

AN INVESTIGATION OF THE SOLVENT  
EXTRACTION KINETICS OF GERMANIUM BY  
7-ALKYLATED-8-HYDROXYQUINOLINE EXTRACTANTS

(VOLUME 2)

By

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3.5. The Effect of the Aqueous Phase Ionic Strength on Germanium Extraction Kinetics by 7-Alkylated-8-hydroxyquinoline Extractants.

There are surprisingly few studies of the effect of ionic strength on the extraction of metal-ions by chelating extractants. As a general rule workers suggest that, provided metal concentrations are low, activity and concentration may be regarded as being equivalent. However, in practical applications (for example leach liquors) where salt concentrations are high ( $> 1 \text{ M}$ ), substantial differences between activity and concentration will occur. Since the knowledge of the relationship between the variation of activity and concentration in such solutions is limited, workers tend to maintain a constant ionic strength for all investigations and thereby circumvent potential problems. The problem of the differences between solution activities and concentration will arise when studies employing low concentrations of metal-ions and extractants are used to predict the outcome of practical situations in which ionic strengths are greater than those in the data set obtained in the laboratory.

As mentioned above, the number of investigations of ionic strength effects with any bearing on this work are limited. Fleming<sup>(59)</sup> observed no change in the observed rate constant for the first order extraction of  $\text{Cu}^{2+}$  by Lix 64N at pH 4 for  $[\text{Na}_2\text{SO}_4]$  concentrations 0 - 0,80 M. Similarly Li and Smith<sup>(204)</sup> observed no change in the observed rate constant for

the complexation of  $\text{Ni}^{2+}$  with 8-hydroxyquinoline in the range of ionic strength 0,124 - 0,204 M. However, Roddy *et al.*<sup>(182)</sup> observed a decrease in the rate of extraction of  $\text{Fe}^{3+}$  by octane solutions of di-(2-ethylhexyl) phosphoric acid ( $\text{D}_2\text{EHPA}$ - Structure (h), Table(4)) when ionic strength was varied. Rates were observed to decrease by a factor of three in the range of ionic strength 0,5 - 3,0 M. Ki and coworkers<sup>(200)</sup> studied the effect of ionic strength on the rate of complexation of  $\text{Fe}^{3+}$  with oxine in methanol and the rate of extraction of  $\text{Fe}^{3+}$  by Kelex 100 in methanol and obtained some interesting results because for the  $\text{Fe}^{3+}$ -oxine system, the value of  $k_{\text{obs}}$  increased for values of ionic strength in the range 0,20 - 0,80 M, while for the  $\text{Fe}^{3+}$ -Kelex 100 system, the rate of extraction decreased for values of aqueous ionic strength from 0,20 - 0,80 M. Clearly, the mechanisms of complex formation for these two systems are different and must in some way be related to the fact that the Kelex complexation is a solvent extraction process while the oxine interaction was an aqueous complexation, however no explanations are offered by the authors for the observed behaviour.

For this study it was decided to investigate the effect of ionic strength on the extraction kinetics of germanium by Lix 26 for ionic strengths in the range 0,715 - 8,2 M. The preparation of solutions of germanium in 0,5 M  $\text{H}_2\text{SO}_4$  and the addition of quantities of  $\text{Na}_2\text{SO}_4$  for ionic strength variations were given in Section 2.4.2.2.4.

An indication of the overall effect is demonstrated by the decrease in percentage extraction with time shown in Figure (76). It is apparent from this plot that the change in ionic strength has a profound effect, both on the initial and equilibrium extraction kinetics. The decline in initial rate and values of  $k_{obs}$  for the slower 'equilibrium' regime calculated via Equation (46) are summarised in Table (42).

| Ionic Strength /M | Initial Rate /((g/l)s <sup>-1</sup> ) | log (Initial Rate) | $k_f(obs)$ /s <sup>-1</sup> | log $k_f(obs)$ |
|-------------------|---------------------------------------|--------------------|-----------------------------|----------------|
| 0,715             | $5,26 \times 10^{-4}$                 | -3,279             | $2,19 \times 10^{-4}$       | -3,700         |
| 2,215             | $5,27 \times 10^{-4}$                 | -3,278             | $2,20 \times 10^{-4}$       | -3,658         |
| 3,715             | $3,92 \times 10^{-4}$                 | -3,407             | $1,59 \times 10^{-4}$       | -3,799         |
| 5,515             | $1,55 \times 10^{-4}$                 | -3,810             | $4,75 \times 10^{-5}$       | -4,323         |
| 8,215             | $2,17 \times 10^{-5}$                 | -4,664             | $2,41 \times 10^{-5}$       | -4,618         |

Table (42). The effect of aqueous phase ionic strength on germanium extraction kinetics by Lix 26. [Lix 26] = 75 g/l, pH ~ 0,24, [Ge]<sub>aq</sub> ~ 0,65 g/l.

Plots of log (Initial Rate) and log  $k_f(obs)$  versus ionic strength are given in Figures (77) and (78) respectively. Examination of these plots reveals that for  $I \leq 2,215$ , the rates of reaction are essentially the same, however linear decreases in rate are apparent thereafter. Hence the initial rate for  $I \geq 2,215$  (Figure (77)) is related to the ionic

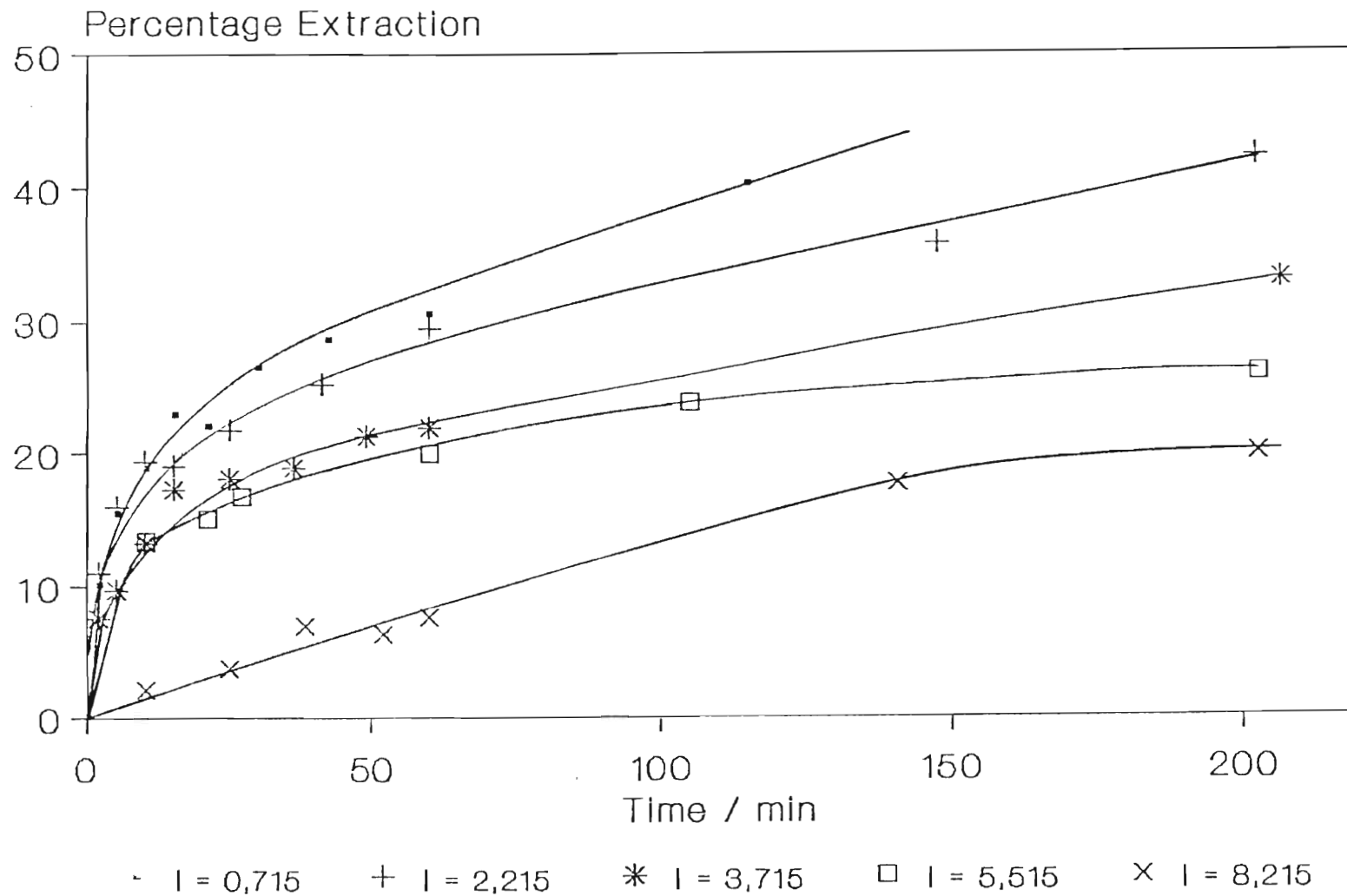


Figure (76). Percentage extraction of germanium by Lix 26 from 0,5 M  $\text{H}_2\text{SO}_4$  aqueous solutions containing  $\text{Na}_2\text{SO}_4$ , as a function of the ionic strength. Aqueous phases :  $\sim 0,65$  g/l Ge in 0,5 M  $\text{H}_2\text{SO}_4$ ; Organic phase : 50 g/l Lix 26. Ionic strength (I) was adjusted by the addition of  $\text{Na}_2\text{SO}_4$  (Section 2.4.2.2.4); units of I are  $\text{mol dm}^{-3}$ .



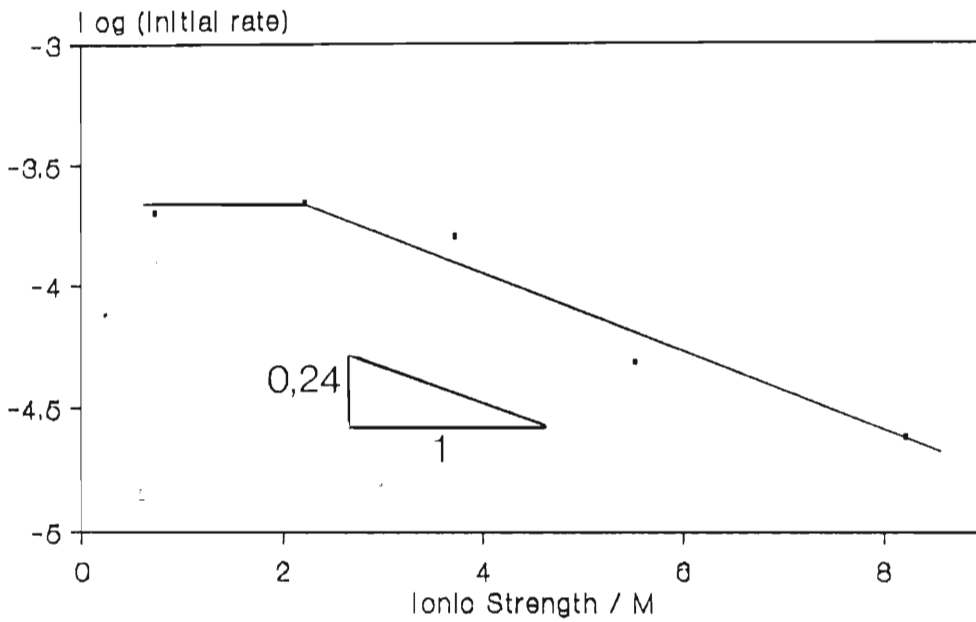


Figure (77). Log(Initial rate) of germanium extraction by Lix 26 as a function of aqueous ionic strength. Initial reaction rates (in  $(\text{g/l}) \text{ s}^{-1}$ ) were calculated from plots of  $[\text{Ge}]_{\text{aq}}$  over the first 5-10 minutes of extraction. Aqueous phases :  $\sim 0,65$  g/l Ge in  $0,5 \text{ M H}_2\text{SO}_4$ ; Organic phase :  $50 \text{ g/l Lix 26}$ .

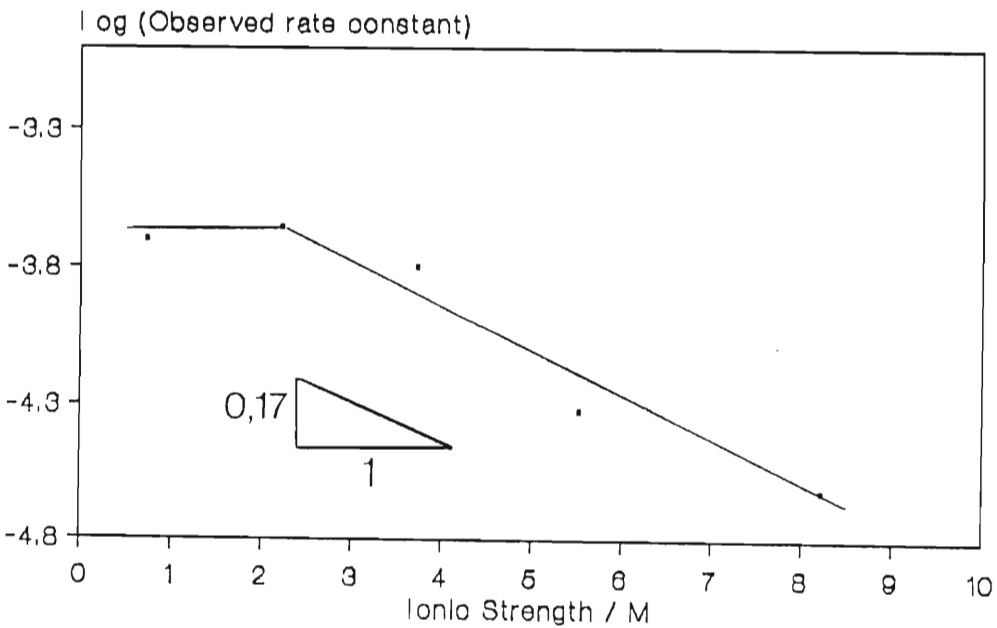


Figure (78). Log(Observed rate constant) for germanium extraction by Lix 26 as a function of ionic strength. Aqueous phase :  $\sim 0,65$  g/l Ge in  $1,5 \text{ M H}_2\text{SO}_4$  with added  $\text{Na}_2\text{SO}_4$  ; Organic phase :  $50 \text{ g/l Lix 26}$ .

strength according to Equation (99):

$$\log(\text{Initial Rate}) = -(0,24I + 2,62) \quad (99)$$

and from Figure (78), the observed forward rate constant,  $k_f(\text{obs})$ , is related to the ionic strength according to Equation (100):

$$\log(k_f \text{obs}) = -(0,17I + 3,26) \quad (100)$$

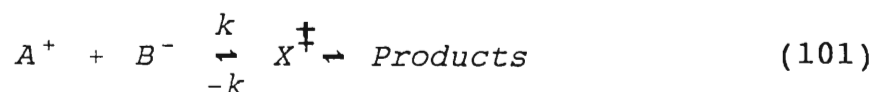
Nazarenko<sup>(94)</sup> has summarised the values of formation constants for germanium hydroxy complexes at a number of ionic strengths, but of particular interest to this work are the value of  $K_i$  for  $I \geq 1,0$  M given in Table (43).

| Constant | I = 1,0 M | I = 8,0 M |
|----------|-----------|-----------|
| $K_1$    | 6,54      | 6,00      |
| $K_2$    | 2,83      | 2,50      |
| $K_3$    | 1,60      | 1,40      |
| $K_4$    | 0,99      | 0,33      |

Table (43). Values of formation constants for the species  $\text{Ge}(\text{OH})_i^{(4-i)+}$  ( $i = 0,1,2,3$ ) at different ionic strengths. (After Nazarenko<sup>(94)</sup>.)

Inspection of the values in this table reveals that increasing ionic strength has only a small effect upon germanium speciation and is therefore unlikely to be the cause of the large observed ionic strength dependence of the kinetic behaviour.

In order to rationalise the changes observed it is necessary to refer to the rate-determining step for the extraction process. This is the stereochemically-controlled formation of  $\text{GeL}_3^+$  (from  $\text{GeL}_2^{2+}$  with HL in the slow reaction regime or  $\text{H}_2\text{L}^+\text{HSO}_4^-$  in the fast kinetic regime). However there is another reaction which must occur prior to the diffusion of this species away from the interface and into the bulk organic phase, viz ion-association in which the charge-neutral species  $\text{GeL}_3^+\text{HSO}_4^-$  is formed. Thus a reaction between  $\text{HSO}_4^-$  and  $\text{GeL}_3^+$  occurs at the interface (and possibly in the organic phase during the initial fast kinetic regime if  $\text{GeL}_2^{2+}$  can exist in the bulk organic). The influence of ionic strength on the rates of reactions between ions in aqueous solution is a well-documented effect<sup>(205)</sup> and is usually referred to as the Primary Salt Effect and has been adopted here in order to quantify the observed rate changes with ionic strength. According to the theory a transition state activated complex  $X^\ddagger$  is formed according to Equation (101):



and kinetic treatment of these equilibria, yields Equation (102) in which the rate constant  $k$  is related to the ionic strength, the charges of the ions reacting,  $z_A$  and  $z_B$  and the value of the rate constant at infinite dilution,  $k_0$ .

$$\log_{10} k = \log_{10} k_0 + 1,02 z_A z_B \sqrt{I} \quad (102)$$

A plot of  $\log_{10}(k/k_0)$  versus  $\sqrt{I}$  is therefore linear with a negative slope if the charged species reacting are of opposite charge and a positive slope if they are of the same charge. Equation (102) also predicts that a reaction between an ion and a neutral molecule should not be affected by the ionic strength of the solution. For this case, where  $\text{GeL}_3^+$  and  $\text{HSO}_4^-$  combine, a slope of -1,02 would be expected, however the constant in Equation (102) is obtained from Debye-Hückel theory which relates the activity coefficient of an ion,  $f$ , to the ionic strength via Equation (103),

$$\log_{10} f = -Qz^2\sqrt{I} \quad (103)$$

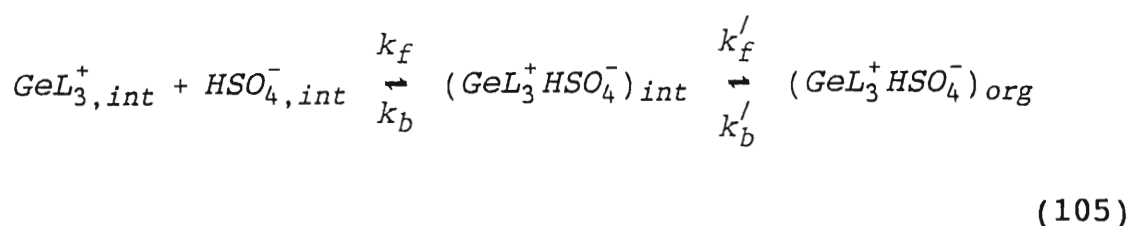
where:

$$Q = \frac{N^2 e^3 \sqrt{2\pi}}{2,303 \sqrt{(\epsilon kT)^3} \sqrt{1000}} \quad (104)$$

in which  $N$  is Avogadro's number,  $k$  is Boltzmann's constant,  $T$  is the temperature in Kelvin and  $\epsilon$  is the permittivity of the medium which is a measurable quantity for most media at any particular temperature. A plot of  $\log k_f(\text{obs})$  versus  $\sqrt{I}$  using the data of Table (42) yields a gradient of -0,75 which proves that the observed decreased rate of reaction cannot be due to an interaction between a neutral (e.g. Lix 26) species and an ion and the negative slope suggests that the interaction is between species of opposite charge. Clearly, since the permittivity of an aqueous/organic interface is not accessible

for measurement, the use of Equation (102) directly to predict the effect of ionic strength upon the observed rate is inappropriate.

An empirical equation relating the observed decrease in the rate of germanium extraction with increasing ionic strength was therefore obtained as follows. If the ionic reaction which occurs at the interface can be summarised by Equation (105):



in which an  $HSO_4^-$  counterion combines with  $GeL_3^+$  at the interface and the ion-association complex formed diffuses away from the interface and into the bulk organic, then, simplifying  $GeL_3^+$  as  $A^+$  and  $HSO_4^-$  as  $B^-$ , Equation (105) can be used to define the rate of formation of the interfacial and bulk ion-pair species as follows:

$$\frac{d[(A^+B^-)_{int}]}{dt} = k_f[A^+][B^-] - (k_b[A^+B^-]_{int} + k'_f[A^+B^-]_{int}) \quad (106)$$

$$\frac{d[(A^+B^-)_{org}]}{dt} = k'_f[A^+B^-]_{int} - k'_b[A^+B^-]_{org} \quad (107)$$

Equating (106) to zero by the Steady State Approximation gives:

$$[A^+B^-]_{int} = \frac{k_f[A^+][B^-]}{k_b + k'_f} \quad (108)$$

and therefore,

$$\frac{d[A^+B^-]_{org}}{dt} = \frac{k'_f k_f[A^+][B^-]}{k_b + k'_f} - k'_b[A^+B^-]_{org} \quad (109)$$

The complex  $A^+B^-$  is highly hydrophobic and charge-neutral, hence it is reasonable to assume that  $k'_b$  would be small and the second term on the right-hand-side of Equation (109) would be negligible. Replacing the combination of constants  $k'_f k_f/k_b + k'_f$  with a new constant  $k''$  simplifies Equation (109) to:

$$\frac{d[A^+B^-]_{org}}{dt} = k''[A^+][B^-] \quad (110)$$

Since for this study, ionic strengths are high, concentration terms must be written as activities i.e.  $a_A = [A^+]\gamma_A^+$  and  $a_B = [B^-]\gamma_B^-$  and therefore a more apt expression for Equation (110) is:

$$\frac{d[A^+B^-]_{org}}{dt} = k''[A^+]\gamma_A^+ [B^-]\gamma_B^- \quad (111)$$

Equation (111) represents the observed rate at which germanium is extracted from aqueous solution by the Lix 26 reagent.

Taking the logarithm of this expression gives:

$$\log(\text{Rate}) = \log k'' + \log[A^+] + \log[B^-] + \log\gamma_{\pm}$$

At constant  $[Ge]_{aq}$ , [Lix 26] and  $[H_2SO_4]$ , the values of  $\log[A^+]$  and  $\log[B^-]$  should be constant, therefore Equation (112) can be simplified to:

$$\log(\text{Rate}) = \log k''' + \log \gamma_{\pm} \quad (113)$$

The product  $\gamma_A^+ \gamma_B^-$ , which is abbreviated  $\gamma_{\pm}$  by convention, is a measurable quantity and is function of all the ions in solution. To date, the Davies Equation<sup>(206)</sup> provides the best approximation for  $\gamma_{\pm}$  at 'high' ionic strength i.e.

$$\log \gamma_{\pm} = -0,513 z_+ |z_-| \left( \frac{\sqrt{(I_m / m^0)}}{1 + \sqrt{(I_m / m^0)}} - 0,30 (I_m / m^0) \right) \quad (114)$$

where  $m^0$  = standard molality of 1 mol  $kg^{-1}$ .

However, this function has only been applied to solutions for which  $I_m \leq 0,1$  mol  $kg^{-1}$ . Inserting the values of ionic strength investigated in this study into Equation (114) gives the following values of activity coefficient:

| Ionic Strength / M | log $\gamma_{\pm}$ |
|--------------------|--------------------|
| 0,715              | -0,125             |
| 2,215              | 0,034              |
| 3,715              | 0,232              |
| 5,515              | 0,483              |
| 8,215              | 0,879              |

Table (44). Values of log  $\gamma_{\pm}$  predicted by the Davies Equation for ionic strengths in the range 0,715 - 8,215 M.  $m^{\circ} = 1 \text{ mol kg}^{-1} \approx 1 \text{ mol dm}^{-3}$ .

If the values of  $\log \gamma_{\pm}$  in Table (44) are inserted into Equation (113), then an increase in rate with increasing ionic strength is predicted, which is not the case for  $I > 2,0 \text{ M}$ . The use of the Davies Equation to give an analytical expression relating rates of reaction of ionic species at an aqueous/organic interface to the ionic strength of the aqueous medium is therefore inappropriate and this is probably because the Davies Equation: (i) begins to fail for  $I > 0,5 \text{ M}$  (where the error in activity coefficients is 5-10 %) and (ii) only really applies to aqueous solutions.

It is clear therefore that a good means of estimating  $\gamma_{\pm}$  at very high ionic strengths is not available. However, an alternate approach is to assume that the empirical Equations (99) and (100) provide an adequate description of the decrease in initial 'fast' and slower 'equilibrium' rates. Inserting Equation (99) into (113) gives:



$$-(0,24I + 2,62) = \log k''' + \log \gamma_{\pm} \quad (115)$$

For  $I = 3,715$  M, for example, the value of the initial rate constant (calculated from the semi-logarithmic plot for the first five minutes of reaction only) is approximately  $6,79 \times 10^{-4} \text{ s}^{-1}$ . Inserting this for  $k'''$  in Equation (115) gives  $\gamma_{\pm} = 0,457$ . Other values of  $\gamma_{\pm}$  calculated in this way for the values of ionic strength investigated in this work are summarised below:

| Ionic Strength / M | $\gamma_{\pm}$ |
|--------------------|----------------|
| 2,215              | 0,705          |
| 3,715              | 0,457          |
| 5,515              | 0,433          |
| 8,215              | 0,501          |

Although these data show a general decrease in the value of  $\gamma_{\pm}$  with increasing ionic strength for the range of ionic strength over which the linear function given by Equation (99) was determined, it is apparent that a limiting value is attained. This does not invalidate the use of Equation (115) for the prediction of the change in observed rate constants with ionic strength because the term in  $I$  becomes more dominant at high ionic strength compared with  $\gamma_{\pm}$ .

In this section of the work (and Section 3.4), the effects of varying parameters in the aqueous phase upon the kinetics of germanium extraction by the chelating reagents of concern to this work were investigated. In the sections which follow, attention is turned to the nature of the organic phase and means by which organic soluble modifiers can be used to enhance extraction characteristics. The next section details

the effect of using different diluents on the kinetic behaviour of the reagents.

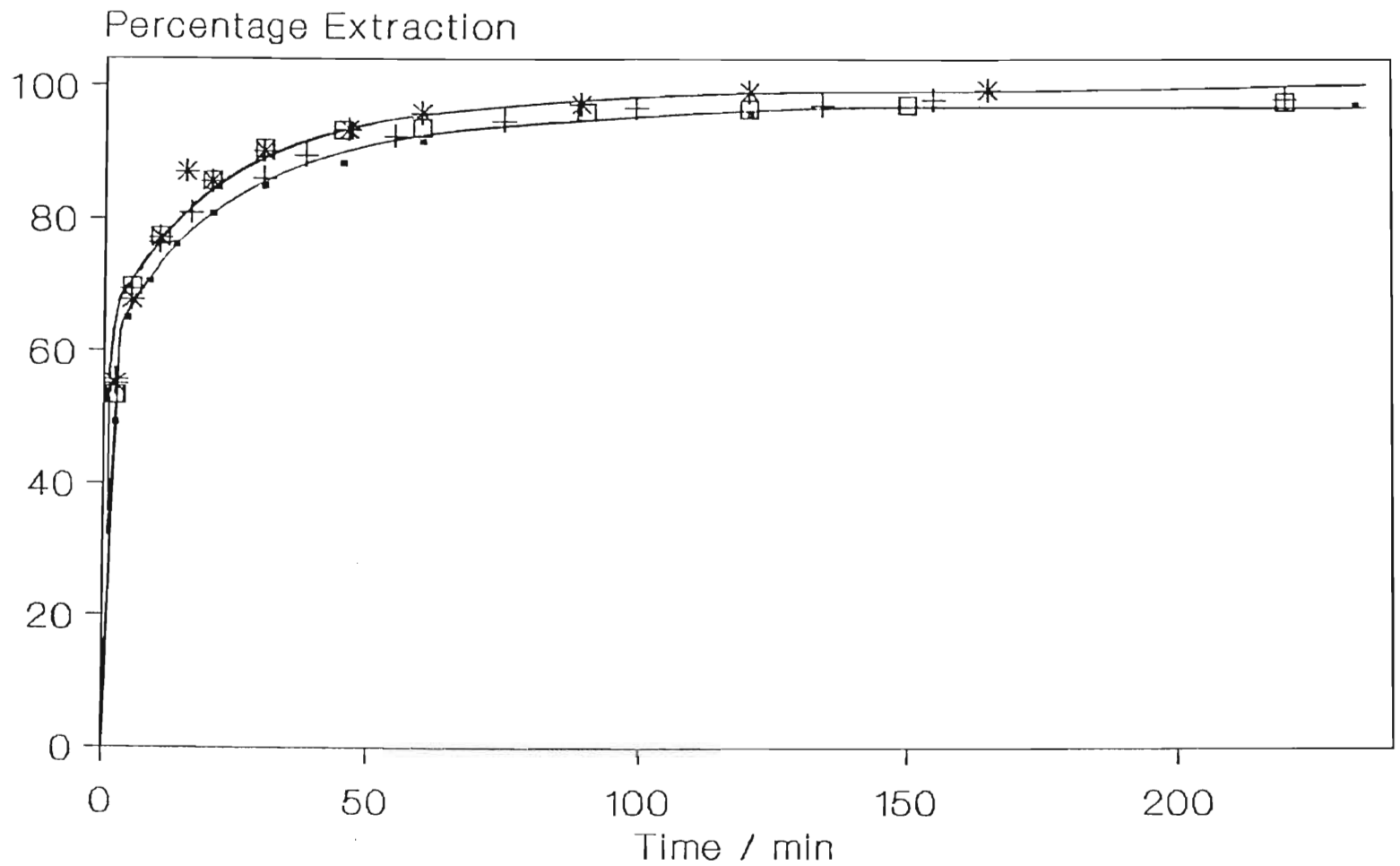
### 3.6. The Importance of the Choice of Diluent on Germanium Extraction Kinetics

In Section 2.4.2.2.6, the characteristics of organic liquids suitable for use as diluents for extractant preparations were given. Although the most important requirements are solubility related, cost and availability are also considered and therefore solvents cheaper than AR toluene were investigated viz. hexane, paraffin and BDH 'Heavy Distillate', the last two of which are mixtures of hydrocarbons with variable composition from batch to batch. The measured relative dielectric constants of the diluents are given below.

| Diluent        | Relative Dielectric Constant |
|----------------|------------------------------|
| Toluene        | 2,37                         |
| Paraffin       | 2,09                         |
| BDH Distillate | 2,06                         |
| Hexane         | 1,87                         |

Table (45). Relative dielectric constants for various diluents.

An indication of the effect of these diluents on the extraction kinetics of germanium by Lix 26 is shown in the plot of Figure (79). For the conditions chosen, all four

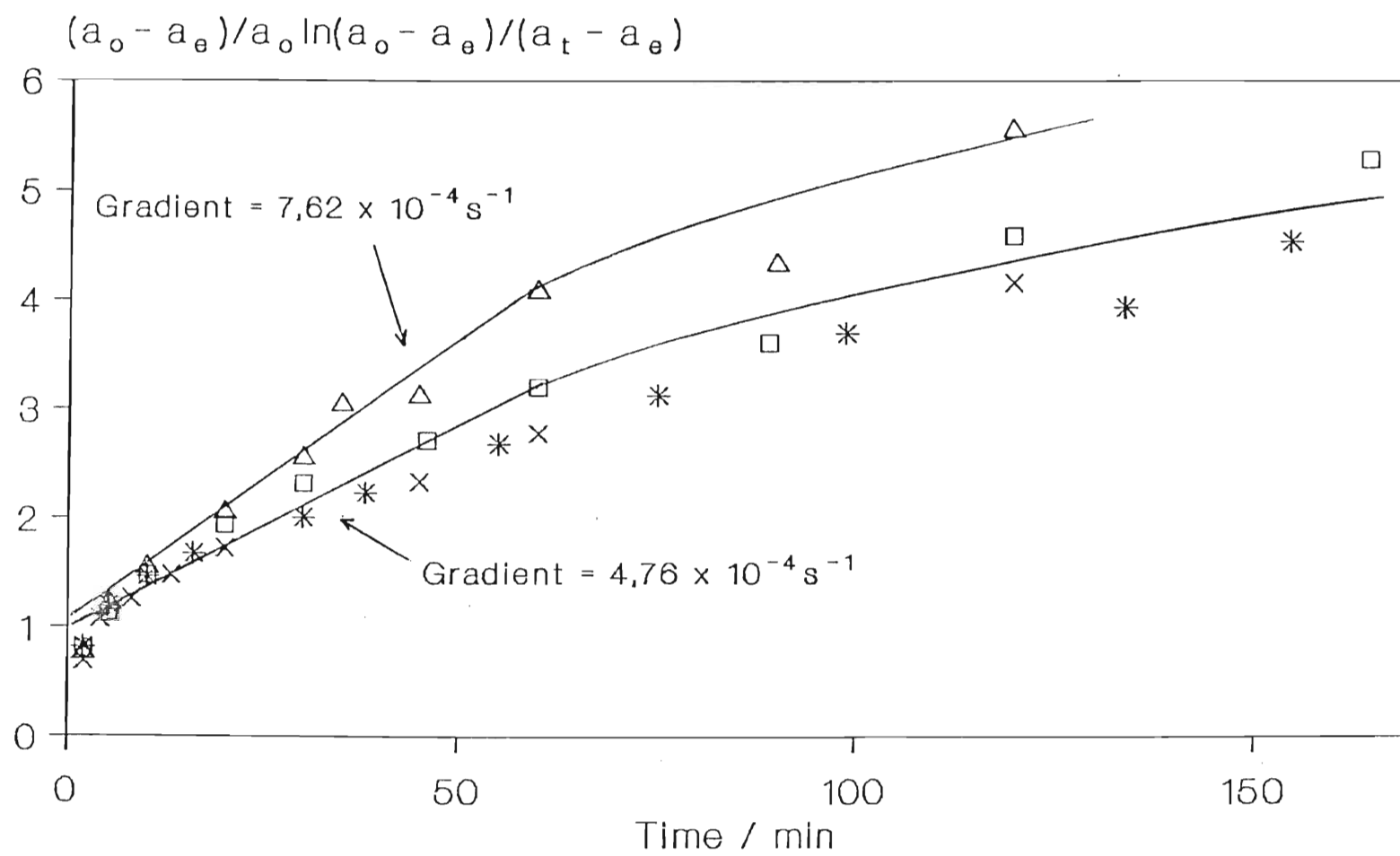


▪ Paraffin    + BDH Heavy Distillate    \* Hexane    □ Toluene  
 (2,09)                    (2,06)                    (1,87)                    (2,37)

Figure (79). Percentage extraction of germanium as a function of time by Lix 26 dissolved in various diluents. Values of relative dielectric constants for these diluents are shown in brackets in the caption. Aqueous phase : ~ 0,65 g/l Ge in 0,5 M H<sub>2</sub>SO<sub>4</sub>; Organic phase : 50 g/l Lix 26 in the diluents listed.

exhibit similar behaviour, however the rate constant observed for the toluene diluent is marginally higher than for the other three (for which the rate constants were approximately the same (Figure (80))). Furthermore, it was observed that for both paraffin and hexane, the Lix 26 active reagent (and probably the metal-ligand chelate formed), coated the sides of the pear-shaped flask after a few minutes of agitation. They are therefore unsatisfactory diluents for this system.

It is suggested that a good indicator of the diluent suitability is the value of the relative dielectric constant. The higher dielectric constant of toluene (there is evidence<sup>(207)</sup> that even small changes in the medium polarity such as the ones given in Table (45), have significant effects upon extractant behaviour), is one factor which contributes to the better solvation ability of the diluent and, *inter alia*, the improved kinetics of extraction, however other factors such as interfacial tension play a role. In the next section, which discusses the improvements in extraction observed by the inclusion of an organic modifier, the relationship between the dielectric constant and extraction performance is examined.



- \* Lix 26/BDH Dist.
- Lix 26/Hexane
- △ Lix 26/Toluene
- × Lix 26/Paraffin

Figure (80). Semi-logarithmic plots of Equation (46) as a function of time for germanium extraction by Lix 26 in various diluents. The plot shows that over a shorter time scale than Figure (79), toluene is the better diluent. Aqueous phase : ~ 0,65 g/l Ge in 0,5 M H<sub>2</sub>SO<sub>4</sub>; Organic phase : 50 g/l Lix 26 in various diluents.

### 3.7. The Enhancement of Extraction Kinetics and Improvement in Percentage Extraction Resulting from the Inclusion of Chemical Modifiers.

The general definition of a 'modifier' as applied to solvent extraction processes is 'any chemical reagent which modifies the extraction characteristics of an extractant'. Modifiers are usually added to solvent systems to overcome the formation of (i) third phases and (ii) emulsions. Third phases are of a density intermediate between the solvent phase i.e. the diluent and extractant and the aqueous phase and result from the effects of the diluent upon the heterogeneous equilibria which are established between the aqueous and organic phases of a system. Most of the available evidence on the formation of third phases suggests that it is solubility related and can be overcome by the addition of a modifier chosen by experiment for its observed ability to augment extraction characteristics.

As with diluents, modifiers are selected for their solubility properties i.e. soluble in the diluent, insoluble in the aqueous phase, physical characteristics such as density, boiling point and flash point, availability and price. The four most common reagents used as modifiers are 2-ethylhexanol, isodecanol, tri-n-butyl phosphate (TBP) and p-nonyl-phenol. The last modifier mentioned is the active reagent added to Kelex 120 (20% v/v Kelex 100 in p-nonyl-phenol) and this was formulated to provide better physical characteristics in solvent extraction operations involving  $\text{Cu}^{2+}$  than were provided by Kelex 100<sup>(208)</sup>.

Besides enhancing the rates of extraction of metal ions by extractants, modifiers are also reported to influence the ability of a stripping reagent to remove loaded metal and also a scrub solution to remove co-extracted metals<sup>(208,209)</sup>. This property is discussed in Section 3.10.3.

There are very few investigations in the available literature detailing the effect of modifiers upon the extraction performance of 7-alkylated-8-hydroxyquinoline chelates. Ritcey and Lucas<sup>(209)</sup>, investigated three modifiers viz. TBP, p-nonylphenol and isodecanol for their effects on phase separation, copper extraction, stripping and selectivity of Kelex 100 with  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Ni}^{2+}$  systems. Their data indicated that a 10% v/v solution of isodecanol provided the best overall properties for a 20 volume percent solution of Kelex 100 in a kerosene-type diluent, Solvesso 150 (a chiefly aromatic diluent sold commercially by Esso and Exxon). Their data also showed that increasing the modifier content beyond a particular concentration caused a decrease in percentage extraction- a phenomenon which has also been reported by other workers<sup>(55)</sup>.

As such, the current understanding of the mechanism by which diluents and modifiers influence the extraction of metals is weak and there is little possibility of predicting the outcome of modifier addition on extraction characteristics from any theoretical viewpoint. Generally speaking, the selection of a modifier is based upon experimental evidence, although trends in behaviour usually emerge in the course of such experiments. For this work, five modifiers were investigated and their solubilities and relative dielectric constants are given in

Table (46).

| Modifier       | Chemical Formula                             | Aqueous Solubility g/100 ml | Relative Dielectric Constant $\epsilon_c^r$ |
|----------------|--|-----------------------------|---|
| n-propanol     | $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ | soluble                     | 35,06                                       |
| n-butanol      | $\text{CH}_3(\text{CH}_2)_3\text{OH}$        | 6,40 <sup>(210)</sup>       | 25,87                                       |
| n-pentanol     | $\text{CH}_3(\text{CH}_2)_4\text{OH}$        | 2,36 <sup>(211)</sup>       | 15,01                                       |
| n-octanol      | $\text{CH}_3(\text{CH}_2)_7\text{OH}$        | *0,0586 <sup>(210)</sup>    | 10,05                                       |
| benzyl alcohol | $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$   | 3,80 <sup>(212)</sup>       | 18,24                                       |
| (toluene)      | $\text{C}_6\text{H}_5\text{CH}_3$            | *0,049 <sup>(213)</sup>     | 2,37  |

Table (46). Physical constants of chemical modifiers and toluene. Solubility data all at 20°C except \* at 25°C.  $\epsilon_c^r$  values measured in this work at 21°C.

Of the modifiers listed, only n-octanol has been investigated in the work of others<sup>(53)</sup>. The list in Table (46) represent an homologous series of aliphatic alcohols and an aromatic alcohol, chosen not for their possible commercial suitability but more to discover the existence of any kind of trend. n-Propanol for example would not be appropriate since its solubility in aqueous solution is high, although the actual quantity which distributes from the toluene diluent to aqueous solution is given by the distribution coefficient. Values of  $K_D$  for these alcohols between toluene and acidic aqueous solutions are not available in the literature, however the



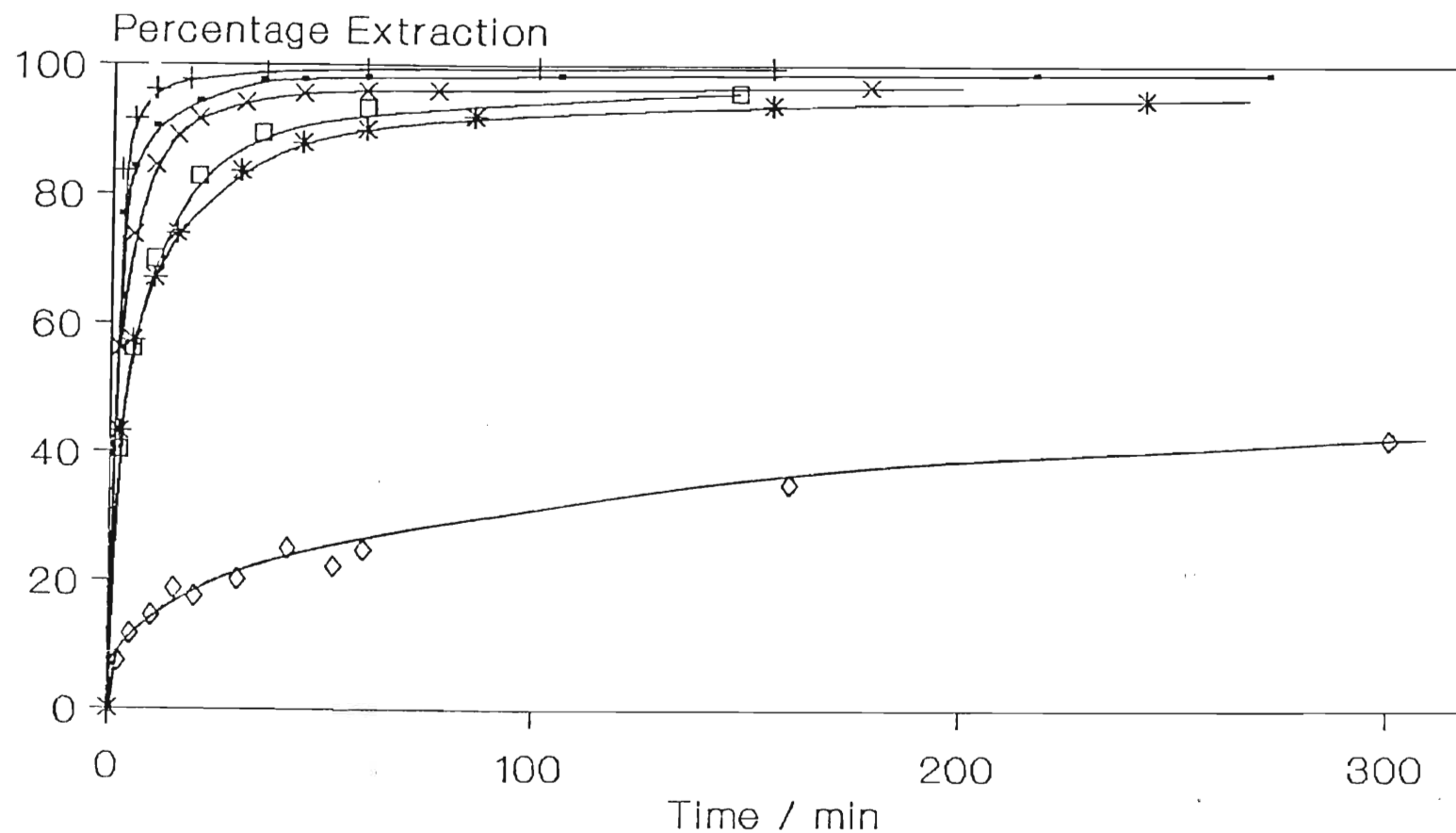
aqueous solubilities yield a relative comparison of the probable values of  $K_D$ . The relative dielectric constant data in the final column of Table (46) is included because there are usually correlations between values of  $\epsilon_c^r$  and extraction performance<sup>(171,207,214)</sup> and it was hoped that this work could demonstrate any relationship which exists between these two. Data appertaining to Lix 26 is presented first, followed by TN 02181/01787 and then a detailed study of one modifier (n-octanol) is given.

### 3.7.1. Kinetic and Equilibrium Data Relating to Lix 26 and Chemical Modifiers

The preparation of the organic phases was described in Section 2.4.2.2.7. Aqueous phases were ~ 0,65 g/l germanium in 0,5 M  $H_2SO_4$ . Although for most of the other parameter studies of this work, an aqueous phase containing 1,5 M  $H_2SO_4$  was selected, it was decided that the study of modifier effects were best performed at a higher pH (approximately 0,24 for 0,5 M  $H_2SO_4$ ), where the extraction rates would be slow enough to facilitate a direct comparison with extraction data obtained in the absence of added modifier. At high aqueous acid concentration, such a comparison would be more difficult to make in view of the fast kinetics characteristic of all the ligand reagents at low pH. Moreover, one of the reasons for including a modifier in a diluent/extractant solution is to achieve reasonable extraction under operating conditions which are not ideal but economically viable and thus it was considered that this study would be appropriate in this regard.

An overall indication of the adverse change in extraction behaviour is illustrated by the percentage extraction plots of Figure (81). For all five modifiers (the upper curves of Figure (81)), the extraction is exceptional compared with extraction data obtained for unmodified organic phase, with extremely fast initial rates of extraction and percentage extractions at equilibrium of  $> 97\%$  ( $< 3$  hours for equilibrium) in the worst case (n-propanol) compared with  $< 59\%$  for Lix 26 alone (equilibrium established after 24 hours!). These data demonstrate one of the major advantages of the use of modifiers viz, higher equilibrium extraction and improved kinetics at a pH which would not normally be considered.

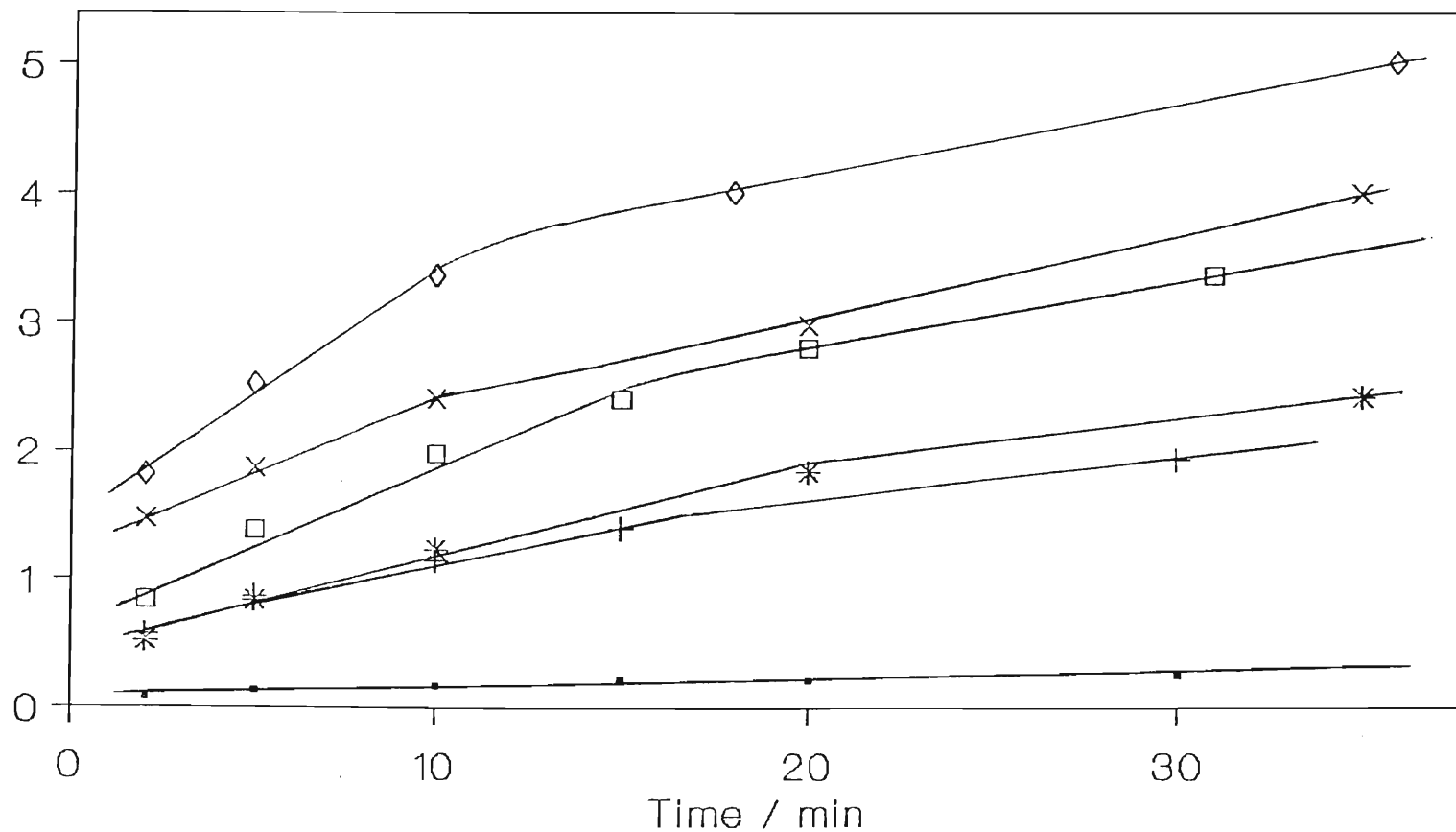
In Figure (82), the semi-logarithmic kinetic plots for these data are presented. The values of observed forward rate constants calculated from the slopes of the linear portions of these curves are summarised in Table (47).



—●— n-Butanol                      —+— Benzyl Alcohol                      —\*— n-Propanol  
 —□— n-Octanol                      —x— n-Pentanol                      ◇ no Modifier

Figure (81). Percentage extraction obtained by varying the nature of the modifier added to Lix 26 in toluene. Organic phase : 45 g/l Lix 26 in toluene containing 10% v/v modifier; Aqueous phase ; ~ 0,65 g.l Ge in 0,5 M H<sub>2</sub>SO<sub>4</sub>. Phase volumes 100 ml.

$$\frac{(a_0 - a_e)}{a_0} \ln \frac{(a_0 - a_e)}{(a_t - a_e)}$$



- Lix 26/no modifier      + n-propanol      ∗ n-octanol
- n-pentanol              × n-butanol      ◇ benzyl alcohol

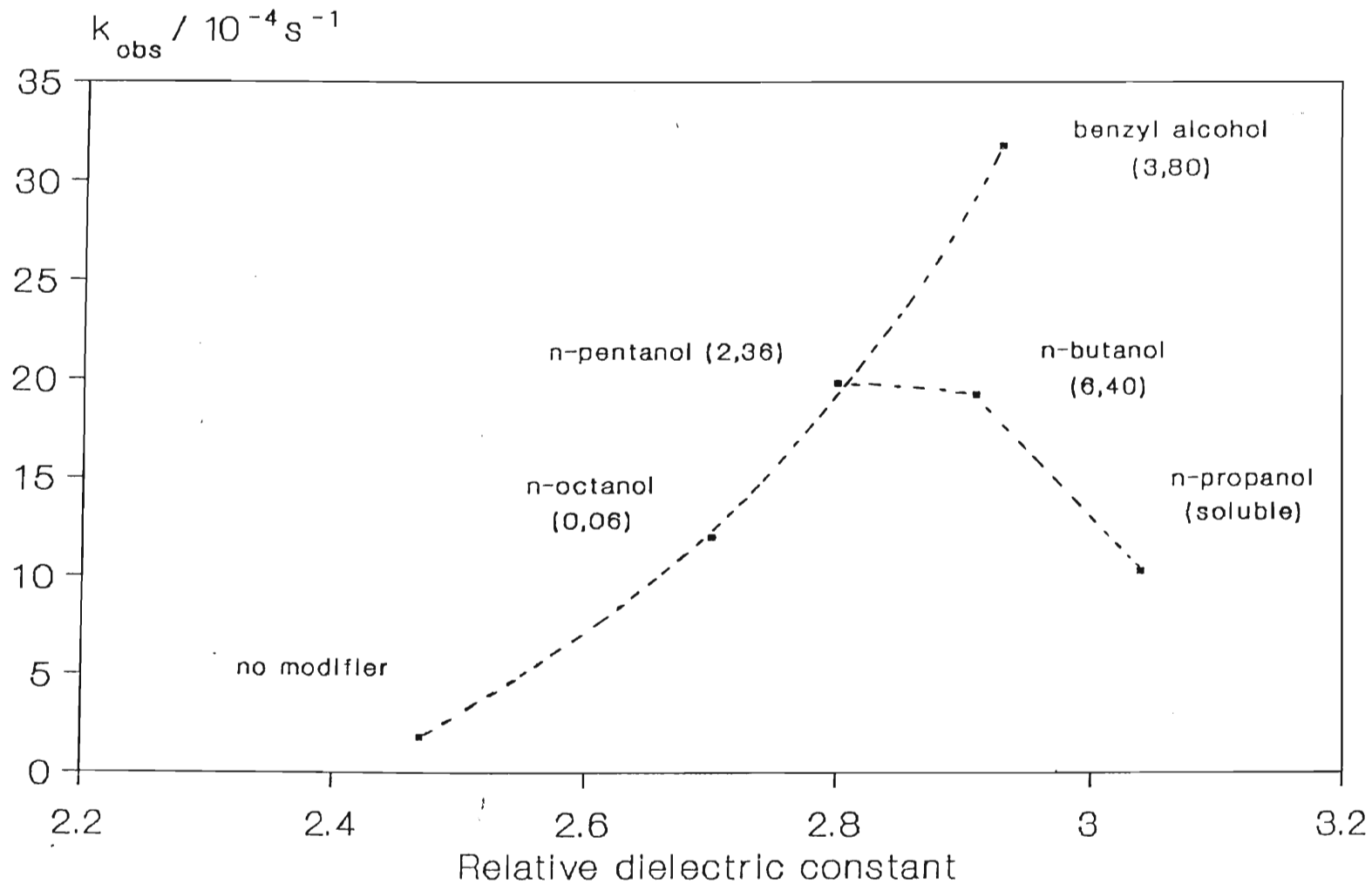
Figure (82). Comparison of the extraction kinetics of germanium by Lix 26 solutions containing various modifiers. Organic phase : 45 g/l Lix 26 in toluene containing 10% v/v modifier; Aqueous phase : ~ 0,65 g/l Ge in 0,5 M H<sub>2</sub>SO<sub>4</sub>.

| Modifier       | $k_f(\text{obs})$<br>/s <sup>-1</sup> | Relative<br>Improvement in<br>Extraction<br>Kinetics | Relative<br>Dielectric<br>Constant |
|----------------|---------------------------------------|--|------------------------------------|
| no modifier    | $1,78 \times 10^{-4}$                 | -  | 2,47                               |
| n-propanol     | $1,03 \times 10^{-3}$                 | x 6  | 3,04                               |
| n-octanol      | $1,20 \times 10^{-3}$                 | x 7  | 2,70                               |
| n-pentanol     | $1,98 \times 10^{-3}$                 | x 11   | 2,80                               |
| n-butanol      | $1,92 \times 10^{-3}$                 | x 11   | 2,91                               |
| benzyl alcohol | $3,17 \times 10^{-3}$                 | x 18   | 2,93                               |

Table (47). Effect of alcohol modifiers on the extraction kinetics of germanium by Lix 26 (45 g/l in toluene with 10 % v/v modifier).

The modifiers have been ordered in the table to reflect their behaviour from worst to best, thus the rate of germanium extraction by Lix 26 containing 10 % v/v benzyl alcohol is 18 times faster than the rate obtained by the ligand alone. The trend in kinetic behaviour and the dielectric constant is illustrated by Figure (83). It is apparent that:

- (i) As  $\epsilon_c^f$  increases, the value of the observed rate constant increases and this is paralleled by the increase in aqueous solubility up to a point. A levelling-off in the improved kinetic behaviour is evident for n-butanol which has a solubility of 6,40 g/ 100 ml aqueous solution



Values in brackets are aqueous solubilities  
 -refer to Table (46)

Figure (83). Forward rate constant for germanium extraction (Equation (46)) as a function of the relative dielectric constant of 10% v/v modifier solutions of Lix 26 (45 g/l) in toluene. Aqueous phase : ~ 0,65 g/l Ge in 0,5 M H<sub>2</sub>SO<sub>4</sub>.

and a decrease in  $k_f(\text{obs})$  is obtained for n-propanol which is ordinarily completely miscible with water.

(ii) The aromatic modifier provides better improvement over the aliphatic alcohol of equivalent relative dielectric constant (cf. benzyl alcohol and n-butanol).

It would not be appropriate to ascribe the increased value of  $k_f(\text{obs})$  solely to the change in dielectric constant, although there is some correlation between  $\epsilon_c^r$  and  $k_f(\text{obs})$ . This effect has also been noted by Rudenko *et al.*<sup>(207)</sup>, who showed that the percentage of germanium extracted by 8-hydroxyquinoline into chloroform, benzene and hexane diluents and mixtures of each with isobutanol, increased with the dielectric constant. Other factors which are also altered by the addition of a modifier such as viscosity and interfacial tension may also play an important role in the improved extraction behaviour. For instance, the interfacial tension between n-octanol/water is  $8,5 \times 10^{-3} \text{ Nm}^{-1}$ <sup>(156)</sup> whereas for toluene/water the value is  $3,61 \times 10^{-2} \text{ Nm}^{-1}$ <sup>(215)</sup>. While these values apply for a static system and therefore of uncertain relevance to vigorously-stirred media, they do indicate that, in principle, the addition of modifiers improves the mass transfer characteristics of an interface. It has already been stated that the current understanding of the mechanism by which modifiers function in improving extraction is inadequate. One possibility is that they interact with the extractant through hydrogen-bonding. This is therefore distinct from the effect of adding surfactants in that the observed change is therefore related directly to a modification of the equilibrium of a chemical reaction. This change in the overall thermodynamic

equilibrium of a system will have ramifications upon the kinetics. It is therefore suggested that for the alcohols studied in this work, one or more modifier molecules hydrogen-bond to the extractant in the manner shown in Figure (84) and therefore render the extractant molecule more surface active. In the figure shown, the alkyl group of the alcohol can align either with the aromatic centres of the quinoline if the alcohol molecule lies in a flat plane perpendicular to the chelate centre or adjacent to the 7-alkyl group. It is suggested that for aliphatic alcohols the latter is more likely, while for benzyl alcohol, proximity to the aromatic centre is more probable. The data for benzyl alcohol would seem to suggest that this latter interaction (Figure (85)), provides the most favourable modification to the extractant molecule at the interface. It is possible that the observed difference between the modifier molecules e.g. n-octanol versus n-butanol, is associated with the number of modifier molecules which can pack around and hydrogen bond to the extractant molecule without hindering the reactive face. Compare for example Figure (84) in which n-octanol interacts with Lix 26, with Figure (86) in which the smaller n-butanol, which is the more effective modifier, hydrogen-bonds to the Lix 26 chelate centre.



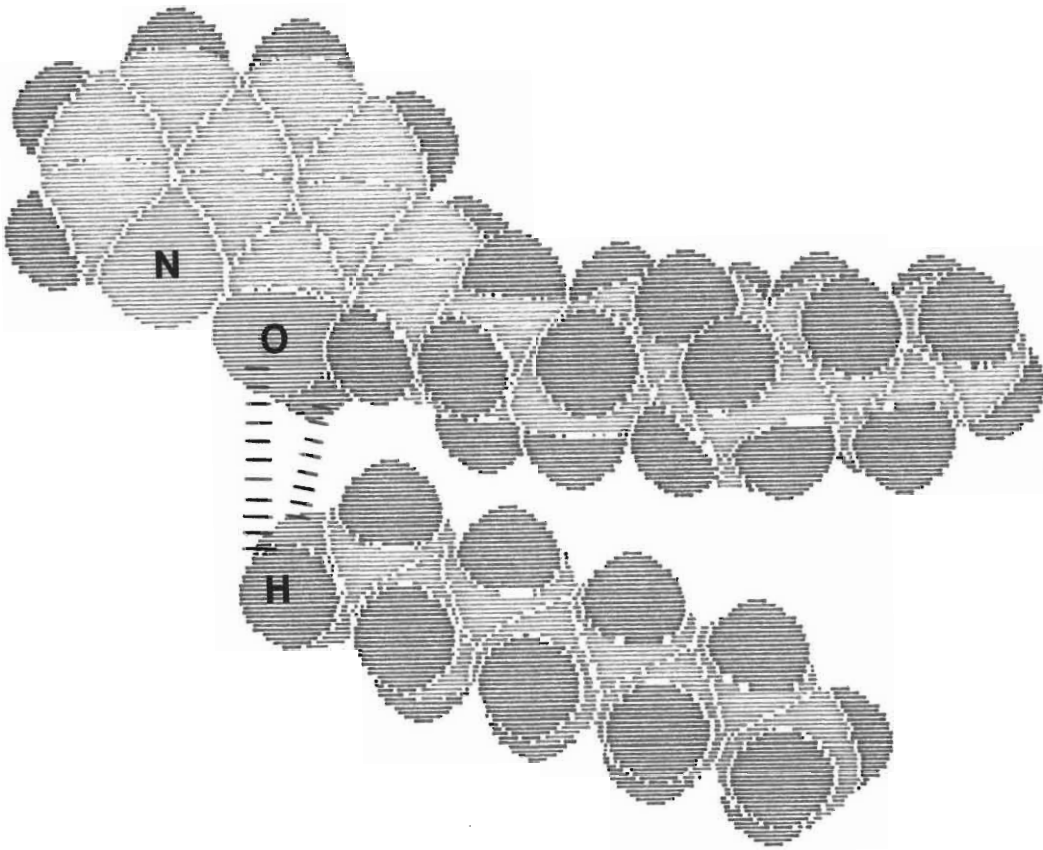


Figure (84). The hydrogen-bonding interaction between n-octanol and Lix 26.

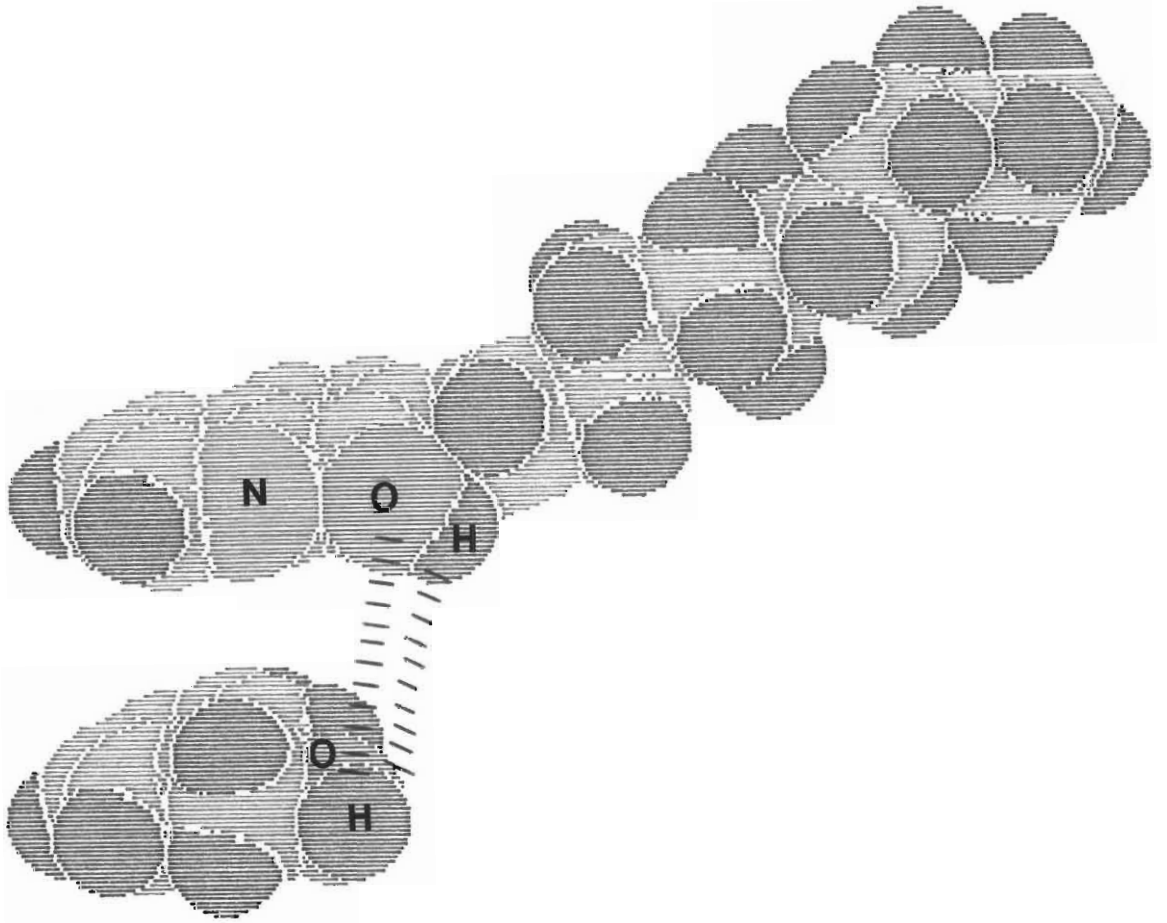


Figure (85). The hydrogen-bonding interaction between a molecule of benzyl alcohol and Lix 26.

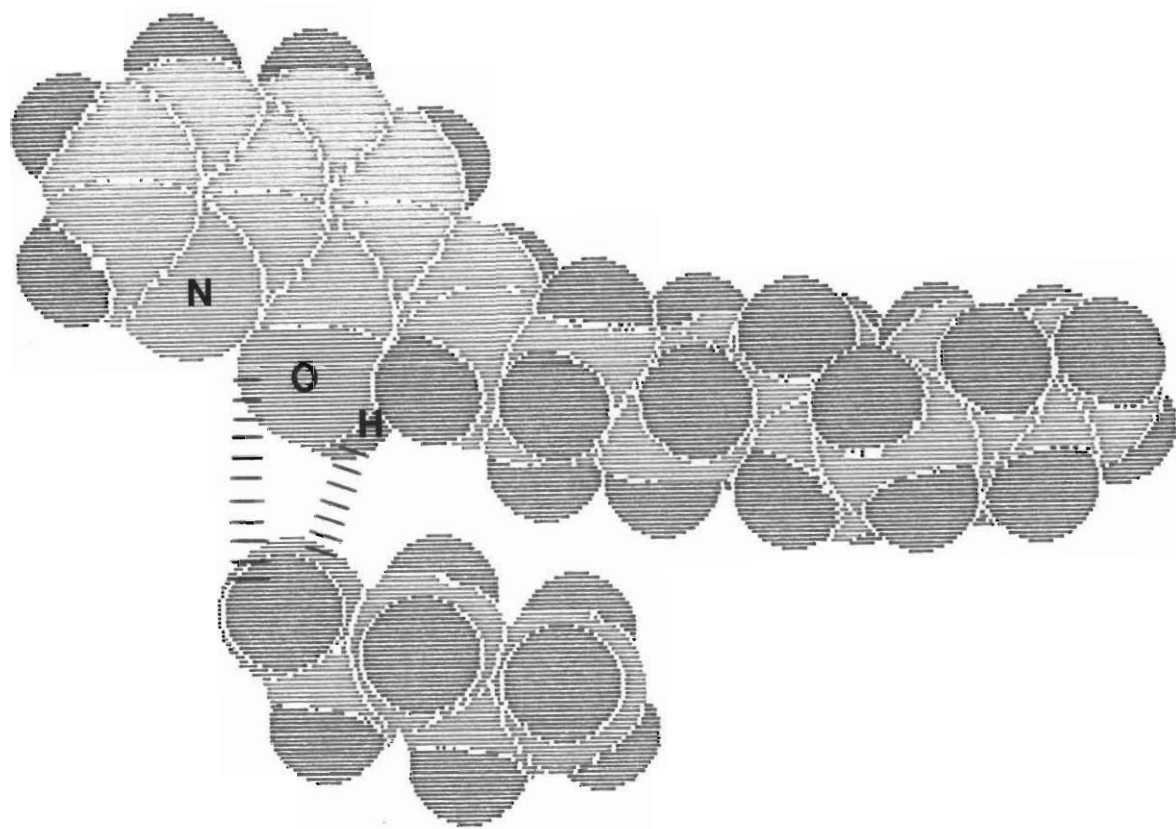


Figure (86). The hydrogen-bonding interaction between a molecule of n-butanol and Lix 26.

In Section 3.4, it was noted that the initial rate and equilibrium percentage extraction of germanium by the ligands of interest to this study increased with increasing  $[H^+]$  and to account for this observation, the change in the speciation of germanium was discussed. It was suggested that the higher hydroxy species extracted at much slower rates (particularly  $GeL_2(OH)_2$ ) than non-hydroxylated  $Ge(IV)$  species. Examination of Figure (81) reveals that fast initial rates and efficient equilibrium extraction are maintained at pH 0,24 and that in fact, observed rate constants are equivalent if not larger than those applicable to extraction of germanium from an 1,5 M  $H_2SO_4$  aqueous phase containing no modifier (cf. Table (47) with Table (30) of Section 3.4.1). The presence of modifiers may, via strong hydrogen-bonding to the ligand, facilitate faster orientation and chelation of these higher hydroxy germanium species at the interface and hence account for the faster overall kinetics.

In the discussion above, the modifier has been described as a carrier molecule which improves the surface activity of the extractant. At the same time, however, the modifier increases the polarity of the diluent (and of the interfacial reaction zone) and therefore renders this medium more receptive to the uptake of charged species viz.  $GeL_3^+$ .

### 3.7.2. The Effect of Modifiers on Germanium Extraction by TN 02181 and TN 01787

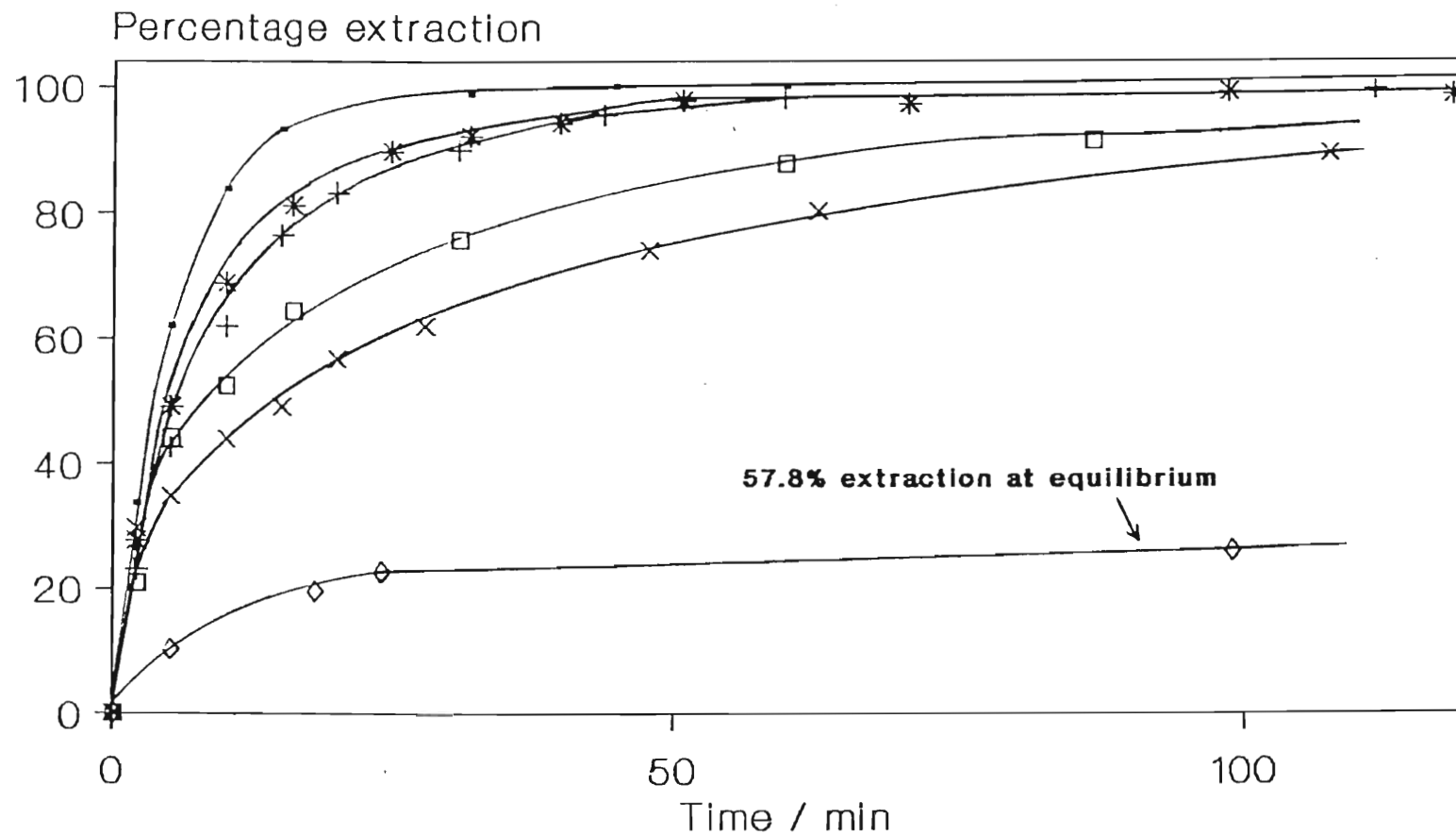
Extraction data pertaining to these two reagents was

manipulated in an analogous manner to Lix 26. Figures (87) and (88) summarise the percentage extraction data for the ligands with 10% v/v solutions of the modifiers. Values of  $k_f(\text{obs})$  calculated from semi-logarithmic plots of Equation (46) and values of relative dielectric constant are included in Table (48).

| Modifier       | $k_f(\text{obs}) / \text{s}^{-1}$ | $\epsilon_c^r$ | $k_f(\text{obs}) / \text{s}^{-1}$ | $\epsilon_c^r$ |
|----------------|-----------------------------------|----------------|-----------------------------------|----------------|
|                | TN 01787                          |                | TN 02181                          |                |
| no modifier    | $1,55 \times 10^{-4}$             | 2,51           | $7,09 \times 10^{-5}$             | 2,51           |
| n-propanol     | $4,18 \times 10^{-4}$ (3x)        | 3,08           | $2,04 \times 10^{-3}$ (28x)       | 3,08           |
| n-octanol      | $9,81 \times 10^{-4}$ (6x)        | 2,71           | $2,07 \times 10^{-3}$ (29x)       | 2,70           |
| n-pentanol     | $1,19 \times 10^{-3}$ (8x)        | 2,83           | $3,64 \times 10^{-3}$ (51x)       | 2,83           |
| n-butanol      | $1,64 \times 10^{-3}$ (11x)       | 2,94           | $3,61 \times 10^{-3}$ (51x)       | 2,94           |
| benzyl alcohol | $2,91 \times 10^{-3}$ (19x)       | 2,97           | $3,59 \times 10^{-3}$ (51x)       | 2,95           |

Table (48). Values of observed forward rate constants for germanium extraction by TN 01787 and TN 02181 in toluene, containing 10 % v/v alcohol modifiers, and dielectric constants of the solutions. Values in brackets indicate the increase in  $k_f(\text{obs})$  relative to extraction with no modifier. Conditions:  $[\text{Ge}] \sim 0,65 \text{ g/l}$  in  $0,5 \text{ M H}_2\text{SO}_4$ ,  $[\text{HL}] = 45 \text{ g/l}$ .

The data in the table parallels the behaviour exhibited by Lix 26 (Table (47)). The relative increases in values of  $k_f(\text{obs})$  for TN 01787 are of the same order as for Lix 26,



▪ Benzyl alcohol      + n-Pentanol      \* n-Butanol  
 □ n-Octanol          × n-Propanol      ◇ no synergist

Figure (87). Percentage extraction obtained by varying the nature of the modifier added to TN 01787 in toluene. Organic phases : 45 g/l TN 01787 in toluene containing 10% v/v modifier; Aqueous phases : ~ 0,65 g/l Ge in 0,5 M H<sub>2</sub>SO<sub>4</sub>. Phase volumes 100 ml.

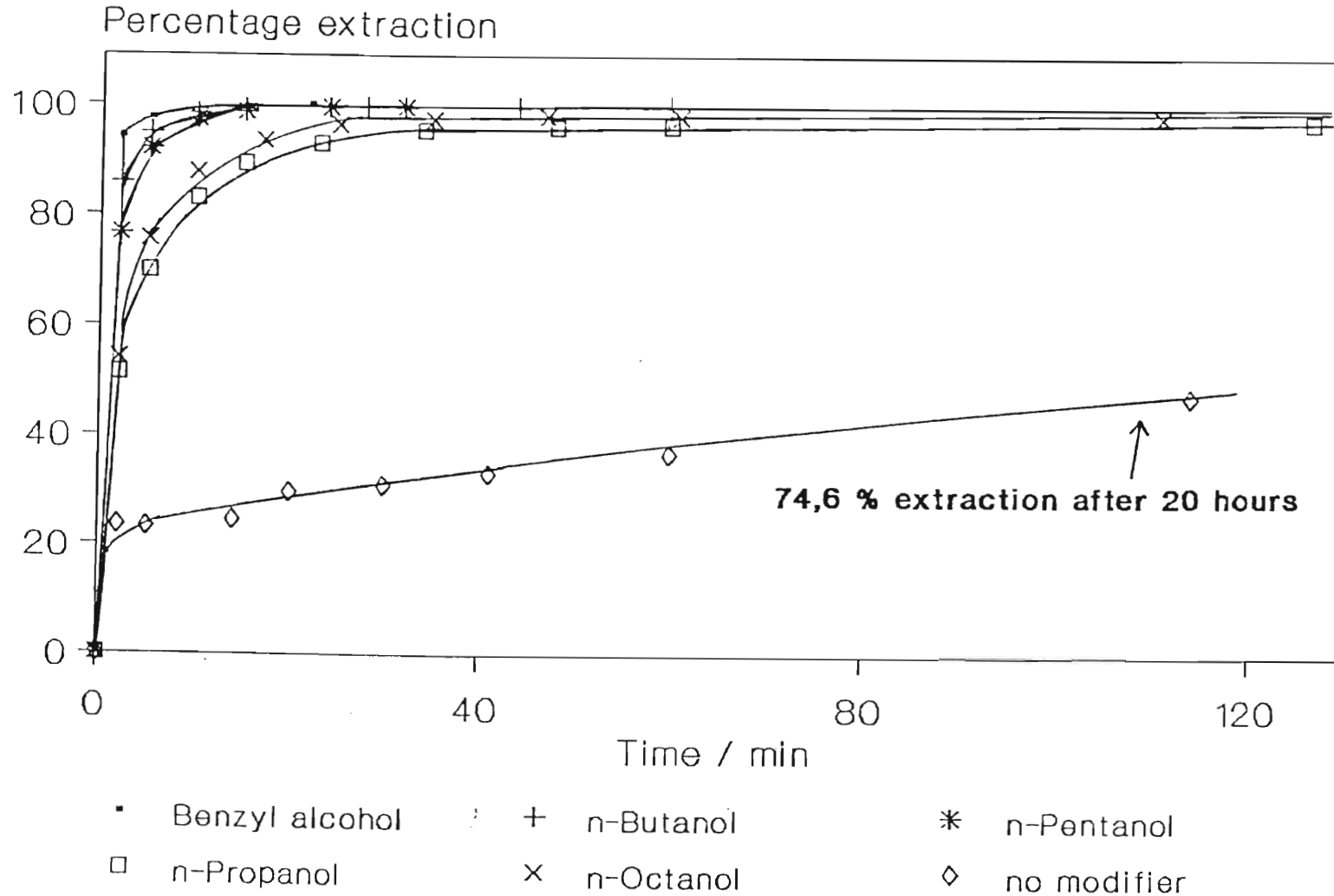


Figure (88). Percentage extraction obtained by varying the nature of the modifier added to TN 02181 in toluene. Organic phases : 45 g/l TN 02181 in toluene containing 10% v/v modifier; Aqueous phases : ~ 0,65 g/l Ge in 0,5 M H<sub>2</sub>SO<sub>4</sub>. Phase volumes 100 ml.

however for TN 02181 they are much larger e.g. 51 times faster rate with benzyl alcohol added as a modifying agent compared with the rate in the absence of any modifier. Again the table has been arranged in order of modifier efficacy. The order shown follows the same pattern as for Lix 26 i.e. the order no modifier < n-propanol < n-octanol < n-pentanol < n-butanol < benzyl alcohol is suggested. Plots of  $k_f(\text{obs})$  versus relative dielectric constant of modifier/toluene solutions (Figure (89)) for TN 01787 show a similar trend to that discussed for Lix 26. For TN 02181, however, the observed rate constant plot levels off at approximately  $3,6 \times 10^{-3} \text{ s}^{-1}$ , which suggests faster kinetics than the observed rate constant ( $k_f(\text{obs}) = 1,60 \times 10^{-3} \text{ s}^{-1}$ , 50 g/l TN 02181) calculated for extraction of germanium from 1,5 M  $\text{H}_2\text{SO}_4$ . In Section 3.2.1.3 an order with respect to ligand of 1,12 was calculated from observed rate data and this suggests that a rate law of the following form:

$$\text{Rate} = k_f(\text{obs}) [\text{Ge}] [\text{HL}]^{1,12} [\text{H}^+]^{-1,18} \quad (116)$$

is appropriate to TN 02181 for  $[\text{TN 02181}] > 20 \text{ g/l}$  (below this concentration the value of  $k_f(\text{obs})$  deviates from the linear behaviour of Equation (116) - see Section 3.2.1.3). Inserting the limiting value of  $k_f(\text{obs})$  above into Equation (116) and concentrations of  $8,95 \times 10^{-3} \text{ M}$  ( $\equiv 0,65 \text{ g/l}$ ) for  $[\text{Ge}]$  and  $1,214 \times 10^{-1} \text{ M}$  for purity-corrected  $[\text{TN 02181}]$  and  $0,575 \text{ M}$  for the concentration of  $\text{H}^+$  in  $0,5 \text{ M } \text{H}_2\text{SO}_4$  gives  
 $\text{Rate} = 5,67 \times 10^{-6} (\text{mol dm}^{-3})^{0,94} \text{ s}^{-1}$  (these unwieldy units arise from the non-integral orders in Equation (116)), which is probably an indication of the limit at which the reaction



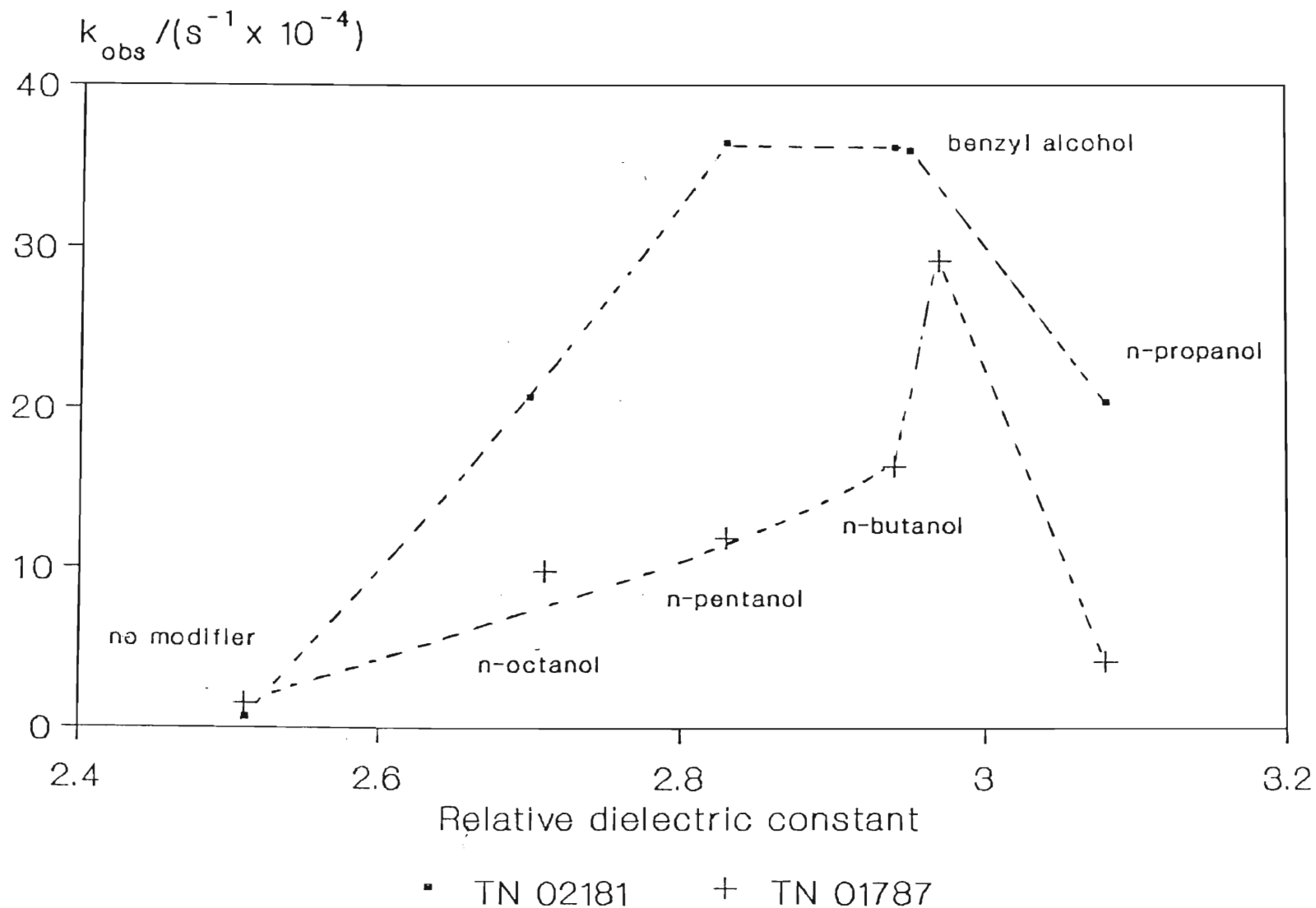


Figure (89). Forward rate constants for germanium extraction (calculated via Equation (46)) as a function of the relative dielectric constant of 10% v/v modifier solutions of TN 02181 (upper curve) and TN 01787 (lower curve) in toluene. Aqueous phases :  $\sim 0,65$  g/l Ge in  $0,5$  M  $\text{H}_2\text{SO}_4$ .

occurs and mass-transfer can progress to and from the interface for these concentrations of germanium and ligand.

There are two points of interest suggested by the plots of these data (Figures (87) to (89)):

(i) The improvement in extraction by TN 02181 by the addition of modifier is far greater than the enhancement observed for TN 01787 and Lix 26, however TN 02181 is generally more efficient than either TN 01787 or Lix 26 e.g. concentration of ligand (Section 3.2.1.3), change in pH (Section 3.4.2) etc. This is partly understandable if the molecular structure of TN 02181 is examined. Figure (90) shows the hydrogen-bonding interaction between one of the isomers of TN 02181 and n-butanol. Comparison with the analogous situation for Lix 26 (Figure (86)) reveals that the modifier has greater freedom of movement about the chelate centre for TN 02181 than for Lix 26. This can be attributed to the compression of the 7-alkyl group of the 8-hydroxyquinoline moiety into a region occupying approximately one third of the space occupied by the 7-alkyl group of Lix 26. It is also worth noting that for all three extractants the observed increase in rate with n-octanol (which as stated before has an aqueous solubility which is sufficiently low as to render this modifier more useful commercially than others investigated here), is poor by comparison with the other modifiers but more importantly, the observed rate constants and relative increases in rate for the smaller alcohols e.g. n-butanol, are comparable for Lix 26 and

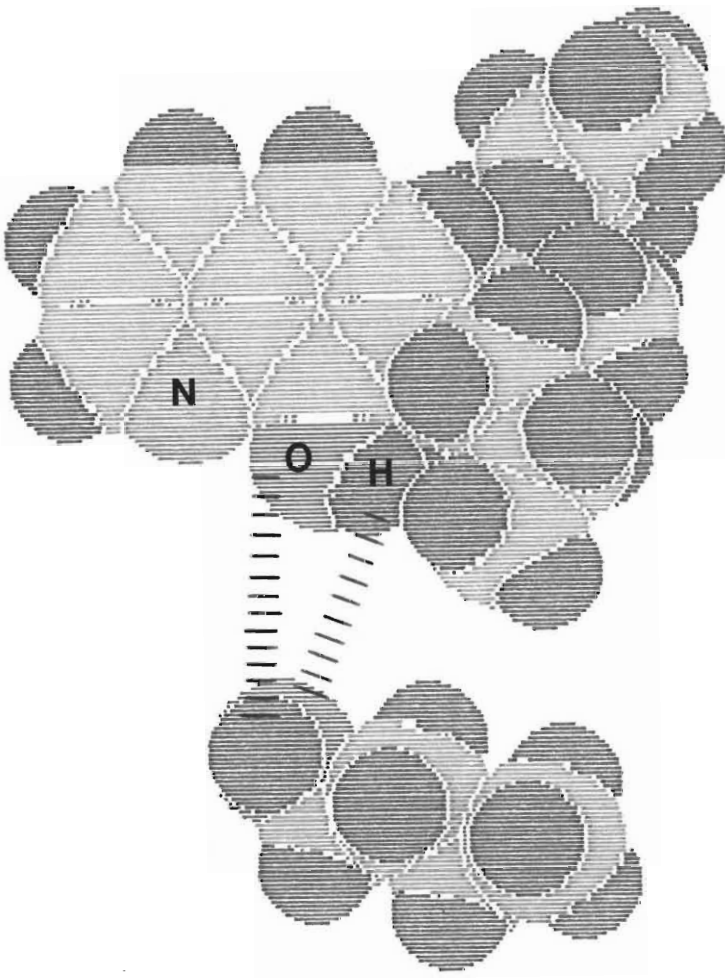


Figure (90). The hydrogen-bonding interaction between n-butanol and TN 02181 (structure A).

TN 01787 (cf. Tables (47) and (48)), but are completely different for TN 02181.

(ii) The extraction kinetic modifying property exhibited by n-propanol shows the least direct comparison between the ligand reagents and it is also the most enigmatic since it affords a better rate of germanium extraction ( $2,04 \times 10^{-3} \text{ s}^{-1}$ ) with TN 02181 than all other modifiers but benzyl alcohol with TN 01787 and Lix 26. It was expected that the high aqueous solubility of the alcohol would reduce its efficacy as a modifier, however the data suggest that it has definite potential in this role.

Thus far, the concentrations of modifiers added to the extractant/diluent solution have been 10 % v/v which is typical of the concentration which would be used in commercial applications. However a detailed study of the effect of increasing the modifier concentration for n-octanol was undertaken to establish an optimal concentration and to determine the effect upon extraction of extremely high modifier concentration. The details of this investigation are summarised in the next section.

### 3.7.3. The Effect of Increasing Modifier Concentration on the Equilibrium Percentage Extraction of Germanium by Lix 26.

It has been mentioned already that the use of modifiers in solvent extraction processes reduces contact times and allows operation under conditions of low ligand concentration and at a pH higher than that which gives the greatest percentage

yield and fastest kinetics in the absence of modifier.

Usually, economics dictate the compositions of aqueous and organic feeds to an hydrometallurgical process and therefore the quantity of modifier added to a ligand solution represents an economic versus efficiency optimum. However, there are also other factors which determine the quantity of modifier which is added to a solvent and one of these is illustrated by the data which follows.

Figure (91) shows the equilibrium percentage extraction of germanium obtained versus the quantity of n-octanol added to a kerosene-type diluent solution of Lix 26 of very low concentration (14,0 g/l). Approximately 64% of the germanium solution is extracted by 40 - 60 % v/v n-octanol solutions compared with 12 % extracted by the ligand with no added modifier. Note that for the experimental conditions given and taking into account the purity of the ligand reagent i.e. 14 g/l  $\equiv$  10,1 g/l purity-corrected Lix 26, the germanium is in stoichiometric excess by approximately 20 %, i.e. 80% extraction is the maximum possible. An important characteristic of Figure (91) is the decrease in extraction which is obtained at very high [n-octanol]. This is probably a result of the formation of a kinetically inactive modifier-extractant adduct species which reduces the quantity of available ligand. This phenomenon has been invoked to explain the reduction in extraction of copper by hydroxyoximes<sup>(216, 217)</sup> and 8-hydroxyquinoline<sup>(218)</sup> systems containing p-nonyl-phenol.

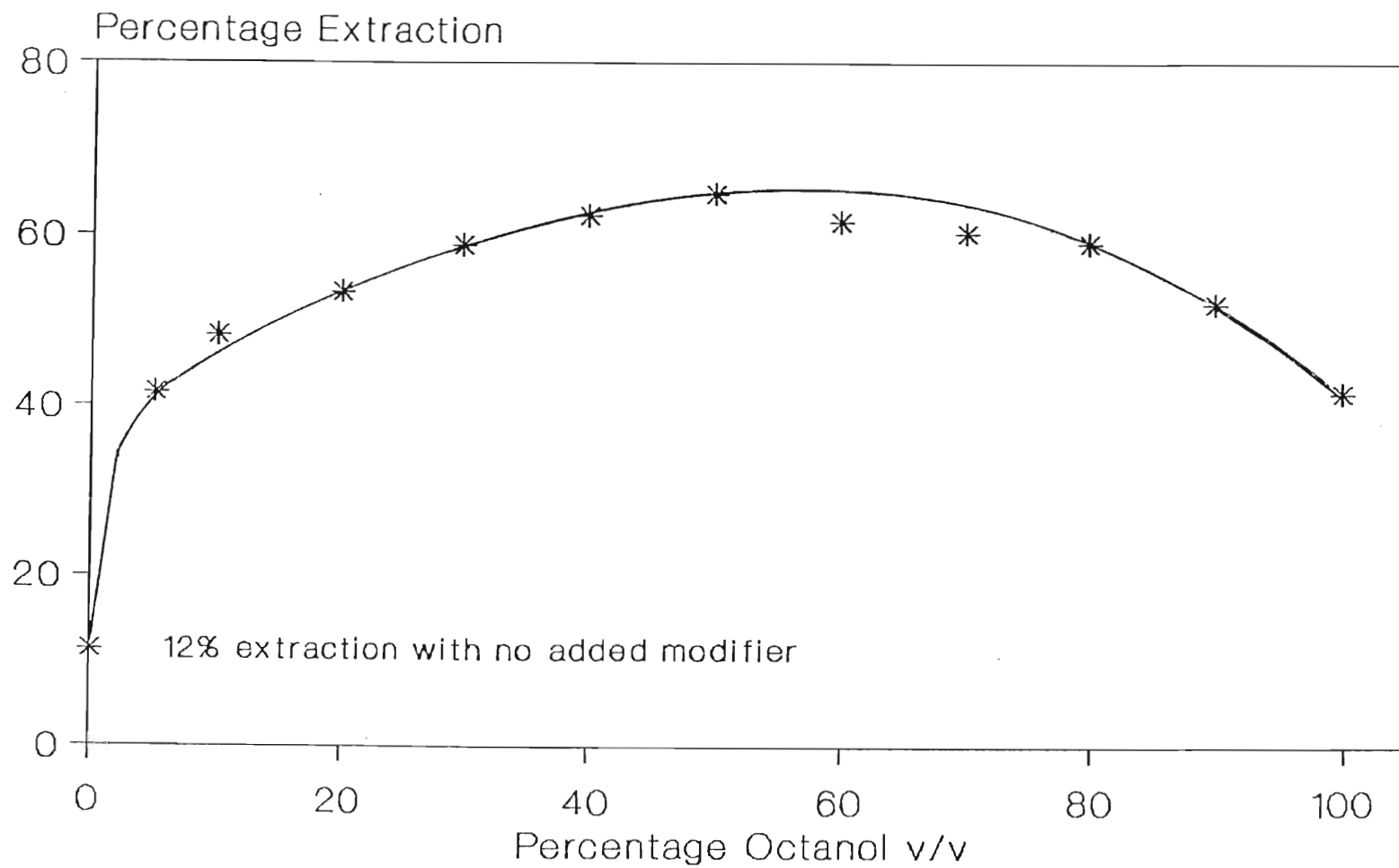


Figure (91). Percentage extraction of germanium by Lix 26 as a function of added n-octanol modifier concentration. Organic phase : 14 g/l Lix 26 in BDH 'Distillate'; Aqueous phase : ~ 1,0 g/l Ge in 0,5 M H<sub>2</sub>SO<sub>4</sub>.

### 3.8. The Extraction Kinetics of 'Acid-Purified' Lix 26.

It is generally recommended<sup>(208)</sup> that commercially available reagents be used for solvent extraction studies since the data obtained is likely to have a greater impact upon the development of an industrial process. However, some workers<sup>(57,127)</sup> recommend that 8-hydroxyquinoline extractants be purified prior to use by washing a toluene solution of the ligand with a number of volumes of acid (1 M H<sub>2</sub>SO<sub>4</sub> or HCl have been utilised). The suggestion is that impurities such as parent oxine and other compounds are protonated and hence removed from the ligand solution. In section 3.3.2, it was shown that free oxine itself does not extract germanium into toluene at low pH although it can affect the initial rate of germanium extraction if present in quantities in excess of 2,0 g/l. It might therefore be expected that an 'acid-purified' solution of extractant would exhibit improved extraction compared with the as-received reagent and this supposition was therefore explored.

Consider the percentage extraction plot of Figure (92). The lower curve shows the extraction behaviour of Lix 26 washed 45 times according to the procedure outlined in Section 2.2.2.4. It is evident from this plot, and a comparison of the values of  $k_f(\text{obs})$  and the initial rate, that the acid-wash procedure removes material which assists extraction. In light of the above discussion, the removal of free oxine should have rendered the ligand solution more efficient yet this is not observed in practice. It is suggested that washing with acid

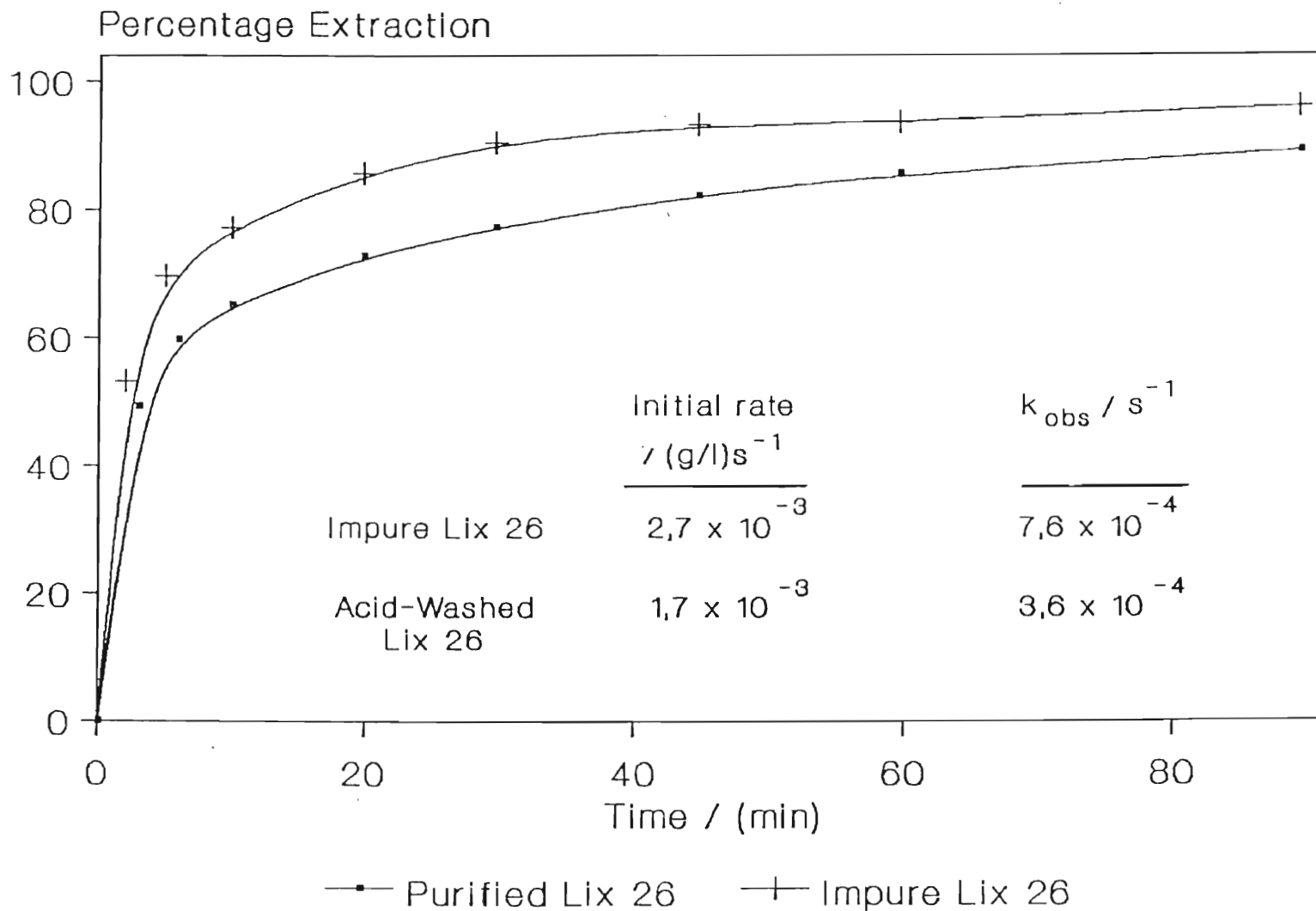


Figure (92). Comparison of the extraction kinetics of acid-purified Lix 26 with the impure as-received commercial material. Organic phase : 50 g/l Lix 26 in toluene; Aqueous phase :  $\sim 0,65$  g/l Ge in 1,5 M H<sub>2</sub>SO<sub>4</sub>. Initial rates and slower 'equilibrium' rate constants ( $k_{obs}$ ) are compared in the plot. The 'purified' sample was washed 45 times with acid according to the procedure outlined in Section 2 2 2 4



alters the composition of the ligand solution through the removal of one or more of the impurities listed in Table (6), which obviously either extract germanium or modify the extractant solution in some beneficial way. Accordingly, it is suggested that acid-washing of ligand solutions offers little simplification for kinetic studies on these systems.

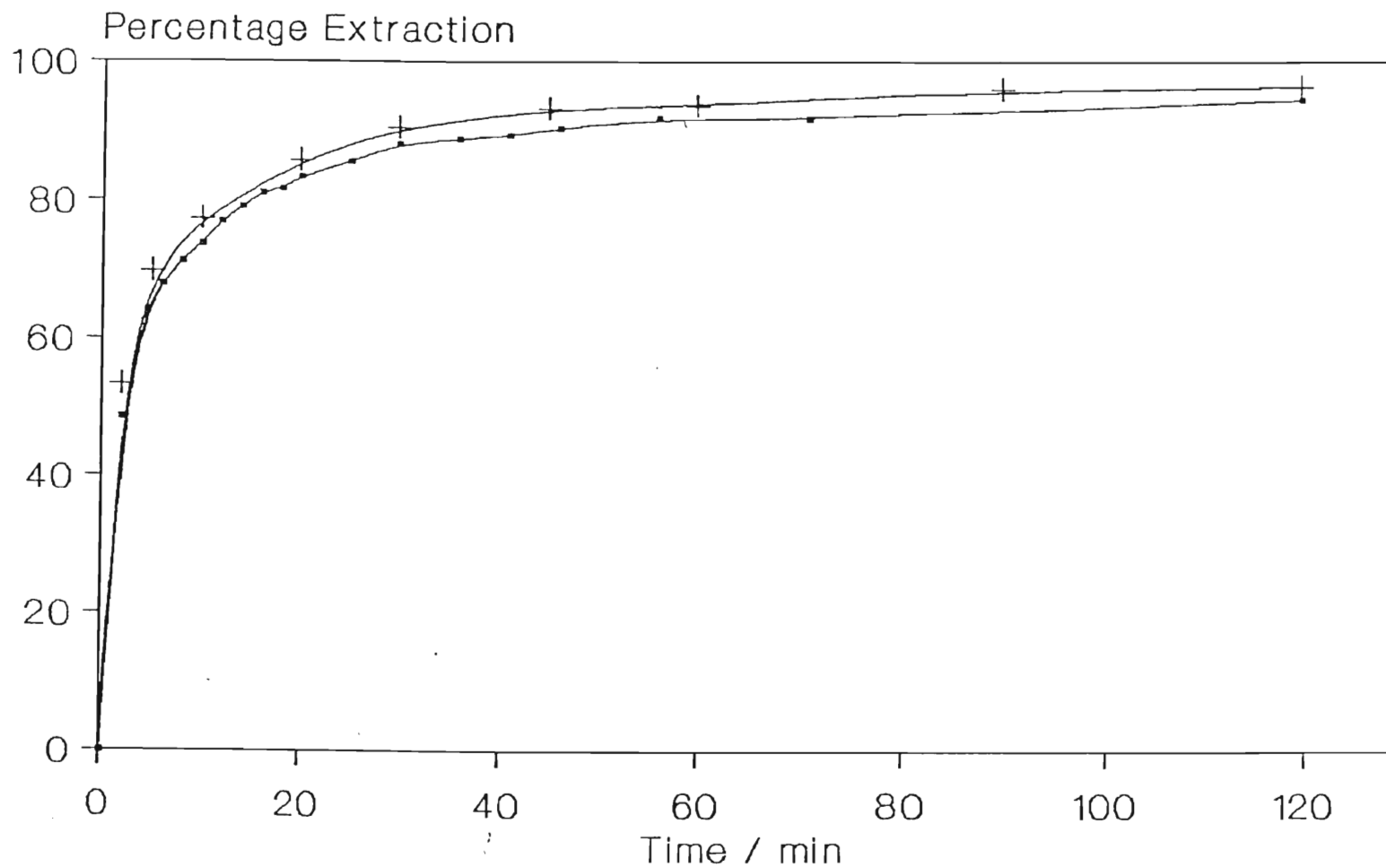
### 3.9. The Use of the AKUFVE Apparatus for Following the Extraction Kinetics of Germanium

A description of the AKUFVE apparatus and the uses to which it has been put by other workers, was given in Section 2.4.2.1. From its introduction to the field of solvent extraction in 1967, the instrument was reported by various workers to be revolutionary in the acquisition of equilibrium, thermodynamic and kinetic data relating to solvent extraction processes. From the point of view of this work, the greatest interest was associated with the use of the instrument to follow the kinetics of germanium extraction by the 7-alkylated-8-hydroxyquinoline derivatives and to determine the enthalpy of extraction. It is worth mentioning that it was intended to utilise this instrument exclusively for the elucidation and mechanistic interpretation of rate data, however for the reasons which are enunciated in Section 3.9.1 it appears that, in retrospect through comparison with shaking data, the method yields rate data which are consistently low compared with a shaking apparatus suggesting that the technique does not achieve the operating conditions manifest by a vigorous shaker. These comparisons of kinetic data are described in the

section following.

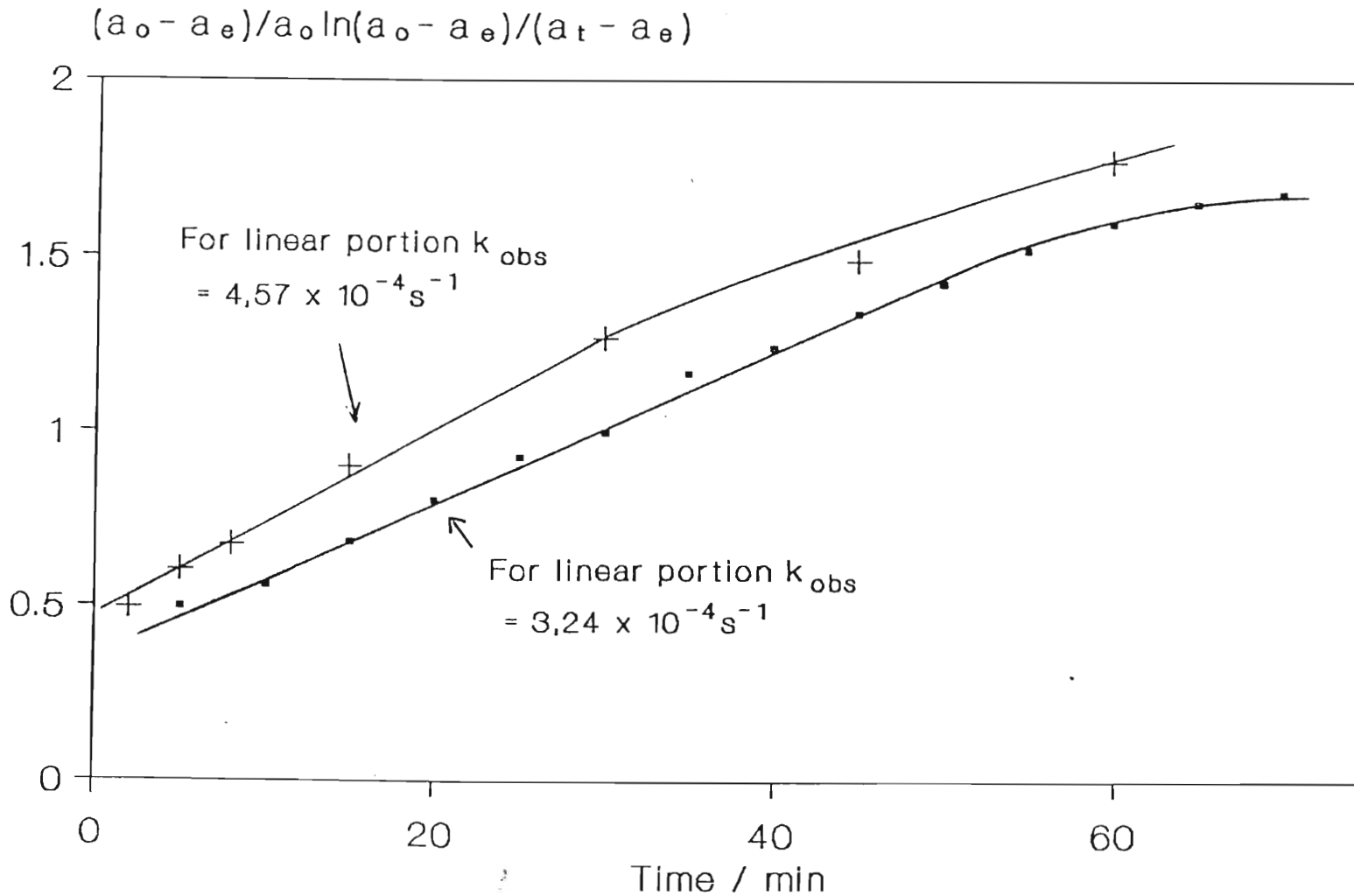
### 3.9.1. A Comparison of the Rate Data Obtained with the AKUFVE and Mechanical Shaker

Figures (93) and (94) show the difference in the observed extraction kinetics for the two techniques. It is evident from these plots that the AKUFVE apparatus apparently retards extraction and yields different values of  $k_f(\text{obs})$  from shaking. In the examples shown, the contrast in behaviour is not too significant, however the observed difference becomes more pronounced as the concentration of ligand increases. In Table (49), values of  $k_f(\text{obs})$  calculated from semi-logarithmic plots are compared for the two sets of apparatus. It is apparent from these data that the AKUFVE apparatus predicts slower kinetics over the full range of extractant concentration studied and that this becomes more important at high [HL].



—■— AKUFVE data    —+— Shaker data

Figure (93). Comparison of the extraction kinetics of Lix 26 in the AKUFVE apparatus with those observed with a mechanical shaker. Aqueous phase : ~ 0,65 g/l Ge in 1,5 M H<sub>2</sub>SO<sub>4</sub>; Organic phase : ~ 50 g/l Lix 26 in AR toluene. Phase volumes 100 ml.



■ AKUFVE Data    + Shaking Data

Figure (94). A comparison of the germanium extraction kinetics observed using the AKUFVE and mechanical shaker. Aqueous phase : ~ 0,20 g/l Ge in 1,5 M H<sub>2</sub>SO<sub>4</sub>; Organic phase : 35 g/l Lix 26 in toluene.

| [Lix 26] / (g/l) | $k_f(\text{obs}) / \text{s}^{-1}$ |                       |
|------------------|-----------------------------------|-----------------------|
|                  | Mechanical Shaker                 | AKUFVE Apparatus      |
| 25,0             | $1,58 \times 10^{-4}$             | $9,21 \times 10^{-5}$ |
| 35,0             | $4,57 \times 10^{-4}$             | $3,24 \times 10^{-4}$ |
| 50,0             | $1,17 \times 10^{-3}$             | $4,95 \times 10^{-4}$ |
| 75,0             | $2,32 \times 10^{-3}$             | $8,53 \times 10^{-4}$ |
| 100,0            | $7,44 \times 10^{-3}$             | $2,06 \times 10^{-3}$ |
| 150,0            | $1,05 \times 10^{-2}$             | $4,21 \times 10^{-3}$ |

Table (49). Comparison of observed forward rate constants for germanium extraction in the slower 'equilibrium' regime by Lix 26 in the AKUFVE apparatus and mechanical shaker. [Ge] ~ 0,200 g/l.

Differences in kinetic behaviour were also observed in experiments where the aqueous phase pH was varied. Compare, for example, the values of  $k_f(\text{obs})$  obtained for the two methods at pH 1,00 and 1,94 viz.

| pH   | $k_f(\text{obs}) / \text{s}^{-1}$ |                       |
|------|-----------------------------------|-----------------------|
|      | Mechanical Shaker                 | AKUFVE Apparatus      |
| 1,00 | $1,90 \times 10^{-4}$             | $3,46 \times 10^{-5}$ |
| 1,94 | $5,67 \times 10^{-5}$             | $2,14 \times 10^{-5}$ |

Table (50). Values of  $k_f(\text{obs})$  for the slow 'equilibrium' region for the mechanical shaker and AKUFVE apparatus at pH 1,00 and 1,94. [Ge] ~ 0,65 g/l; [Lix 26] : 50 g/l.

It is clear from these data that the experimental techniques are not equivalent and that the way in which phases mix, equilibrate and separate influences the overall kinetic behaviour.

Consider first the contact time of the solute-containing aqueous phase with the ligand-containing organic phase. The instrument specifications (Table (17)) quote an average hold-up time from centrifuge exit and re-entry into the mixing chamber of 1,5 seconds. For reactions with half-life  $> 2$  minutes this is experimentally acceptable, however such a hold-up time for some of the kinetic runs performed in this work (high ligand concentration and 1,5 M  $\text{H}_2\text{SO}_4$  where  $t_{\frac{1}{2}} < 2$  minutes) may be a contributing factor to the increased difference in value of observed rate constants summarised in Table (49). Another important point to consider for the AKUFVE apparatus are the volumes which are in contact in the assembly. During cyclisation of the dual phase mixture, in this work 600 ml in total, 120 ml resides in the centrifuge and approximately 50 ml in the interleading tubes and sampling ports at any particular time. Essentially then, at any particular time, 30% of the phase mixture is variously in contact varying from completely separated (in the collecting chambers of the H-centrifuge-see Figure (33) and during the 1,5 second period mentioned above) to incompletely separated in the bowl of the H-centrifuge. An interesting question arises concerning the fate of interfacially adsorbed species in the centrifuge. As the organic/aqueous mixture separates in the centrifuge baffles, do adsorbed species such as  $\text{GeL}^{3+}$  and  $\text{GeL}_2^{2+}$ , both of which are relatively hydrophobic, accompany the

organic phase or are they returned to be subsequently equilibrated with the two-phase mixture in the mixer? The procedures which have been adopted in this work cannot resolve this question and therefore it is impossible to predict to what extent the phenomenon affects data acquired.

Another consideration which should be noted is the fluctuation in interfacial area which occurs between the mixer and centrifuge. In the mechanical shaker, the area of contact between the aqueous and organic phases is at a maximum at all times except for a few seconds during sampling, however for the AKUFVE system, the phase contact areas fluctuate according to locality. It would be impossible therefore to make any judgements regarding the dependence of the rate on the interfacial area.

Notwithstanding the inherent problems listed above, the AKUFVE apparatus can still be a useful tool (e.g. in the determination of equilibrium data, partition coefficients and thermodynamic constants where relative rates are utilised), however other techniques are more likely to be representative in kinetic studies.

### 3.9.2. The Determination of Thermodynamic Parameters via AKUFVE Data.

The effect of temperature on the observed reaction kinetics of a solvent extraction process is an important study since calculated values of activation energy, entropy, enthalpy and Gibbs free energy changes are illuminating in the interpretation of spontaneity of a process and a necessary

prerequisite to thermodynamic model development.

Various workers have calculated values of activation energy,  $E_a$ , for solvent extraction processes using various ligands, diluents, metal-ions and practical assemblies. Some of the more important results to this work are summarised in Table (51). The data presented in Table (51) indicates first that values of  $E_a$  are positive and second that they are of the order of approximately 20-30 kJ mol<sup>-1</sup> which is within the 'rule-of-thumb' range (< 32 kJ mol<sup>-1</sup>) for diffusion-controlled processes<sup>(220)</sup>.



| Reaction. (metal-ligand/diluent)        | Reaction Cell Type | $E_a$ / kJ mol <sup>-1</sup> | Reference |
|---|--------------------|------------------------------|-----------|
| Fe <sup>3+</sup> - Kelex 100/methanol   | S-F.Spec           | 64,0                         | 200       |
| Fe <sup>3+</sup> - 8-HQ/methanol        | S-F.Spec           | 23,0                         | 200       |
| Cu <sup>2+</sup> - Lix 65N/toluene      | AKUFVE             | 25,1                         | 150       |
| Cu <sup>2+</sup> - Kelex 100/toluene    | AKUFVE             | 28,0                         | 57        |
| Cu <sup>2+</sup> - Lix 64N/xylene       | Single-Drop        | 27,2                         | 219       |
| Fe <sup>3+</sup> - 8-HQ/chloroform      | Lewis Cell         | 26,4 (pH 1,20)               | 127       |
| Fe <sup>3+</sup> - 8-HQ/chloroform      | Lewis Cell         | 10,7 (pH 2,35)               | 127       |
| Ni <sup>2+</sup> - 8-HQ/aqueous         | S-F.Spec           | 37,2                         | 204       |
| Cu <sup>2+</sup> - Kelex 100/chloroform | Lewis Cell         | 12,5                         | 59        |
| Cu <sup>2+</sup> - Lix 64N/chloroform   | Lewis Cell         | 19,5                         | 59        |

Table (51). Activation energies for various metal-ligand chelate complexation solvent extraction reactions and reaction assemblies. S-F.S : Stopped-Flow Spectrophotometry.

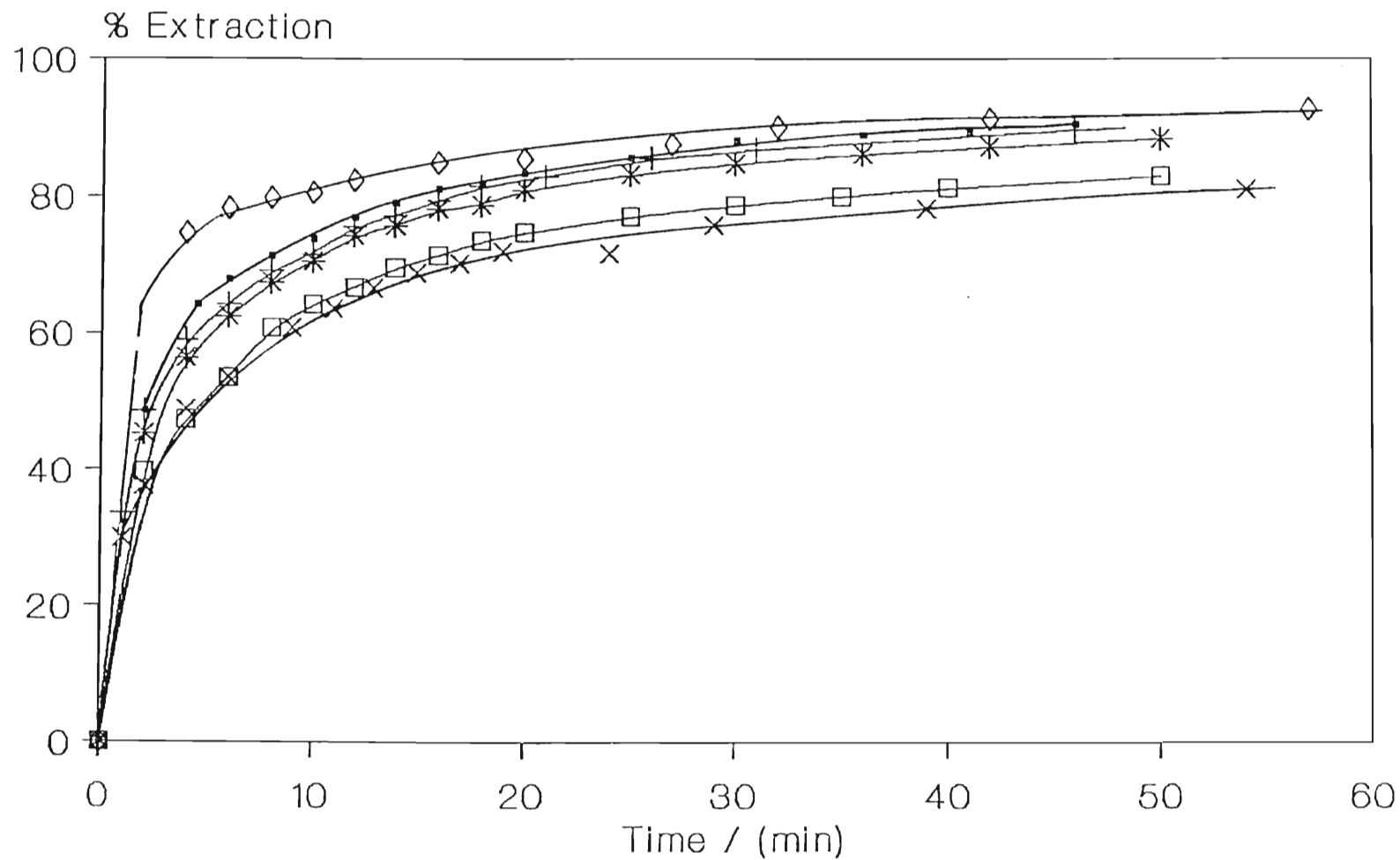
8-HQ : 8-hydroxyquinoline.

An indication of the effect of increasing temperature on the extraction kinetics of germanium by Lix 26 is given in Figure (95), where it is evident that increasing the temperature lowers the rate of extraction and equilibrium percentage extraction. Semi-logarithmic plots of these data yielded the values of  $k_f(\text{obs})$  for the slow equilibrium regime given in Table (52).

| Temperature<br>/K | 1/T / K <sup>-1</sup>  | $k_f(\text{obs})$ / s <sup>-1</sup> | ln $k_f(\text{obs})$ |
|-------------------|------------------------|-------------------------------------|----------------------|
| 288,15            | $3,470 \times 10^{-3}$ | $1,500 \times 10^{-3}$              | -6,502               |
| 298,15            | $3,354 \times 10^{-3}$ | $1,353 \times 10^{-3}$              | -6,605               |
| 303,15            | $3,299 \times 10^{-3}$ | $1,212 \times 10^{-3}$              | -6,715               |
| 308,15            | $3,245 \times 10^{-3}$ | $1,079 \times 10^{-3}$              | -6,832               |
| 313,15            | $3,193 \times 10^{-3}$ | $1,051 \times 10^{-3}$              | -6,858               |
| 318,15            | $3,143 \times 10^{-3}$ | $9,172 \times 10^{-4}$              | -6,994               |

Table (52). Observed values of forward rate constants for germanium extraction by Lix 26 as a function of temperature (pH ~ -0,21, Phase Volumes : 300 ml, [Lix 26] = 50 g/l, AKUFVE apparatus).

The activation energy can be determined from the experimental data by plotting ln  $k_f(\text{obs})$  versus 1/T. Figure (96) shows that a decrease in reaction rate with increasing temperature is observed. A linear plot with gradient 1502 K<sup>-1</sup> and intercept



◇ 15° C • 25° C + 30° C \* 35° C □ 40° C × 45° C

Figure (95). The effect of temperature on percentage extraction of germanium by Lix 26. All plots obtained with the AKUFVE assembly. Aqueous phase : ~ 0,65 g/l Ge in 1,5 M H<sub>2</sub>SO<sub>4</sub>; Organic phase : 50 g/l Lix 26 in AR toluene; Phase volumes 300 ml.

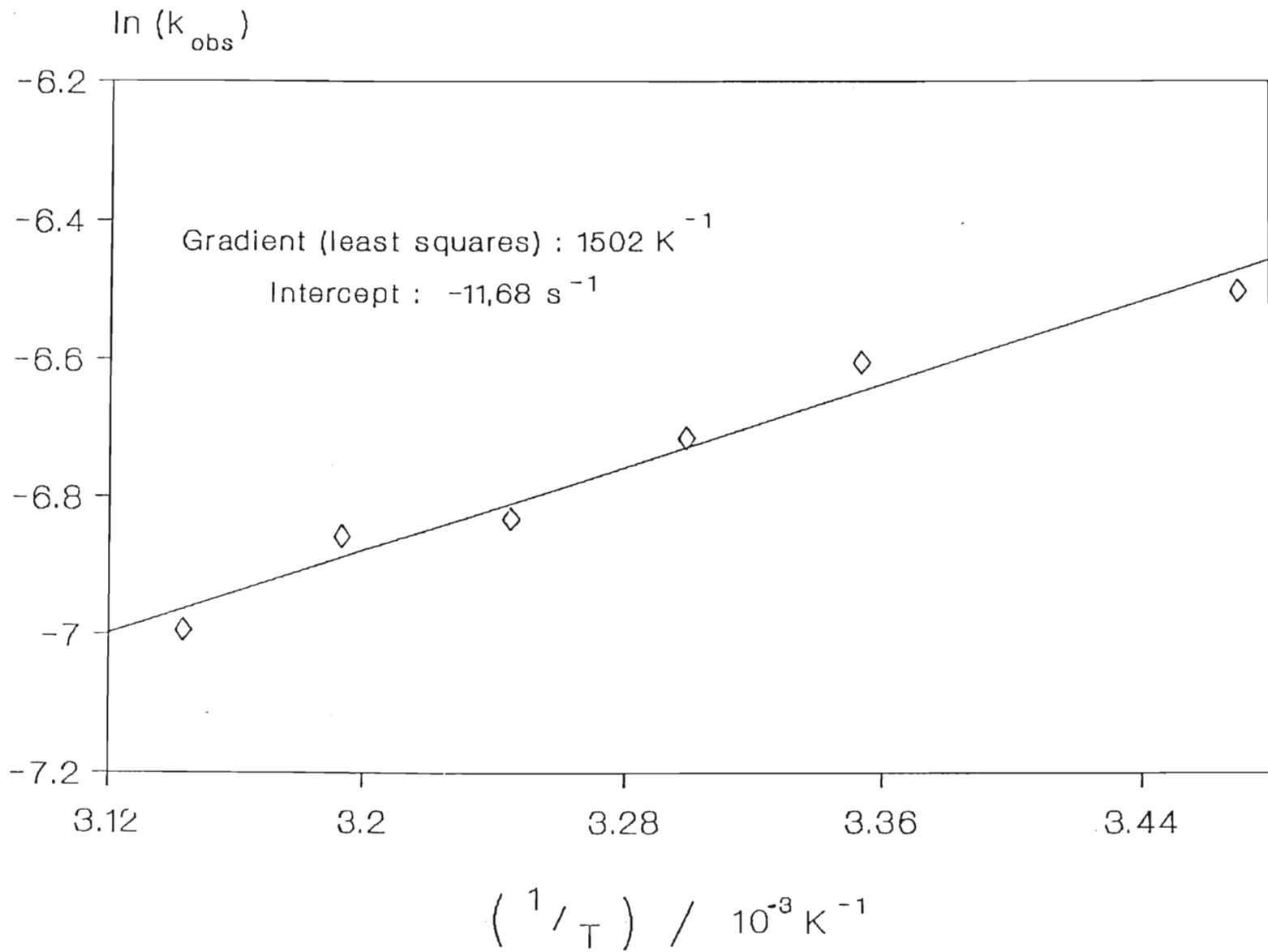


Figure (96). Arrhenius plot of  $\ln(k_{\text{obs}})$  vs  $1/T$  for the extraction of germanium from 1,5 M  $\text{H}_2\text{SO}_4$  solutions by 50 g/l Lix 26 solutions in toluene using the AKUFVE apparatus.

$-11,68 \text{ s}^{-1}$  is obtained. Using the linear form of the Arrhenius equation  $k = Ae^{-(E_a/RT)}$  gives  $E_a = -12,49 \text{ kJ mol}^{-1}$  and  $A = 8,5 \times 10^{-6} \text{ s}^{-1}$ . Note that although the discussion in the previous section indicated acquisition of low experimental values of  $k_f(\text{obs})$  associated with the AKUFVE apparatus, it is improbable that data from a shaking apparatus would yield a different gradient, although the intercept may show a slight difference.

Following the calculation of  $E_a$  it is possible to calculate the enthalpy of activation,  $\Delta H^\ddagger$ , at any temperature using Equation (117):

$$\Delta H^\ddagger = E_a - RT \quad (117)$$

The molecularity of the rate-determining step for germanium extraction (see Equation (57)) is taken to be unity because  $\Delta(PV)$  for a liquid phase reaction is essentially zero. The entropy and free energy of activation can then be calculated via Equations (118) and (119) respectively:

$$\Delta S^\ddagger = R \ln \left( \frac{N_o h}{R T} k_f e^{\Delta H^\ddagger / RT} \right) \quad (118)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger \quad (119)$$

where  $N_o$  = Avogadro's Number

$h$  = Planck's Constant

At  $25^\circ\text{C}$ , these equations yield the following :  $\Delta H^\ddagger = -14,97 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -350,0 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\Delta G^\ddagger = +89,4 \text{ kJ mol}^{-1}$ . The negative value of  $\Delta H^\ddagger$  implies that an increase in temperature favours the reverse reaction of

Equation (57) i.e.  $\text{GeL}_3^+$  disproportionates into free ligand and  $\text{GeL}_2^{2+}$ . The positive value of  $\Delta G^\ddagger$  and negative value of  $\Delta S^\ddagger$  suggest that the reaction is not entropy driven and neither is it thermodynamically favourable.

It is important to remember that the process which is being thermodynamically modelled involves reaction at an aqueous/organic interface. There are very few reports of a decrease in extraction rate with increasing temperature for solvent extraction processes. Cote and Bauer<sup>(203)</sup> observed a decrease in the extraction rate of germanium by Kelex 100. This offers support for the observations reported here but no data was presented by these authors. It was therefore decided to examine this effect more closely. Figure (97) shows the change in the distribution coefficient with increasing temperature, where  $D = [\text{Ge}]_{\text{org}} / [\text{Ge}]_{\text{aq}}$  at equilibrium. Additionally Figure (98) shows the change in initial extraction rate with increasing temperature. It is clear from these plots and Figure (95) that the rate of extraction is affected in the initial and slower 'equilibrium' regions and that the overall percentage extraction decreases with temperature. The following explanations are postulated for this behaviour:

- (i) An increase in the temperature increases the mobility of the ligand at the interface resulting in a decrease in the available ligand at the interface due to less tight packing.
- (ii) The back-reaction kinetics become more significant as the temperature increases.

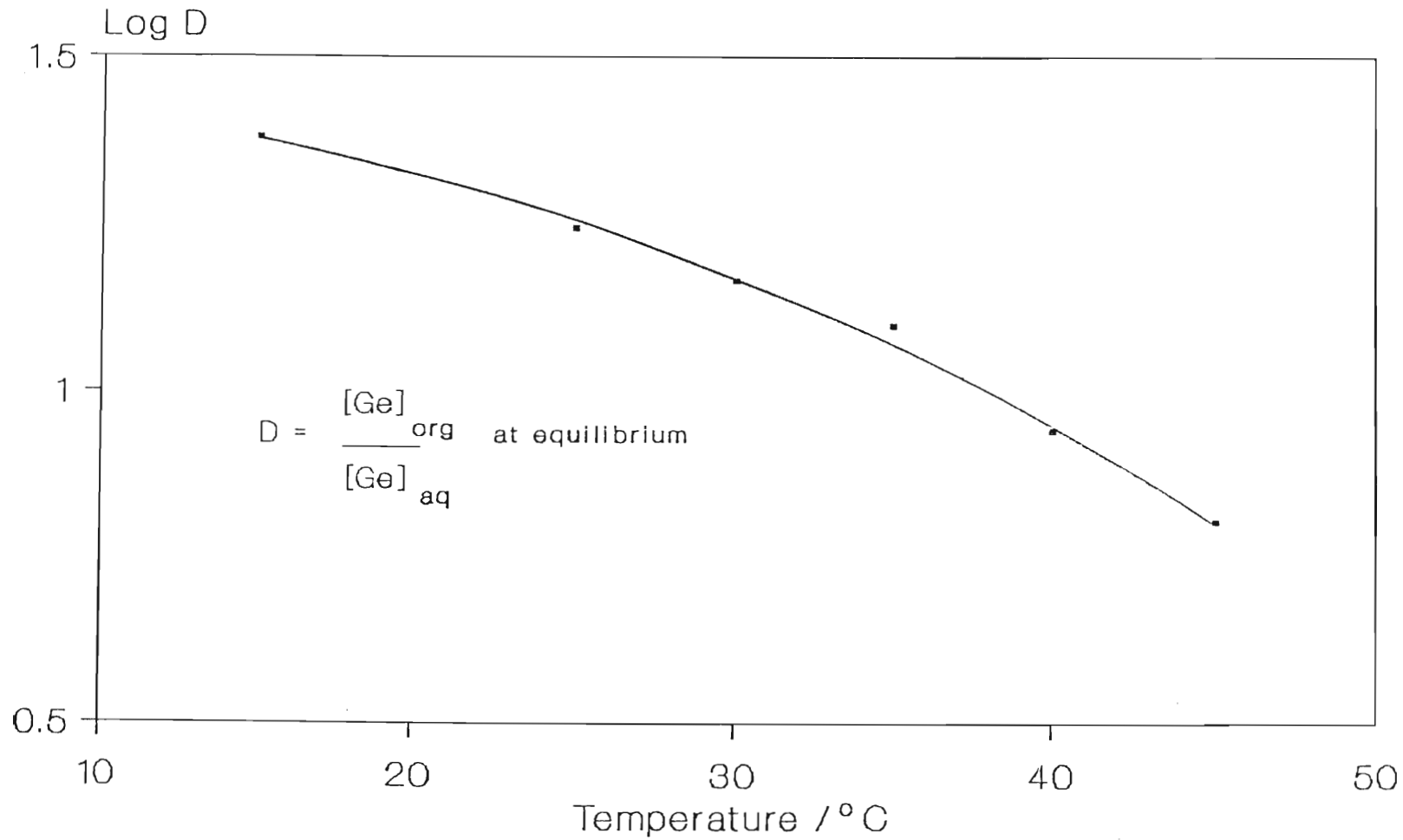


Figure (97). Log of the distribution coefficient (as defined in the figure) as a function of temperature for a 50 g/l solution of Lix 26 in toluene. Aqueous phase : ~ 0,65 g/l Ge in 1,5 M H<sub>2</sub>SO<sub>4</sub>.; Phase volumes : 300 ml.

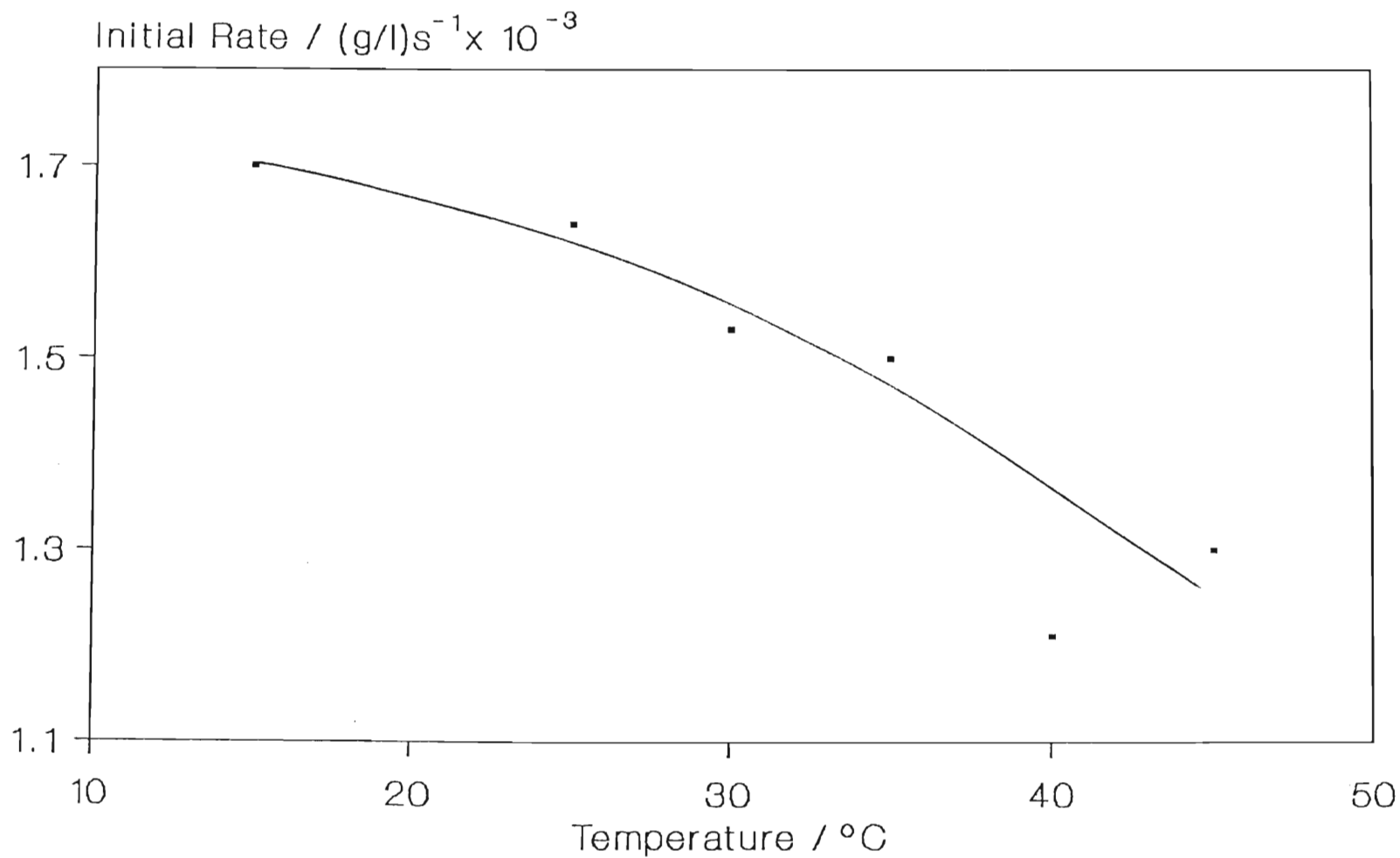


Figure (98). Observed initial rate for the complexation of germanium by Lix 26 as a function of temperature in the AKUFVE apparatus. Organic phase : 50 g/l Lix 26 in AR toluene; Aqueous phase : ~ 0,65 g/l Ge in 1,5 M H<sub>2</sub>SO<sub>4</sub>; Phase volumes 300 ml.

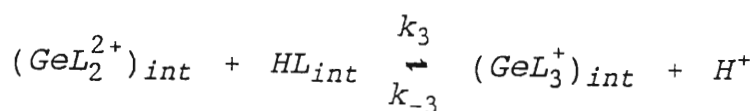


It is also possible that the germanium speciation shown in Figure (67) is altered in some way which favours the shifting of the equilibria towards higher hydroxy species.

An indication of the importance of (ii) above is given by the semi-logarithmic plots of  $a_e/a_o \ln (a_o - a_e)/(a_t - a_e)$  versus time of Figure (99). Values of  $k_b(\text{obs})$  calculated from the slopes of the linear regions of these data are presented in Table (53).

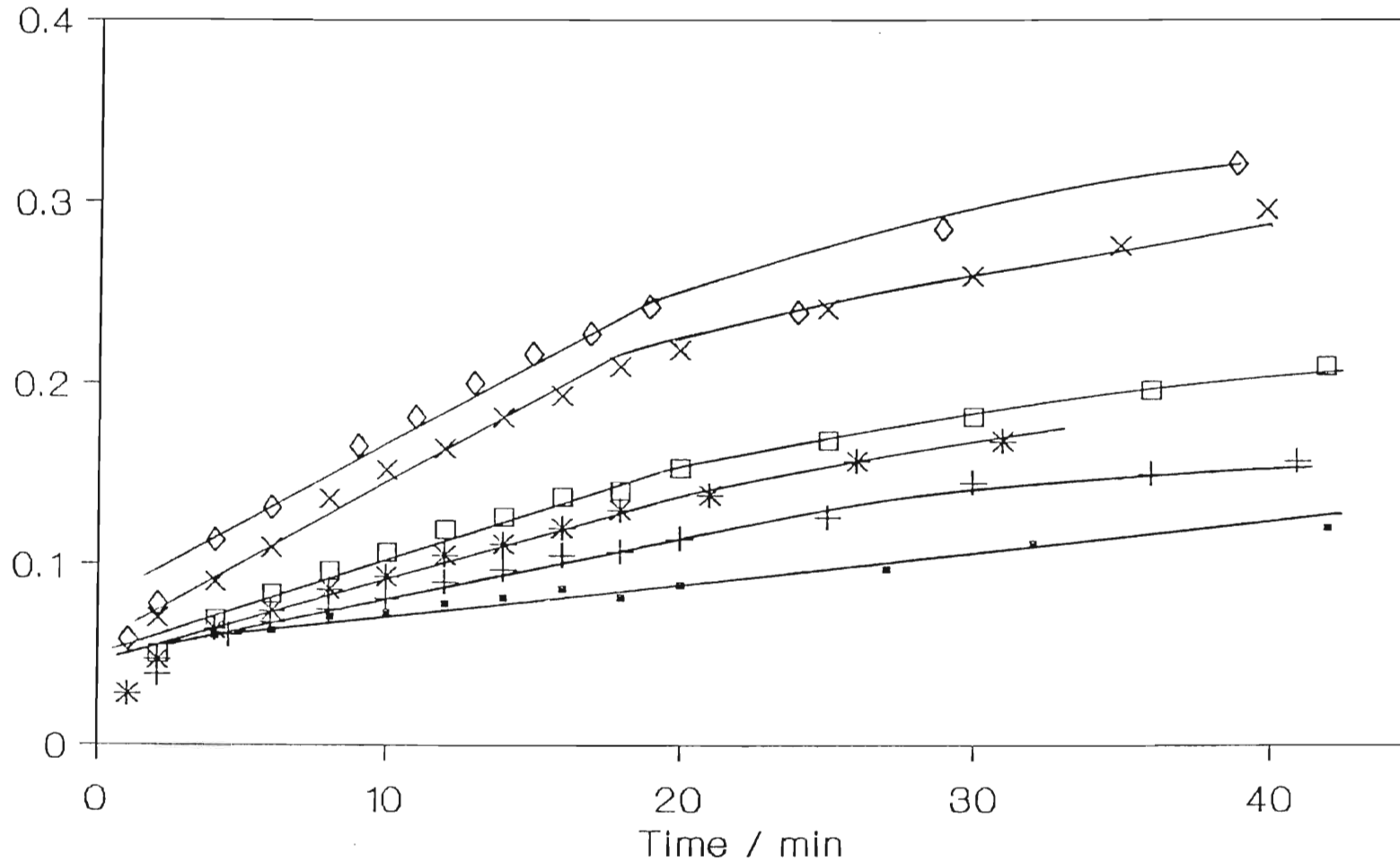
| Temperature /K | 1/T /K <sup>-1</sup>   | $k_b(\text{obs}) / \text{s}^{-1}$ | ln $k_b(\text{obs})$ |
|----------------|------------------------|-----------------------------------|----------------------|
| 288,15         | $3,470 \times 10^{-3}$ | $2,37 \times 10^{-5}$             | -10,65               |
| 298,15         | $3,354 \times 10^{-3}$ | $4,32 \times 10^{-5}$             | -10,05               |
| 303,15         | $3,299 \times 10^{-3}$ | $7,39 \times 10^{-5}$             | -9,51                |
| 308,15         | $3,245 \times 10^{-3}$ | $9,08 \times 10^{-5}$             | -9,31                |
| 313,15         | $3,193 \times 10^{-3}$ | $1,38 \times 10^{-4}$             | -8,89                |
| 318,15         | $3,143 \times 10^{-3}$ | $1,66 \times 10^{-4}$             | -8,71                |

Table (53). Values of observed reverse reaction rate constants for the rate determining step, summarised below, at various temperatures for the extraction of germanium by Lix 26 in the AKUFVE apparatus.



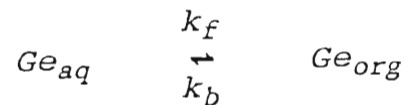
Values of  $k_b(\text{obs})$  were calculated using Equation (47).

$$a_e / a_o \ln(a_o - a_e) / (a_t - a_e)$$



■ 15°C    + 25°C    \* 30°C    □ 35°C    x 40°C    ◇ 45°C

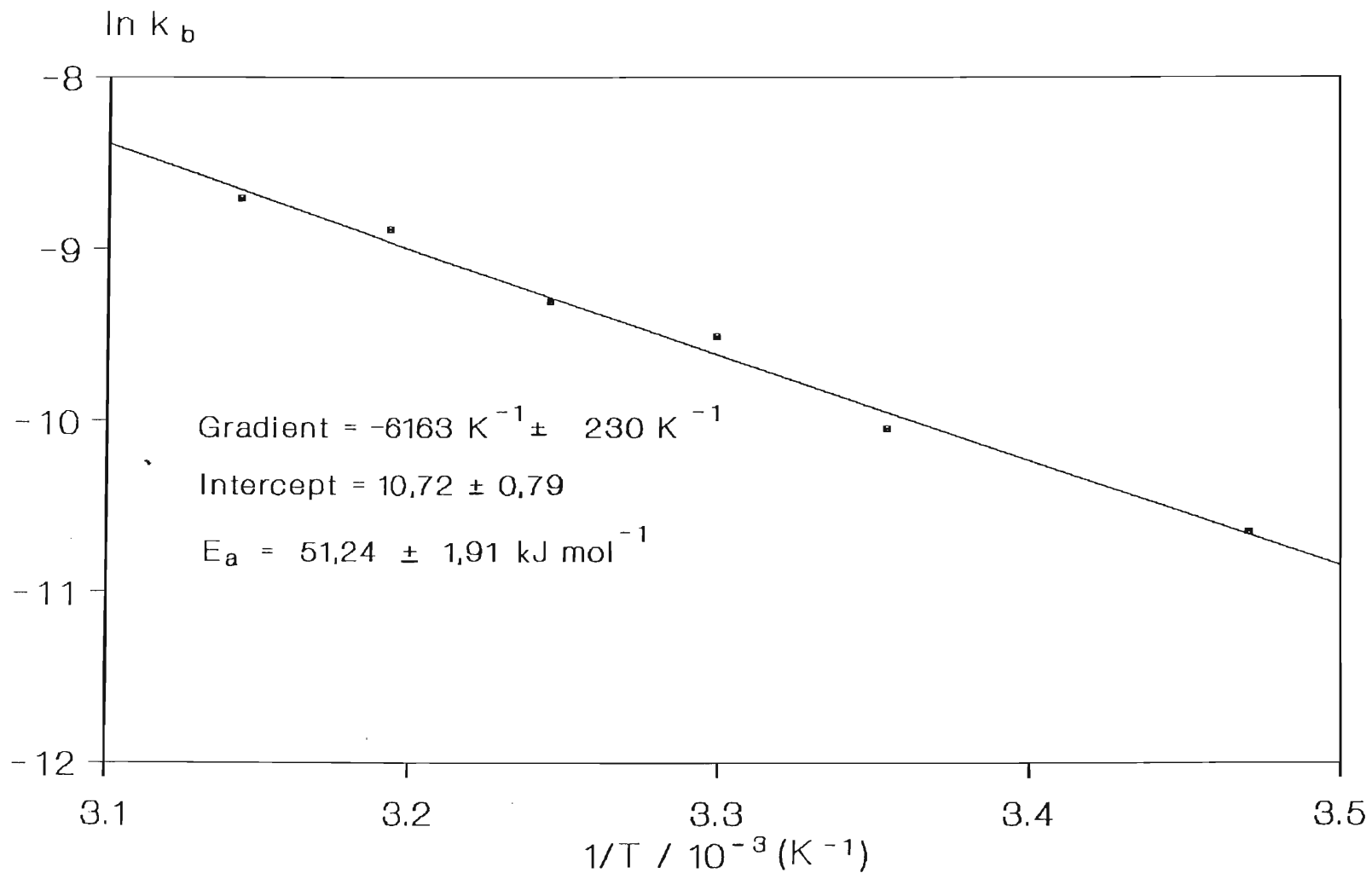
Figure (99). Observed reverse rate constants  $k_b$ , calculated via plots of Equation (47), for the germanium extraction process:



as a function of time for various temperatures in the AKUFVE apparatus. Organic phase : 50 g/l Lix 26 in AR toluene; Aqueous phase : ~ 0,65 g/l Ge in 1,5 M H<sub>2</sub>SO<sub>4</sub>; Phase

Figure (100) shows the plot of  $\ln k_b(\text{obs})$  vs  $1/T$  obtained using these data. This is linear over the temperature range investigated (15-45°C) with a gradient of  $-6163 \pm 230 \text{ K}^{-1}$  and intercept  $10,72 \pm 0,79 \text{ s}^{-1}$ . The activation energy can therefore be calculated as  $+51,24 \pm 1,91 \text{ kJ mol}^{-1}$ . For the reverse rate process therefore, a positive activation energy is apparent. Calculating other thermodynamic parameters via Equations (117) to (119) gives,  $\Delta H^\ddagger = 48,76 \pm 1,91 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -(166,3 \pm 7,8) \text{ J K}^{-1} \text{ mol}^{-1}$ , and  $\Delta G^\ddagger = +98,3 \pm 3,0 \text{ kJ mol}^{-1}$  at 25 °C. Comparing these values with those for the forward reaction process of Equation (57), shows that at 25°C the reverse process is more entropically favoured i.e. less negative  $\Delta S^\ddagger$ , but less energetically favoured (higher positive value of  $\Delta G^\ddagger$ ), than the forward rate process.

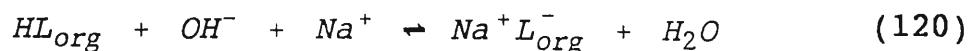
In conclusion, it must be noted that while these data indicate a low feasibility of extraction as the temperature is raised, the thermodynamic treatment which has been utilised here is relevant to a homogeneous reaction mechanism, hence the values of activation parameters calculated above reveal little information about the complex equilibria which exist between the two phases in contact - this point is further discussed in Section 3.15 in which an holistic kinetic model of the extraction processes and partitioning effects are described.



**Figure (100).** Observed change in the reverse rate constant as defined for Figure (99), as a function of temperature in the AKUFVE apparatus. Organic phase : 50 g/l Lix 26 in toluene; Aqueous phase :  $\sim 0,65 \text{ g/l Ge}$  in  $1,5 \text{ M H}_2\text{SO}_4$ ; Phase volumes : 300 ml.

### 3.10. The Kinetics of Germanium Stripping by Aqueous Hydroxide Solutions

Stripping is the reverse process to extraction in which 'loaded' ligand is stripped of its metal ion by contact with an appropriate aqueous species, usually  $\text{OH}^-$  or  $\text{H}^+$ . In Section 3.4, the effect of pH on extraction and the nature of the species extracted were discussed. In order to demonstrate what conditions would be suitable to strip the metal ion from the ligand i.e. favour the back-reactions, it is necessary to review some of the details which were summarised there. First consider Equations (83) - (89) on page 257 and Equation (120) below:

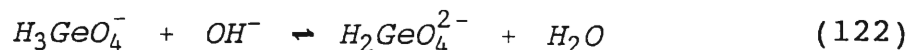
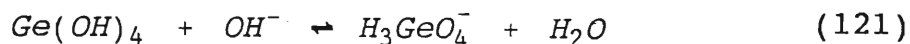


In this scheme Equation (83) represents extraction of germanium for  $\text{pH} \geq 3$ , Equations (84) to (88) summarise extraction for  $\text{pH} \leq 2$  and Equations (89) and (120) indicate extraction of  $\text{H}^+$  and  $\text{Na}^+$  respectively. For pH 2-3 a combination of Equations (83) to (88) constitute the overall reactions.

Examination of Equations (86) to (88) shows that an increase in acidity should promote back-extraction and the formation of species  $\text{Ge}(\text{OH})_i^{(4-i)+}$  for  $i = 0, 1, 2$ . Furthermore the uptake of  $\text{H}^+$  via Equation (89) and the concomitant utilisation of HL favours a shift to the left of Equations (83) to (88). Essentially then, at high acidity, back extraction is favoured and is a possible route toward stripping the metal ion from

the ligand. Cote and Bauer<sup>(53)</sup> determined the percentage stripping of germanium from Kelex 100 by this method and concluded that even at very high acidities (4 M H<sub>2</sub>SO<sub>4</sub>), the method was inefficient.

Consider now the effect of raising the pH on the equilibria of Equations (83)-(89) and (120). If the acidity is decreased then GeL<sub>3</sub><sup>+</sup>HSO<sub>4</sub><sup>-</sup> will be transformed into Ge(OH)<sub>4</sub> and for pH > 3 the only species residing in the organic phase will be GeL<sub>2</sub>(OH)<sub>2</sub> and since this complex extracts to a much lesser degree than GeL<sub>3</sub><sup>+</sup>HSO<sub>4</sub><sup>-</sup>, much of the Ge(IV) will be present in the aqueous phase. Thus for 3 < pH < 8, reasonable stripping can be expected, however to completely strip the organic phase of germanium requires that the pH be increased to 11 or greater. Consider Figure (101) which summarises the germanium species existing for pH > 4. At pH > 11, the only species which can exist in aqueous solution are H<sub>3</sub>GeO<sub>4</sub><sup>-</sup> and H<sub>2</sub>GeO<sub>4</sub><sup>2-</sup> which are both complex anionic molecules and do not react with HL. Thus, under conditions of high pH, Equation (83) shifts to the left and the anionic species begin to form via Equations (121) and (122).



Hence, when germanium loaded ligand, GeL<sub>3</sub><sup>+</sup>HSO<sub>4</sub><sup>-</sup> is contacted with an OH<sup>-</sup> solution of sufficient concentration, the

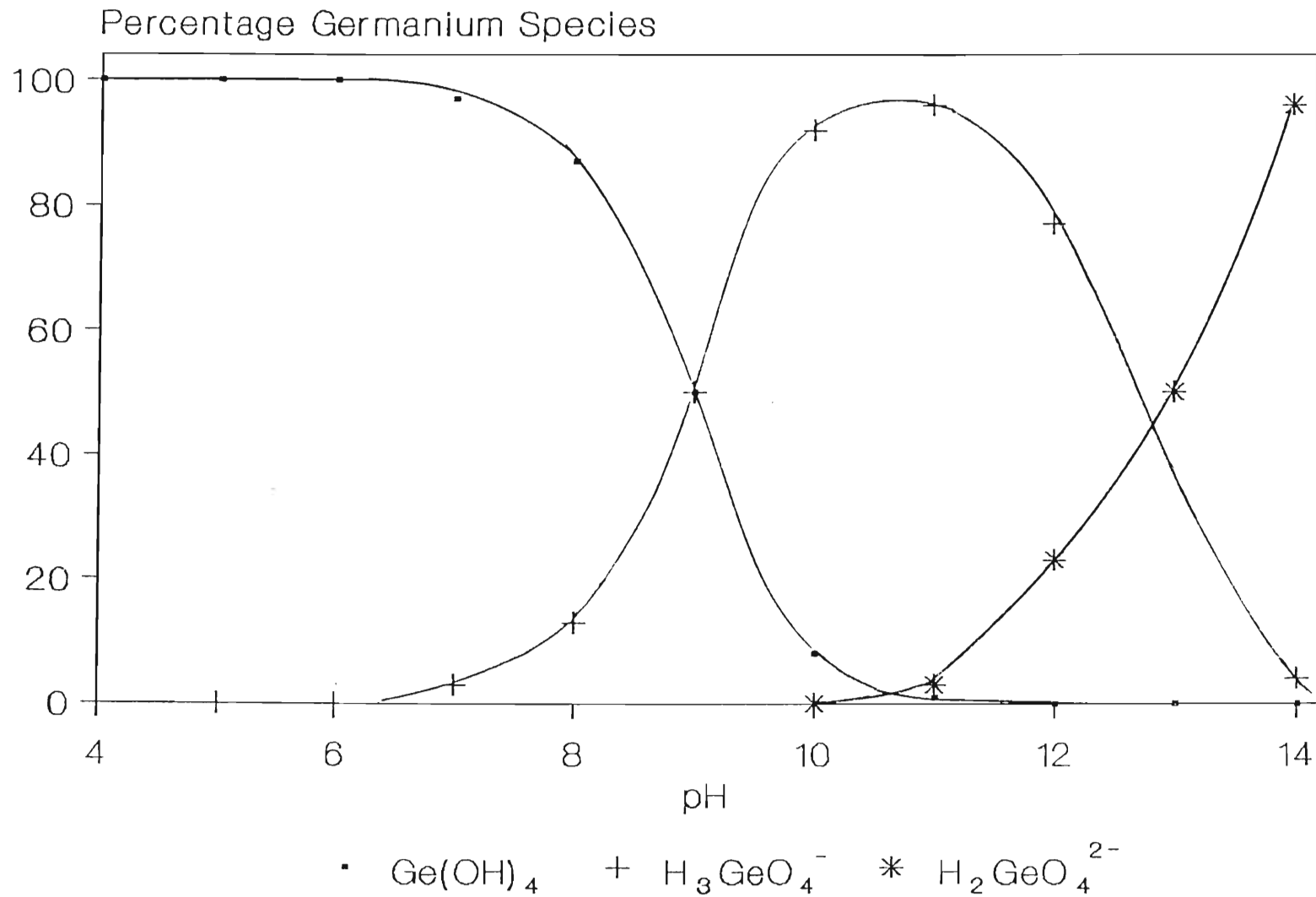
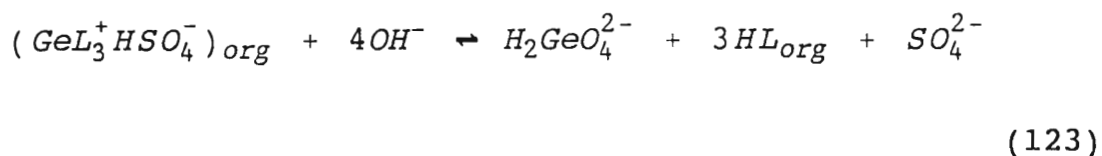


Figure (101). The species distribution of germanium in the pH range 4-14<sup>(94)</sup>.

following overall reaction occurs:



At the same time however,  $Na^+$  is extracted into the organic phase as an association complex  $Na^+L^-$  via Equation (120). This occurs for  $pH \geq pK_a'$  (acid-dissociation constant at the interface) of the ligand which is approximately 10,14 - calculated from interfacial tension measurements, Section 3.11.2.4. The sections which follow detail some of the pertinent characteristics of hydroxide stripping of germanium-loaded Lix 26.

### 3.10.1. The Effect of Hydroxide Concentration on the Rate and Equilibrium Percentage of Stripping.

Table (54) summarises the percentage of germanium stripped from loaded ligand by 0,5; 1,0; 2,5 and 5,0 M NaOH solutions.

| % Germanium Stripped From Organic Phase |            |            |            |            |
|---|------------|------------|------------|------------|
| Time /min                               | 0,5 M NaOH | 1,0 M NaOH | 2,5 M NaOH | 5,0 M NaOH |
| 5                                       | 2,6        | 1,3        | 0          | 0          |
| 10                                      | 2,8        | 4,2        | 0          | 0          |
| 20                                      | 4,5        | 7,5        | 1,1        | 0          |
| 30                                      | 9,9        | 10,4       | 1,9        | 0          |

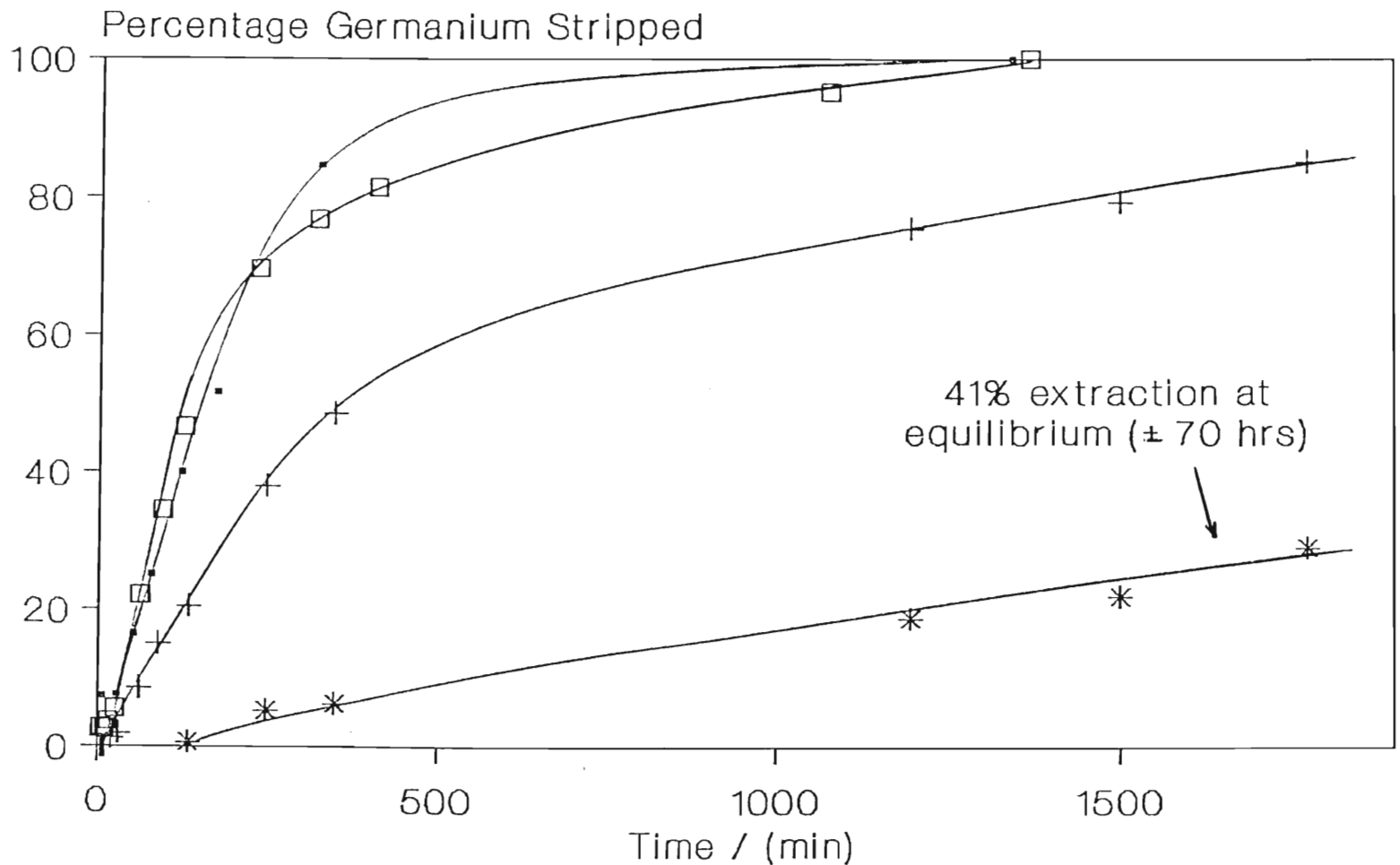


| Time /min | % Germanium Stripped From Organic Phase |            |            |            |
|-----------|---|------------|------------|------------|
|           | 0,5 M NaOH                              | 1,0 M NaOH | 2,5 M NaOH | 5,0 M NaOH |
| 60        | 22,0                                    | 16,3       | 8,4        | 0          |
| 90        | 34,4                                    | 25,1       | 15,0       | 0          |
| 120       | 46,6                                    | 39,9       | 20,4       | 0,6        |
| 300       | 76,8                                    | 80,0       | 42,5       | 6,1        |
| 1440      | 100,0                                   | 100,0      | 79,4       | 21,9       |

Table (54). Percentage germanium stripped by NaOH solutions of various concentration as a function of time. Phase Ratio 1:1 aq:org ;  $[\text{Ge}]_{\text{org}}^{\text{initial}} \sim 0,65 \text{ g/l}$  ;  $[\text{Lix } 26] = 50 \text{ g/l}$  ; Temperature =  $\pm 21^\circ\text{C}$ .

There are a number of points to note from these data, the plot of percentage stripping versus time of Figure (102) and other observed events:

- (i) The stripping process must consist of a number of steps. It was noted that soon after phase contact, the brown ligand-containing organic phase assumed a reddish colouration - this has been attributed by Cote and Bauer<sup>(53)</sup> to the uptake of  $\text{Na}^+$  by the ligand (Equation (120)) for Kelex 100.
- (ii) Following this initial reaction, the reddish colouration slowly disappeared.
- (iii) The stripping process is characterised by a very slow 'induction period', followed by faster kinetics. At high hydroxide concentration (5,0 M NaOH), < 1% !



□ 0,5 M NaOH    + 1,0 M NaOH    + 2,5 M NaOH    \* 5,0 M NaOH

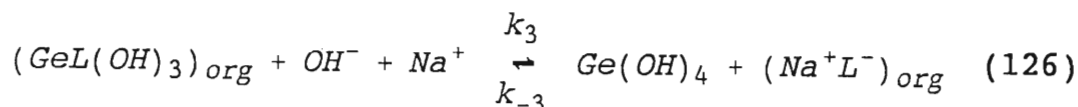
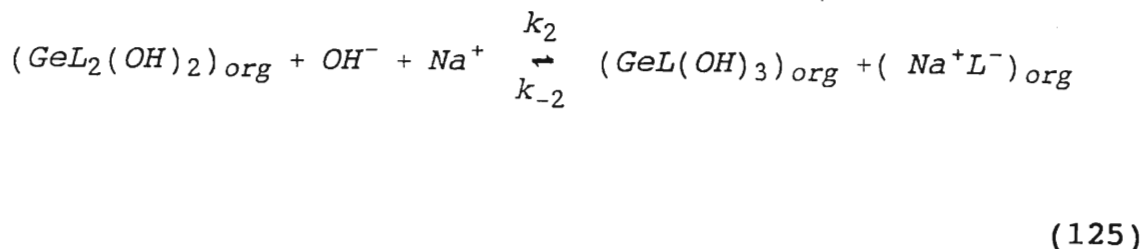
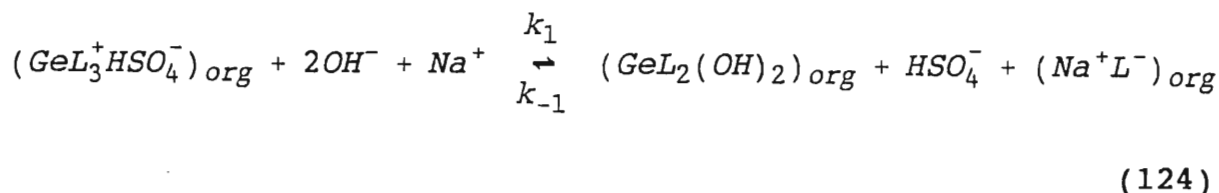
Figure (102). Percentage germanium stripped from germanium-loaded Lix 26 by various concentrations of NaOH in the aqueous phase (pH = 13,7-14,7). Organic phase :  $\sim 0,65$  g/l Ge in 50 g/l Lix 26/toluene; Aqueous phase : NaOH solution. Phase volumes : 100 ml.

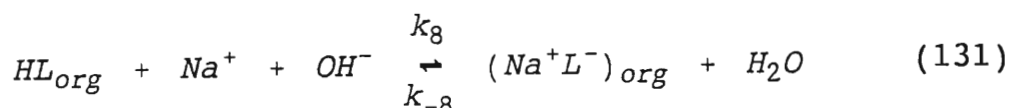
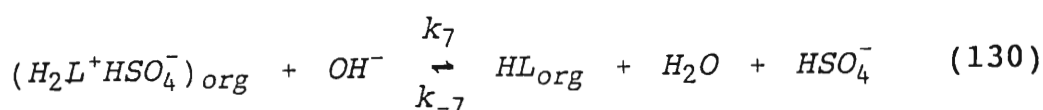
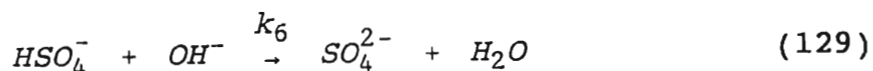
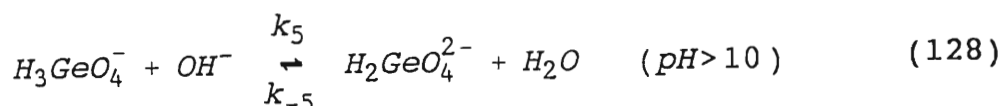
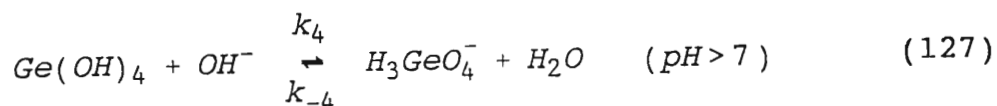
germanium is stripped in the first two hours of phase contact.

(iv) Both the rate at which germanium is stripped and the percentage of germanium in the aqueous phase at equilibrium are highest at the lowest  $\text{OH}^-$  concentration (pH  $\sim$  13,7).

(v) After a period of contact depending upon the initial concentration of  $\text{OH}^-$ , the phases were observed to form an emulsion. The stability of these emulsions - the observed time required for complete phase separation, which varied from approximately 5 minutes for  $[\text{OH}^-] = 0,5 \text{ M}$  to approximately 30 minutes for  $[\text{OH}^-] = 5,0 \text{ M}$ , increased with increasing hydroxide concentration.

A possible mechanism for the stripping process is suggested below:





In this scheme, Equation (124) represents the uptake of  $\text{OH}^-$  by the extracted germanium complex to form  $\text{GeL}_2(\text{OH})_2$  which reacts with further  $\text{OH}^-$  to give, eventually  $\text{Ge}(\text{OH})_4$  via Equations (125) and (126). Germanic acid anionic species are then formed via Equations (127) and (128) and these do not complex with free ligand. Equation (129) represents neutralisation of  $\text{HSO}_4^-$  while Equation (130) indicates the release of  $\text{H}^+$  from any protonated ligand species formed via Equation (89).  $\text{Na}^+\text{L}^-$  is formed via Equation (131) and as a steadily increasing by-product of Equations (124) - (126). It is proposed that the build-up of the reddish-brown complex in the organic phase during the initial reaction stages is a result of the presence of one or a number of hydroxylated or complexed  $\text{Na}^+$  species (i.e. of the type  $\text{Na}^+\text{L}^-$ ) of the impurities given in Table (6). It is not likely that the

coloured complex is a result of the formation of either (i)  $\text{Na}^+\text{L}^-$  or (ii) the intermediates  $\text{GeL}_2(\text{OH})_2$  and  $\text{GeL}(\text{OH})_3$  since in the first case the appearance of the complex would persist throughout the reaction and in the second case no such complex was observed during extraction runs performed at the pH ( $\geq 2-3$ ) at which  $\text{GeL}_2(\text{OH})_2$  is the extracted species. Moreover, the formation and subsequent disappearance of the complex occurs within the first 5 minutes of the stripping reaction, during which time little stripping occurs (Table (54)). It is concluded therefore that the colouration must be due to the presence of an intermediate complex formed between NaOH and the impurities in Lix 26.

With regard to the nature of the rate-determining step during the stripping scheme of Equations (124) to (131), a first model which was envisaged was that the cleavage of the first ligand molecule from the germanium ion, represented by Equation (124), would be rate limiting on stereochemical grounds for exactly the same reasons that the process of the chelation reaction of the third ligand during extraction is rate limiting. The ionic species  $\text{GeL}_3^+\text{HSO}_4^-$  is highly hydrophobic (Figure (70)) and must therefore equilibrate with its component ions at the interface during stripping. It is therefore necessary for the stripping reaction, that  $\text{OH}^-$  becomes available in the interface (or in the bulk organic). Equation (131) is a possible source of  $\text{OH}^-$  in the organic phase and this reaction is offered as an explanation for the slow initial kinetics. This rationale does not however explain why the initial and subsequent rates of stripping decrease with increasing  $[\text{OH}^-]$ . If the above assertions vis-à-vis the

rate-determining step are correct then, following  $\text{OH}^-$  uptake by free ligand, the rate of reaction is given by Equation (132).

$$\text{Rate} = -\frac{d[\text{GeL}_3^+\text{HSO}_4^-]}{dt} = k_1[\text{GeL}_3^+\text{HSO}_4^-][\text{OH}^-]^2[\text{Na}^+] - k_{-1}[\text{GeL}_2(\text{OH})_2][\text{HSO}_4^-][\text{Na}^+\text{L}^-] \quad (132)$$

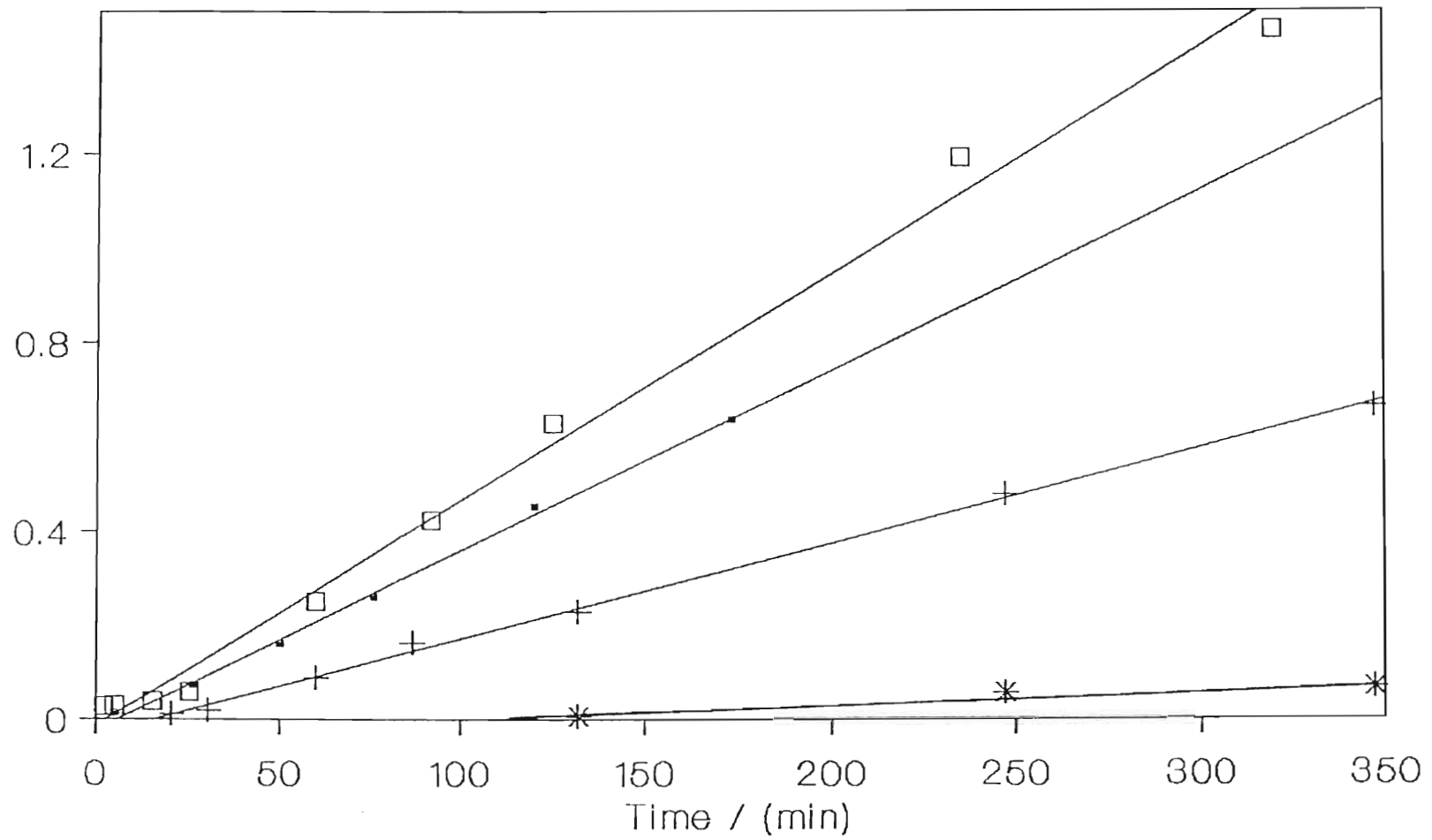
It is assumed in this rate equation that the order with respect to  $[\text{OH}^-]$  is two i.e. the process represented is elementary.

Equation (132) represents the slow step for the overall process of germanium distribution:



and thus as a first attempt to linearise the kinetics of stripping by hydroxide, first order plots analogous to the those used for the extraction process were investigated i.e. Equation (46) is used to obtain  $k_f'$ (obs) - the observed forward stripping rate constant, except in this case the components  $c_e$ ,  $c_o$ , and  $c_t$  of the equation refer to the concentration of germanium in the organic phase at equilibrium, initially and at some intermediate time respectively. Figure (103) shows semi-logarithmic plots for the four hydroxide concentrations investigated. Values of  $k_f'$ (obs) calculated from the slopes of these plots are summarised in Table (55).

$$(c_o - c_e)/c_o \ln(c_o - c_e)/(c_t - c_e)$$



□ 0,5 M NaOH    ▪ 1,0 M NaOH    + 2,5 M NaOH    \* 5,0 M NaOH

Figure (103). Semi-logarithmic kinetic plots for germanium-loaded toluene/Lix 26 stripping by various NaOH solutions.  $c_o$ ,  $c_e$  and  $c_t$  refer to the concentrations of germanium in the loaded organic phase initially, at equilibrium and some intermediate time respectively. Organic phase : ~ 0,65 g/l Ge in 50 g/l Lix 26/toluene; Aqueous phase : NaOH solution; Phase volumes 100 ml.

| [NaOH] / M | log [OH <sup>-</sup> ] | k <sub>f</sub> '(obs) /s <sup>-1</sup> | log k <sub>f</sub> '(obs) |
|------------|------------------------|--|---------------------------|
| 5,0        | 0,699                  | 3,54 x 10 <sup>-6</sup>                | -5,48                     |
| 2,5        | 0,398                  | 1,96 x 10 <sup>-5</sup>                | -4,71                     |
| 1,0        | 0,000                  | 6,35 x 10 <sup>-5</sup>                | -4,20                     |
| 0,5        | -0,301                 | 7,99 x 10 <sup>-5</sup>                | -4,10                     |

Table (55). Values of observed stripping rate constants for germanium stripping from metal loaded Lix 62 at various hydroxide concentrations. [Ge]<sub>org</sub><sup>initial</sup> ~ 0,65 g/l; phase volume ratio 1:1 (100 ml quantities). k<sub>f</sub>'(obs) is used as the symbol for the forward rate constant for stripping.

The values of observed stripping rate constants in Table (55) show only a marginal increase as [OH<sup>-</sup>] is decreased below 1,0 M. Stripping for [OH<sup>-</sup>] < 0,5 M is not efficient because germanium is converted into its most aqueous soluble and least ligand extractable form, H<sub>2</sub>GeO<sub>4</sub><sup>2-</sup> at pH > 13,5 whereas for pH < 13,0, the species H<sub>3</sub>GeO<sub>4</sub><sup>-</sup> dominates and this is not as soluble in the aqueous phase.

Figure (104) shows a plot of log k<sub>f</sub>'(obs) versus log [OH<sup>-</sup>] of these data with an apparent reaction order of inverse 1,8 for [OH<sup>-</sup>] > 1,0 M. The linearity of the semi-logarithmic plots of Figure (103) prove that the stripping reaction, once initiated, is indeed first order in germanium, however the expected second-order with respect to [OH<sup>-</sup>] is not observed in practice- in fact inverse second-order is suggested by these results.



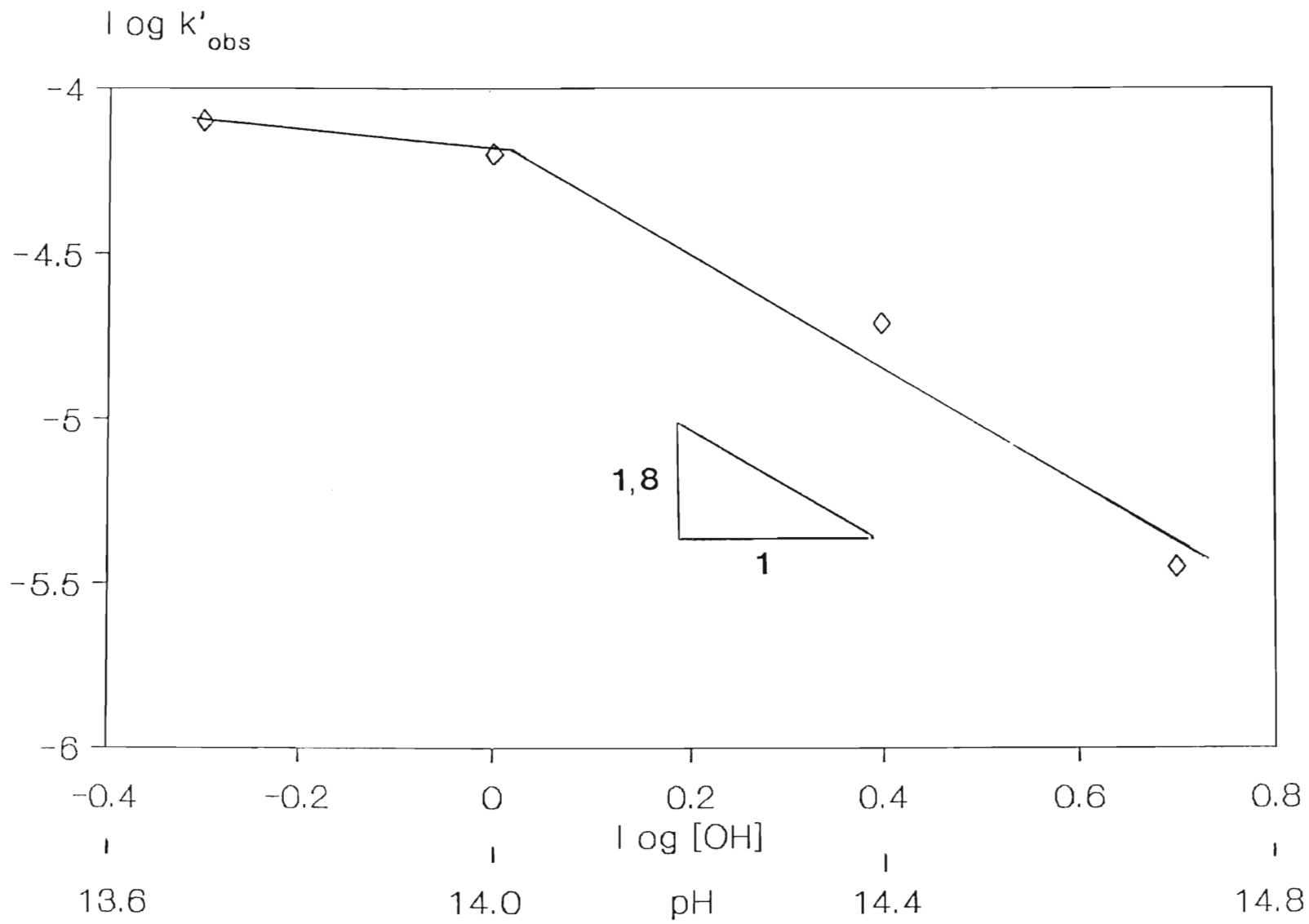


Figure (104). Log(Observed rate) for the stripping of germanium from loaded Lix 26 as a function of  $\log[\text{OH}]$  in the aqueous phase. Initial concentration of Ge in organic phase  $\sim 0,65$  g/l; [Lix 26] : 50 g/l in AR toluene; Aqueous phases : NaOH solutions 0,5-5,0 M (pH = 13,7-14,7).

An inverse second order in hydroxide cannot be correlated with the proposed rate-determining step indicated by Equation (132). Indeed, the entire stripping scheme which is proposed cannot explain the observed decrease in rate with increasing  $[\text{OH}^-]$ , therefore there are other reactions participating in the stripping process. A possible explanation lies in the consideration of the events which occur during the initial stages of phase contact. The initial reactions which occur following phase contact are given by Equations (129) - (131) i.e. the hydroxide solution: (i) neutralises any  $\text{H}_2\text{L}^+\text{HSO}_4^-$  formed during the acidic extraction (Equation (130)) and (ii) reacts with free HL and HL formed as a result of (i) above to form  $\text{Na}^+\text{L}^-$  (L = Lix 26 and any impurities which react with sodium hydroxide). It is likely that these events occur very quickly i.e.  $k_6$ ,  $k_7$  and  $k_8$ , are proposed to be diffusion-controlled rate constants. The build-up of  $\text{Na}^+\text{L}^-$  which results, shifts Equation (124) to the left i.e. favouring the preservation of  $\text{GeL}_3^+\text{HSO}_4^-$  concentration. The higher the initial hydroxide concentration in the aqueous phase, the faster the rate at which ligand is converted via the abovementioned processes (Equations (130) and (131)) into  $\text{Na}^+\text{L}^-$  and the greater the extent to which the stripping process is retarded. This rationale is supported by the increase in the so-called 'induction-period' for the stripping process as a function of  $\text{OH}^-$  concentration. For instance, extraction is not observed for a 5.0 M NaOH strip solution over a period of 90 minutes. After all available ligand has been converted into  $\text{Na}^+\text{L}^-$ , hydroxide then becomes available in the organic phase via Equation (131). Because it exists as a neutral species in

the organic medium, the possibility of  $\text{GeL}_3^+\text{HSO}_4^-$  being surface active and reacting with hydroxide at the interface is not entirely ruled out, but is less likely than reaction in the organic phase.

Another reaction which contributes to the overall slowness of germanium stripping, is the formation of  $\text{Na}^+\text{L}^-$  as a product of Equations (124) - (126). The formation of  $\text{Na}^+\text{L}^-$  by these reactions would sustain its concentration for a period long enough to retard Equation (124) significantly and this competing equilibrium process is offered as one possibility for the overall slow rate of germanium removal from the ligand.

The only reactions which directly remove  $\text{Na}^+\text{L}^-$  during the stripping process are the reverse reactions of Equations (124) - (126) and (131) and these are likely to be slower than the forward rate processes resulting in the formation of the species (otherwise stripping would not be observed at all). These forward reactions which reduce the rate of stripping will always be in operation at the high pH required to produce the anionic species of Equations (127) and (128) and very high hydroxide concentrations will increase their participation.

Slow stripping kinetics have been reported by Cote and Bauer<sup>(53)</sup> for germanium-loaded Kelex 100 with a 3 M NaOH solution. Boateng *et al.*<sup>(221)</sup> suggest a strip liquor of 120 - 200 g/l NaOH i.e. 3-5 M NaOH. In view of the above discussion, it is suggested that these authors have recommended hydroxide concentrations that are too high - it appears that a 1 M NaOH solution maintains an optimal balance between slow stripping

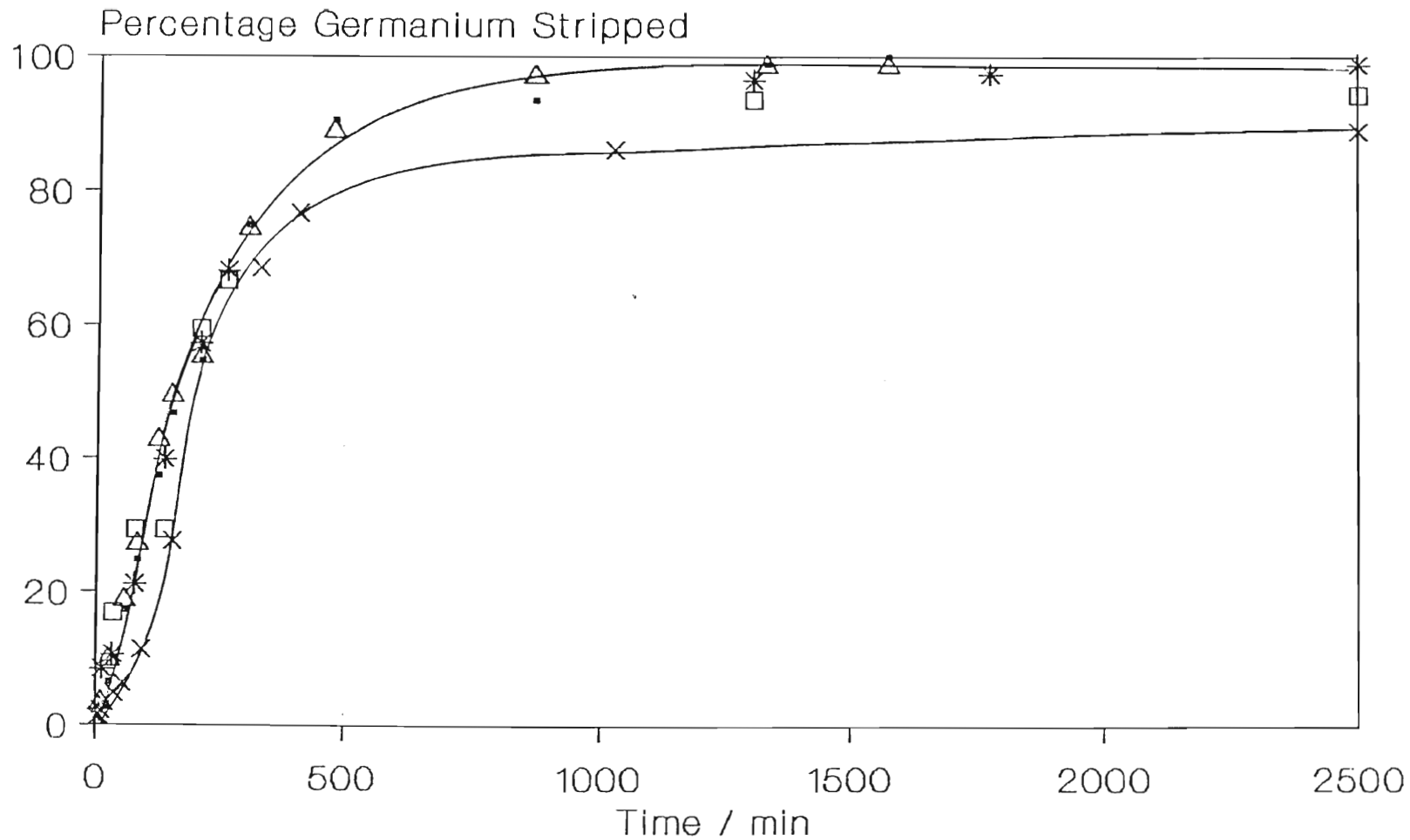
and sufficient hydroxide to enforce the formation of the unextractable germanic acid species.

An important aspect of any stripping process is the determination of an optimum phase ratio. This topic is dealt with in the next section.

### 3.10.2. Determination of an Optimum Aqueous:Organic Phase Ratio for Germanium Stripping of Lix 26 by Sodium Hydroxide.

In Section 2.4.2.2.9, it was noted that it is desirable to reduce the handling volume of an extraction/stripping process such that (i) during extraction a minimum volume of organic phase (o) is used and (ii) for stripping, a minimum volume of aqueous phase (a) is utilised. In principle, therefore an optimum a:o ratio is readily determined, but in practice there are a number of other considerations which deserve attention e.g. solubility of the stripped metal or metal-hydroxy species in the aqueous strip liquor, emulsion formation at very low or high a:o phase ratios and finally economic factors associated with transferring, separation, precipitation, filtering etc. of the phases concerned.

Details of the experimental procedure adopted to determine the effect of the a:o ratio on the stripping kinetics were given in Section 2.4.2.2.9. Figure (105) summarises the data obtained by varying the a:o ratio from 1:4 to 5:1. The plots indicate that strip ratios over the entire range investigated are suitable, however at the lowest a:o ratio the kinetics are noticeably retarded and at equilibrium ( $\pm$  42 hours) only 90%



• 1:1    △ 2:1    \* 3:1    □ 5:1    × 1:4  
 Aqueous:Organic Phase Ratio

Figure (105). Percentage germanium stripped from a loaded  $\text{LiX}$  26/toluene organic phase by 1,0 M NaOH as a function of contact time and a:o phase ratio from 5:1 to 1:4.  $[\text{Ge}]_{\text{org}}$  (initial):  $\sim 0.65 \text{ g/l}$

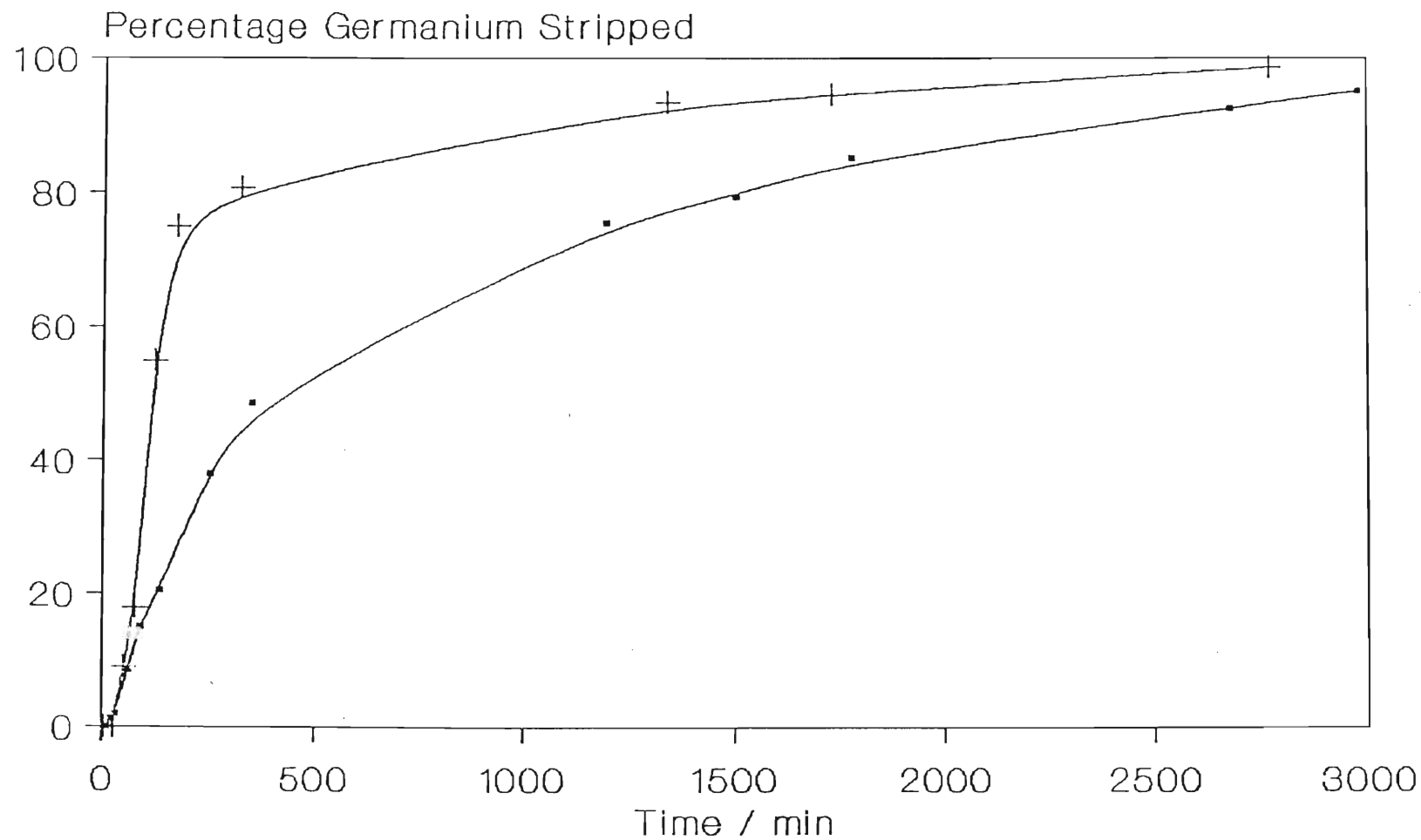
of the germanium is stripped. After 500 minutes 75% of the germanium is stripped by the 1:4 ratio compared with approximately 85% for 1:1 and above and although the latter is inherently more attractive, the lower extraction obtained at low a:o ratios is offset by the advantages of handling smaller volumes of strip liquor subsequent to and during alkaline stripping.

In Section 3.7, the advantages of modifier addition to extractant solutions were discussed. The next section details the effect of the modifier on the stripping process.

### 3.10.3. Comparison of the Germanium Stripping Rates by NaOH from Loaded Lix 26 Organic Solution With and Without an Added Modifier.

The characteristics of modifiers and their effect upon germanium extraction kinetics by the 7-alkylated-8-hydroxyquinoline derivatives concerned in this work, were discussed Section 3.4.7. For all the modifiers tested, accelerated kinetics and improved equilibrium percentage extraction were noted and mechanistic details for their action were proposed. The current section is concerned with the effect of added modifiers on the stripping kinetics.

Consider for example the plots of Figure (106) which show the percentage germanium stripped with time by 2,5 M NaOH from metal-loaded Lix 26 solutions of the same concentration (50 g/l) containing no organic modifier (lower curve) and 30% v/v n-octanol modifier (upper curve). Semi-logarithmic plots



—•— Lix 26    —+— Lix 26/ n-octanol

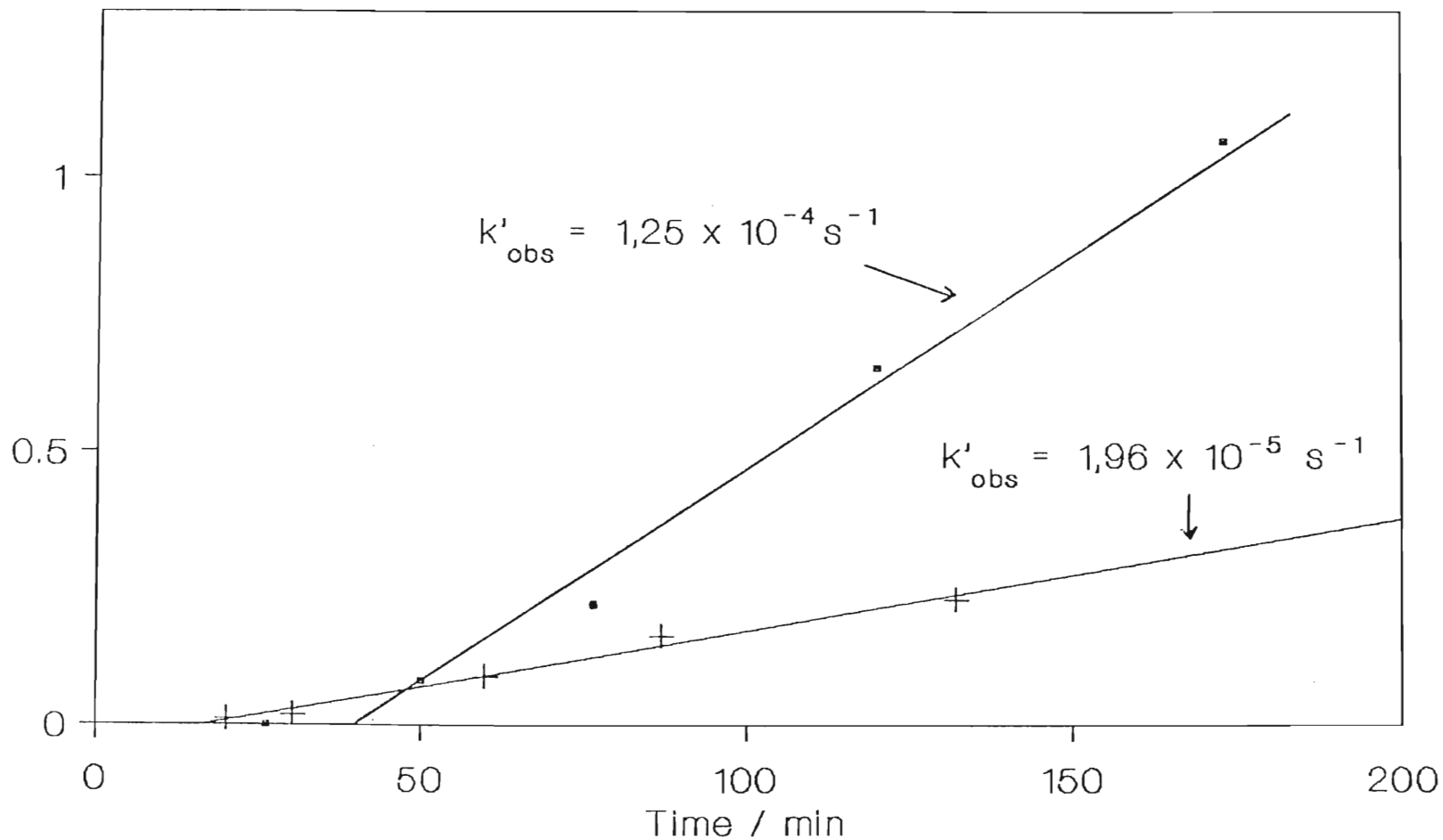
Figure (106). The effect of an organic modifier (n-octanol) on the stripping kinetics of germanium from loaded Lix 26. [NaOH] = 2,5 M; Organic phase : ~ 0,65 g/l Ge in 50 g/l Lix 26/toluene (lower curve) and 50 g/l Lix 26/toluene containing 30% n-octanol (upper curve); Phase volumes 100 ml.

of these data are presented in Figure (107). It is apparent from these figures that, in a manner similar to the extraction phenomenon, the presence of the modifier enhances the observed rate, in this case a six-fold increase in the observed stripping rate constant is obtained (cf.  $k_f'(\text{obs}) = 1,25 \times 10^{-4} \text{ s}^{-1}$  with modifier and  $1,96 \times 10^{-5} \text{ s}^{-1}$  without). Figure (107) shows that this increase in rate is not associated with the entire stripping period i.e. no germanium is detected in the aqueous phase for the first 30 minutes for both situations, however thereafter the observed rate increases markedly for the ligand solution containing added modifier.

In section 3.7.1, it was proposed that during germanium extraction, the modifier causes the ligand to become more surface-active via hydrogen bonding. During stripping it is proposed that modifier reagents behave in an analogous fashion by accelerating the rate at which  $\text{GeL}_3^+\text{HSO}_4^-$  comes into contact with hydroxide at the interface and in the bulk organic phase. Thus the affinity of the  $\text{C}_8$  - alkyl group of n-octanol for the  $\text{C}_{12}$  - 7-alkyl group of the three ligand molecules of  $\text{GeL}_3^+$  results in the formation of ligand complex/modifier aggregates which, by virtue of the polar groups of the modifier molecules is of a greater surface activity than the relatively hydrophobic tri-ligand chelate and therefore more amenable to a ligand replacement reaction by  $\text{OH}^-$ . The suggestion which is therefore offered to account for the enhanced stripping kinetics associated with the presence of the modifier in the metal-loaded ligand solution is that the modifier increases



$$(c_o - c_e)/c_o \ln(c_o - c_e)/(c_t - c_e)$$



▪ Lix 26/ n-octanol    + Lix 26

Figure (107). Semi-logarithmic plot for the first-order stripping of germanium from Lix 26/toluene and Lix 26/toluene/n-octanol systems by 2,5 M NaOH.  $[Ge]_{org}(\text{initial})$  :  $\sim 0,65 \text{ g/l}$ ; Phase volumes : 100 ml. Note the 6-fold increase in  $k'_{obs}$  for the upper (n-octanol) curve.

the rate at which the chelated metal encounters  $\text{OH}^-$  (Equations (124) - (126)) in the organic bulk and at the interface. If reaction of the  $\text{GeL}_3^+$  chelate with  $\text{OH}^-$  at the interface is a faster process than reaction of these species in the organic bulk, then the intervention by the modifier may account for the improved observed stripping kinetics.

Although no attempts were made in this work to determine the optimum conditions for germanium stripping from a modifier-containing organic phase and further the reduction which could be made in  $[\text{OH}^-]$  in the strip liquor, as a result of the presence of an organic modifier, while still obtaining fast kinetics and reasonable equilibrium stripping, some suggestions for future work are presented in Chapter 5.

Throughout this work, reference has been made to the importance of the physical properties of interfaces and the bulk aqueous and organic phases. The sections following describe the relevance of the organic viscosity, interfacial tension, dielectric constant and the possibility of ligand aggregation effects on the development of a kinetic model for the solvent extraction of germanium and to the interpretation of the effect of other parameters on the extraction processes which have already been described.

### 3.11. Physical Parameters Important for the Development of a Solvent Extraction Model.

The transfer of a solute species across a phase boundary is usually a function of a number of chemical and physical events

which are not independent of one another. Thus far the importance of interfacial tension and relative dielectric constant of the organic medium have been mentioned (Sections 3.2.1.7 and 3.2.1.2 respectively), however, the viscosity of the ligand/diluent solution and the possibility of polymerization of ligand molecules in the organic diluent also require consideration. The sections which follow deal with each of these in turn and also considers their contribution towards aspects of a kinetic model for solvent extraction which is presented in Section 3.15.

#### 3.11.1. Infra-red Spectrophotometric Investigation of Ligand Aggregation.

The aggregation of extractant molecules in the solvent phase affects the metal loading capacity of the solvent because it results in a lowering of the availability of the form of extractant which is involved in metal complexation. In general, the formation of extractant aggregates such as  $(HL)_2$ , increases with increasing ligand concentration and results in a lower metal-loading capacity than expected. Ashbrook and Ritcey<sup>(222)</sup> for example, determined the extraction isotherms for  $Co^{2+}$  and various concentrations of  $D_2EHPA(Na)$ -the sodium salt of structure (h) in Table (4). Using a 20% v/v solution of this ligand in kerosene, the maximum loading capacity of the solvent was  $21 \text{ kg m}^{-3}$  whereas for 30% v/v and 40% v/v solutions, this figure rose to  $28 \text{ kg m}^{-3}$  and  $33 \text{ kg m}^{-3}$  respectively. The results of their study are typical of the behaviour which is demonstrated by a number of other aggregating extractants viz. carboxylic and sulphonic acids,<sup>(173,174)</sup>  $\beta$ -hydroxyoximes<sup>(175)</sup> etc. in that metal-loading

capacities are not linear with increasing ligand concentration.

One of the aims of this work is to present a complete model for the solvent extraction of germanium by 7-alkylated-8-hydroxyquinoline derivatives and to give an account of the parameters which are of direct relevance to the process to facilitate the proposal of optimum operating conditions. In view of the comments made above and also considering that 7-alkylated-8-hydroxyquinoline derivatives contain groups which would be amenable to hydrogen-bonding, it was considered necessary to determine to what extent, if any, ligand was present in the organic phase as inaccessible dimeric species. The infra-red procedures detailed in Section 2.5.4 were chosen to examine this.

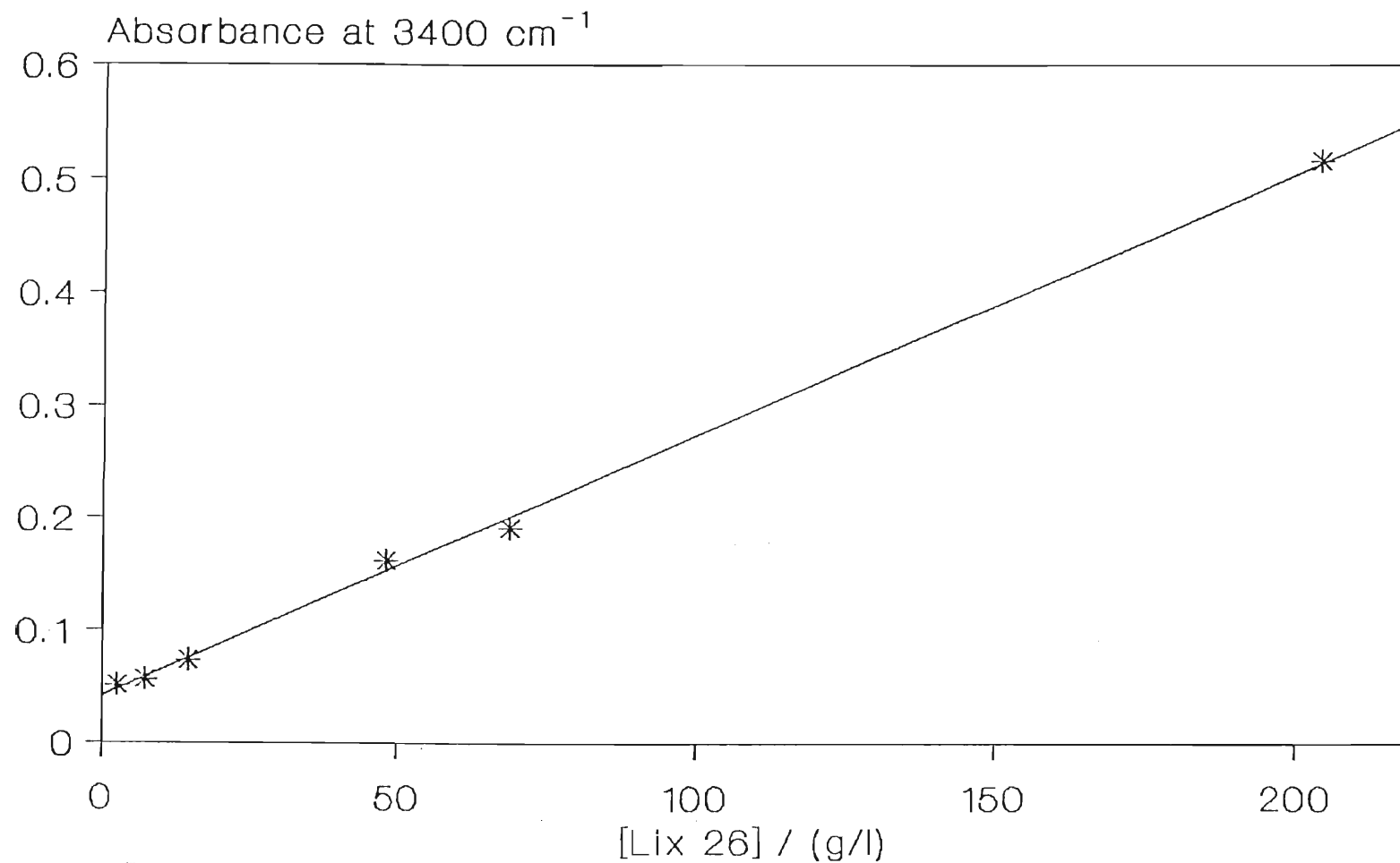
Consider first the infrared spectrum of Lix 26 in  $\text{CCl}_4$  of Figure (10b). Dimerization of organic molecules can be detected by the disappearance and shifting of one OH band on the i.r. spectrum and the appearance of another as the concentration of the organic molecule decreases<sup>(176)</sup>. In general, a sharp band at  $3570 \text{ cm}^{-1}$  is characteristic of free OH stretch, while a broad band at  $3350 \text{ cm}^{-1}$  is associated with hydrogen-bonding. If intermolecular hydrogen-bonding is present, then the intensity of the band at  $3350 \text{ cm}^{-1}$  usually decreases faster than the concentration (i.e. Beer's law plot is not linear) and the free OH band at  $3570 \text{ cm}^{-1}$  becomes more pronounced as the concentration decreases and more OH moieties are free to stretch in their normal mode. In Figure (10b), the following can be noted: (i) the absence of the sharp band at

3570  $\text{cm}^{-1}$  is evidence that no free OH is present and (ii) the band at  $\sim 3400 \text{ cm}^{-1}$  indicates that the molecule is intramolecularly hydrogen-bonded. Table (56) shows the change in percentage transmittance of the  $3400 \text{ cm}^{-1}$  peak of Lix 26 with changing concentration. The absorbance of the peak at  $3400 \text{ cm}^{-1}$  is plotted against [Lix 26] in Figure (108). The linear decrease in absorbance with decreasing ligand concentration demonstrates that the ligand is intramolecularly bonded. In addition, free OH stretching in the  $3600 \text{ cm}^{-1}$  region does not appear with decreasing ligand concentration.

| [Lix 26]<br>/ (g/l) | % Transmittance<br>( $3400 \text{ cm}^{-1}$ peak) | Absorbance |
|---------------------|---|------------|
| 205,02              | 30,5  | 0,516      |
| 68,82               | 64,5  | 0,190      |
| 48,01               | 69,0  | 0,161      |
| 14,48               | 84,5  | 0,073      |
| 6,97                | 88,0  | 0,056      |
| 2,52                | 89,0  | 0,051      |

Table (56). Percentage Transmittance and Absorbance ( $A = -\log_{10} (T/100)$ ) of the  $3400 \text{ cm}^{-1}$  peak of varying concentration of Lix 26 in  $\text{CCl}_4$ .

Analogous results were also obtained for TN 01787 and TN 02181 in the concentration range 1,0 - 250,0 g/l in  $\text{CCl}_4$ , hence covering the range of concentration reported in this work.



Lix 26 concentrations corrected for active components

Figure (108). Absorbance of the intramolecular H-bonding peak (3400 cm<sup>-1</sup>) as a function of Lix 26 concentration in CCl<sub>4</sub>. 0,1 mm pathlength liquid cell with NaCl windows, Pye-Unicam SP-300 Infrared spectrophotometer.

Like Lix 26 these two reagents therefore bond intramolecularly.

Since intermolecular bonding is absent over the concentration range used in germanium extraction, the possibility of the occurrence of species such as  $(HL)_2$  can be precluded from any final kinetic model. It must be noted however, that it is tacitly assumed in the above discussion that the active ligand behaves in a similar manner in  $CCl_4$  as it would in toluene. This is a reasonable assumption since the two solvents have almost identical relative dielectric constants:  $CCl_4 = 2,24$  ; toluene =  $2,38^{(156)}$ , and are therefore of similar polarity and likely to affect dissolved ligand species to a similar extent.

### 3.11.2. The Use of Interfacial Tension Data in the Interpretation of Surface Population of 7-Alkylated-8-hydroxyquinoline Extractants and in the Determination of the Area Occupied per Molecule at the Interface.

In order to understand the mechanism of any solvent extraction process, it is necessary to provide an adequate description of the manner in which adsorbates pack at the interface and also the relationship between increasing bulk concentration and ligand availability at the phase boundary. Kinetic data alone are usually inadequate for the deduction of an extraction mechanism when interfacial rate processes dominate. Clearly, to facilitate an understanding of such mechanisms, rate data must be augmented by physico-chemical data about the interfacial phenomena themselves. Although interfacial concentrations of extractant cannot be determined by a direct

experimental technique, they may be estimated indirectly via interfacial tension measurements using the Gibbs Adsorption Isotherm and this is discussed in the next section.

### 3.11.2.1. The Gibbs Adsorption Equation.

Equation (133) summarises the relationship between the lowering of the interfacial tension between immiscible phases by an amphiphilic adsorbant and the bulk concentration of the amphiphilic species (Gibbs, 1876<sup>(223)</sup>).

$$\Gamma = \frac{-1}{2,303RT} \frac{d\gamma_{int}}{d\log_{10}[HL]_{int}} \quad (133)$$

Examination of Equation (133) shows that a plot of interfacial tension ( $\gamma$ ) versus  $\log_{10}[HL]$  is linear with slope  $-2,303RT\Gamma$ , where  $\Gamma$  is the Excess Interfacial Population Density (EIPD) or Surface Excess and gives an indication of the interfacial occupancy by the extractant molecule.

The following must be noted with respect to Equation (133) since the interpretation of data is subject to these proviso's:

- (i) The 'Surface Excess' is the excess amount per unit area of the surface and not a concentration in the conventional sense. The estimation of  $\Gamma$  therefore, via tensiometer measurements provides a relative result if the same dish is used for all measurements but can be scaled up (or down) in a linear fashion to estimate the surface coverage of larger or smaller dimension and this



is because the value of  $\Gamma$  calculated applies to a monolayer of extractant at the liquid-liquid interface.

(ii) It is assumed that solutions are dilute such that concentrations and not activities can be used in the calculation of  $[\text{HL}]_{\text{int}}$ .

Measurement of interfacial tension permits both a qualitative assessment of the nature and packing of the interface and a quantitative estimation of  $\Gamma$  and thence the area occupied by the extractant, the interfacial dissociation constant of the surface active material ( $K_a^{\text{int}}$ ) and information concerning the energy of adsorption of the surface active material at the interface (via the Langmuir Isotherm). Each of these quantities yield complementary information *vis-à-vis* the interfacial properties of extractant molecules and are discussed in the sections following.

### 3.11.2.2. Interfacial Tension Data Pertaining to Ligand Solutions in Contact with Aqueous Phases 1,5 M in $\text{H}_2\text{SO}_4$ .

In Section 3.1.3, it was shown that at low  $[\text{HL}]$ , the order of efficiency of germanium extraction by the extractant reagents of interest to this work in the Lewis Cell was:

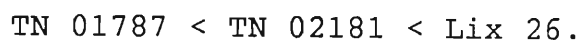
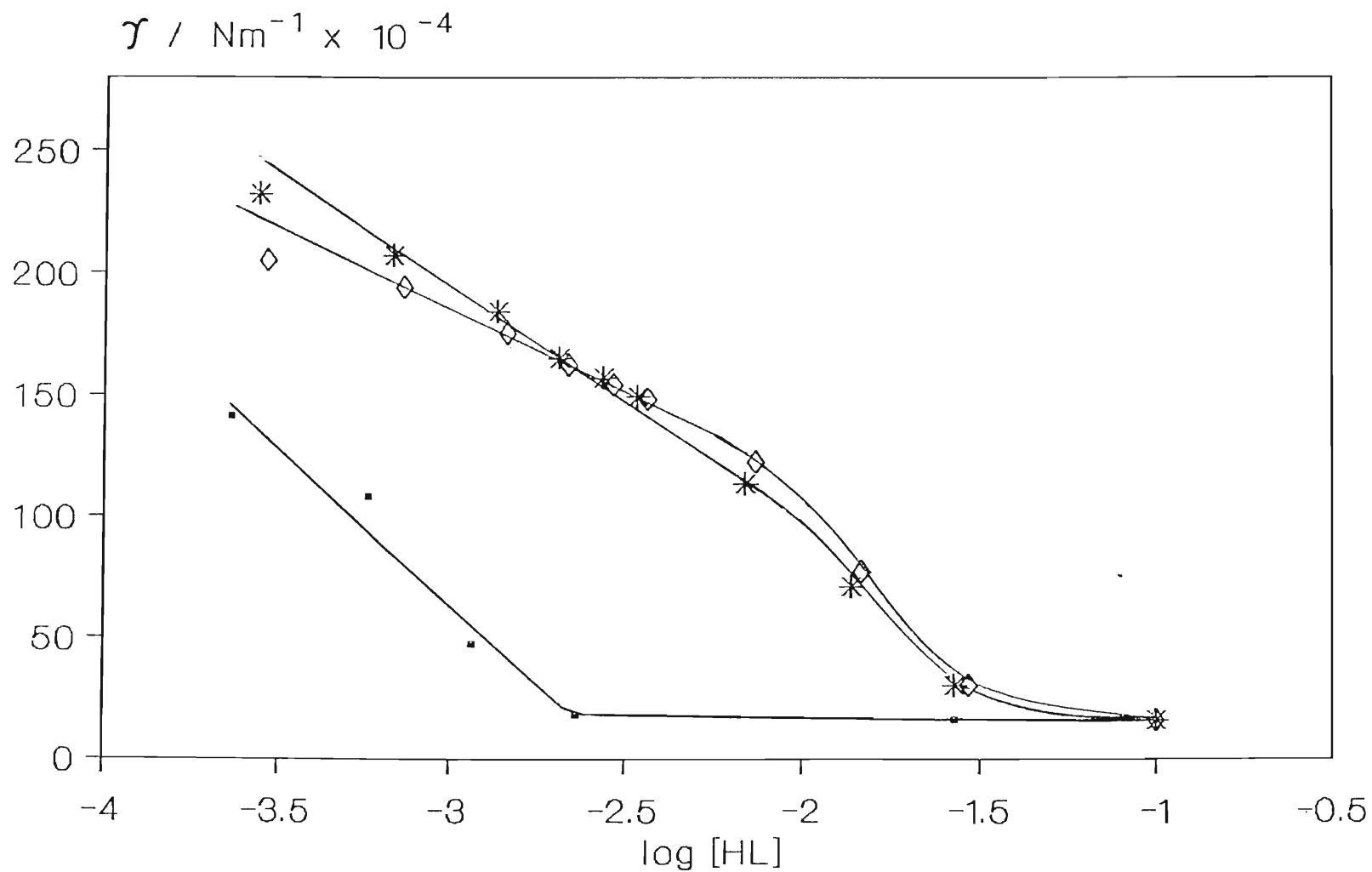


Figure (53) showed plots of  $\gamma$  versus  $[\text{HL}]$  for these three reagents, where it is clear that Lix 26 is more surface active than the TN products over the concentration range examined. While Figure (53) gives a qualitative representation of the relative surface activity of the reagents, Figure (109) facilitates the calculation of the interfacial excess. Values of the gradients of  $\gamma_c$  vs  $\log[\text{HL}]_{\text{org}}$ , the interfacial excess  $\Gamma$



▪ Lix 26      ◇ TN 01787      \* TN 02181

(all concentrations corrected for purity)

Figure (109). Interfacial tension ( $\gamma_c$ ) as a function of [HL] for Lix 26, TN 02181 and TN 01787. Aqueous phases : 1,5 M  $\text{H}_2\text{SO}_4$ ; Organic phases : ligand reagent in AR toluene. Data recorded at 21°C.

and the molecular coverage per area calculated by multiplying  $\Gamma$  by Avogadro's number, are summarised in Table (57).

| Ligand   | Gradient / $\text{Nm}^{-1}$ | Interfacial Excess $\Gamma$<br>/ $\text{mol m}^{-2}$ | Area Coverage<br>/ $\text{molecules m}^{-2}$ |
|----------|-----------------------------|--|--|
| Lix 26   | $-1,29 \times 10^{-2}$      | $2,29 \times 10^{-6}$                                | $1,38 \times 10^{18}$                        |
| TN 01787 | $-8,69 \times 10^{-3}$      | $1,54 \times 10^{-6}$                                | $9,30 \times 10^{17}$                        |
| TN 02181 | $-1,03 \times 10^{-2}$      | $1,84 \times 10^{-6}$                                | $1,11 \times 10^{18}$                        |

Table (57). Interfacial parameters calculated from interfacial tension measurements for Lix 26, TN 02181 and TN 01787 in AR toluene. Aqueous phase : 1,5 M  $\text{H}_2\text{SO}_4$ .

It is clear from these data that Lix 26 has a greater surface activity than TN 01787 or TN 02181 at the pH of the measurements. This surface activity could be associated with a number of chemical and physical (i.e. size, conformation etc.) properties of the ligand. Two suggestions are offered to explain this higher interfacial activity:

- (i) The protonated species  $\text{H}_2\text{L}^+\text{HSO}_4^-$  (Equation (89)) of Lix 26 is more surface active than that of TN 02181 and TN 01787 and
- (ii) The higher interfacial activity (at this pH) for Lix 26 is an indication of greater impurity occupancy at the phase boundary- Lix 26 is the least pure of the reagents.

As mentioned above, physical size is another factor which determines the value of  $\Gamma$ . Table (58) summarises values of

ligand area calculated by multiplying the inverse of the final column of Table (57) by  $1 \times 10^{20} \text{ \AA}^2$  (which converts  $\text{m}^2 \text{ molecule}^{-1}$  into  $\text{\AA}^2$ ) and areas calculated via the use of the Alchemy Molecular-Modelling Program, further discussed in Section 3.13.

| Ligand   | Area of molecule ( $\text{\AA}^2$ )<br>Tensiometer Measurements | Area of molecule<br>( $\text{\AA}^2$ ) Alchemy |
|----------|---|--|
| Lix 26   | 72,4  | 125,5  |
| TN 01787 | 107,6   | 77,4   |
| TN 02181 | 90,4  | 70 - 106                                       |

Table (58). Extractant areas predicted by the Gibbs adsorption treatment of interfacial tension data and molecular modelling by Alchemy.

Areas calculated via interfacial tension measurements correlate closely with observed extractant behaviour since Lix 26, being the smallest ligand molecule would be more available at the interface than e.g. TN 01787, however the agreement between such molecular areas and those calculated via Alchemy is poor. The discrepancies are a function of a number of attributes both of the measurement technique and of the Alchemy software viz.

(1) Alchemy predicts the most stable conformation, hence area and volume, of a neutral molecule utilising crystal data. The package cannot therefore account for any interaction with solvents (in the case of extractant molecules oriented at the interface there are two

solvents to consider), nor can it account for forces of attraction and repulsion (including any hydrogen-bonding interactions) between adjacent extractant molecules and between extractant molecules and species in the aqueous phase e.g.  $\text{Ge}^{4+}$ ,  $\text{H}^+$ ,  $\text{HSO}_4^-$ ,  $\text{H}_2\text{O}$  etc. The measurement of interfacial tension, on the other hand, yields data relevant to the actual situation - in this case ligand is protonated and the measurements are thought to be indicative of population of the interface by predominantly  $\text{H}_2\text{L}^+\text{HSO}_4^-$  and some neutral HL.

(2) The interfacial tension measurements are greatly affected by surface active impurities. This is likely to affect Lix 26, which is the least pure reagent, to a greater extent than TN 02181 or TN 01787.

An additional piece of information which can be deduced from the plots of  $\gamma$  vs  $\log[\text{HL}]$  of Figure (109) is the minimum bulk organic concentration of extractant required to maximally populate the interface. This is indicated by the point at which the Gibbs Isotherm plot deviates from linearity. For the reagents shown in Figure (109), such a deviation occurs at  $\log[\text{HL}]_{\text{org}} = -2,6$  for Lix 26 and  $-1,8$  (approx) for TN 01787 and TN 02181. These values are equivalent to  $[\text{Lix } 26]_{\text{org}} = 1,10$  g/l;  $[\text{TN } 01787]_{\text{org}} = 5,41$  g/l;  $[\text{TN } 02181] = 5,88$  g/l for complete saturation of the interface by a monolayer of the as-supplied reagents. These values apply to population of an interface with surface area  $23,76 \text{ cm}^2$  (diameter of dish used for interfacial tension measurements =  $5,5 \text{ cm}$ ). Since surface excess is a linear property, the concentration of ligand required to completely populate the interface of the Lewis

cell (Area : 103,87 cm<sup>2</sup>) can be calculated by proportionation. Hence, using the values above, concentrations of 4,8 g/l, 23,7 g/l and 25,7 g/l of the impure reagents are required to fully occupy the aqueous/organic interface. For the studies which were performed with the Lewis Cell (Section 3.1.2) to determine reaction orders with respect to ligand, a minimum concentration of 50,0 g/l was utilised and although the organic phase was stirred in order to constantly supply the interface with active ligand (while interfacial tension measurements apply to a static equilibrium), it is reasonable to assume that ligand availability at the interface was not a limiting or rate determining factor.

At this point it must be noted that while the interfacial excess expresses the amount of ligand adsorbed at the interface per unit area, the measurement of this quantity at a static interface by interfacial tension measurements cannot be correlated with the interfacial excess which applies to droplets of a vigorously-stirred dispersion as exists in a mechanical shaker. A number of practical assemblies have been designed by various workers to facilitate such a measurement-one technique involves making use of the light scattering properties of dispersions<sup>(224,225)</sup> but is limited in application because only fluids of sufficient transparency render such measurement possible<sup>(226)</sup>. By far the most satisfactory arrangement for the measurement of  $\Gamma$  in a dispersed system is the Microporous Teflon Phase Separator (MPTS)<sup>(78,162,227-231)</sup>, because it permits the isolation and sampling of the bulk organic phase under conditions of high interfacial area<sup>(78,227,232)</sup>. Investigators using this apparatus usually monitor the absorbance of the organic phase (proportional to

the bulk ligand concentration) as the stirring rate is varied - hence the amount of interface generated as a function of stirring can be determined. A number of suggestions to further the work presented here and using such an apparatus are given in Chapter 5.

### 3.11.2.3. Interfacial Excess of 7-Alkylated-8-hydroxyquinoline Extractants at the Aqueous/Toluene Interface as a Function of Aqueous Phase pH.

The population of an aqueous/organic interface by a surface-active ligand is a function mainly of: (a) the bulk concentration of the ligand in the organic phase, (b) the nature of the diluent, (c) the solubility of the ligand in the aqueous phase and (d) the pH of the aqueous phase. Since the ligand reagents of interest to this work can associate with a proton to give  $H_2L^+$  or dissociate at the phenolic group to give  $L^-$ , and since such species might be expected to exhibit higher interfacial activity than the neutral forms, an investigation of the interfacial behaviour of Lix 26 as a function of pH was initiated. Two features of this investigation have relevance: (i) the determination of the relationship between  $\Gamma$  and pH, which will establish whether the low percentage extraction and observed germanium extraction rate at  $pH > 2$  is a function, not only of the low extractability of the species  $GeL_2(OH)_2$  which is the predominant metal chelate species formed in this range of pH (Section 3.4.6), but also a function of the low surface activity of the extractant and (ii) to evaluate the acid dissociation constant,  $K_a^{int}$ , at the interface- this latter has implications in describing the processes occurring during stripping because at  $pH > pK_a^{int}$ , the ligand will

deprotonate to form  $L^-$  which associates with  $Na^+$  to give  $Na^+L^-$ , the extractable species:- Section 3.10.1 discussed the relevance of the formation of this species.

Consider first the plots of interfacial tension versus [Lix 26] at various values of pH in Figure (110). There are a number of interesting features associated with these data:

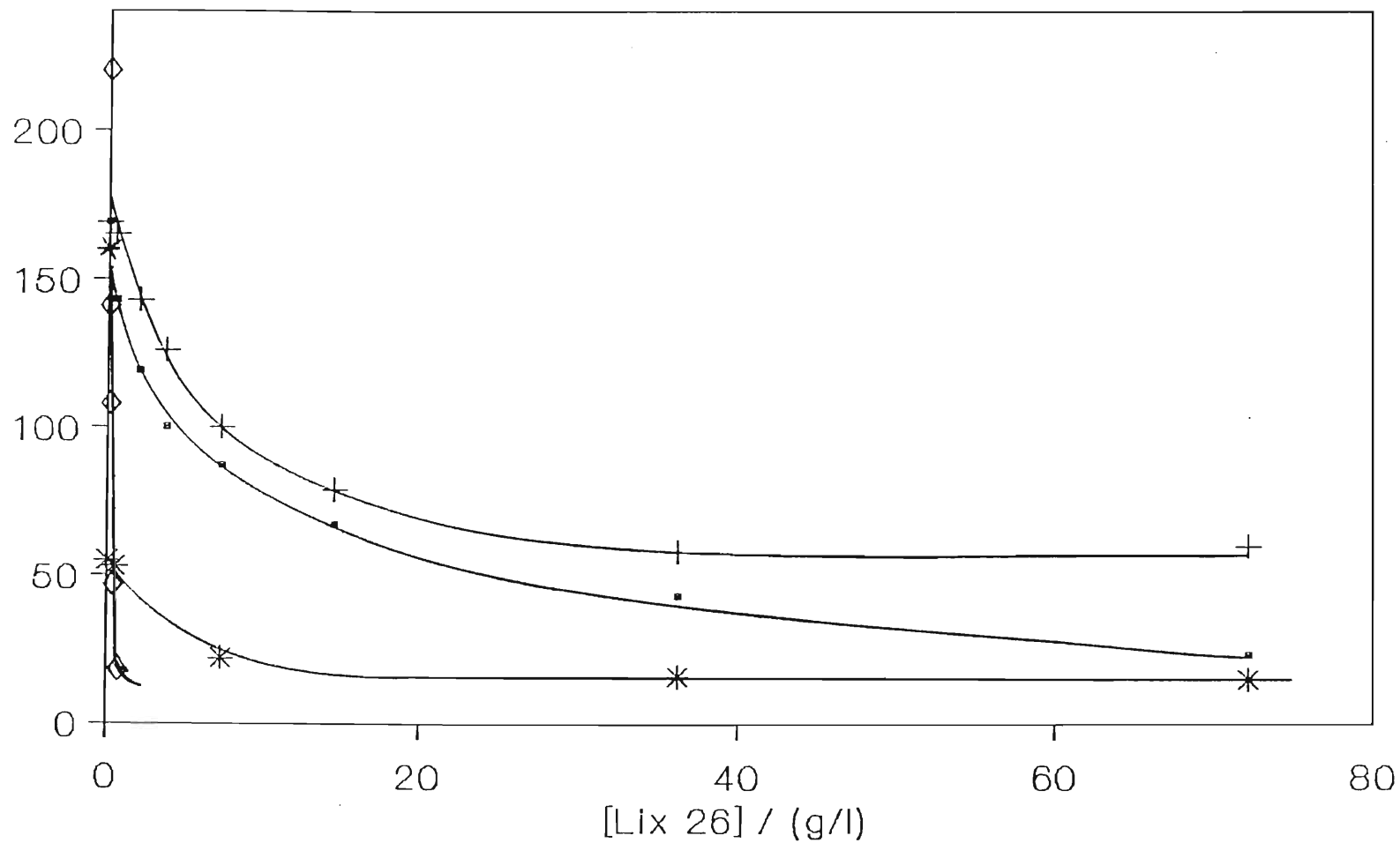
(i) Rapid declines in the values of  $\gamma$  are evident at very low (-0,21) and high (12,20) pH for [Lix 26]  $\leq$  1,0 g/l. Unlike the low pH (range) curve (which tends to zero interfacial tension), the curve at pH 12,20 levels off to approximately  $2,5 \times 10^{-3} \text{ Nm}^{-1}$ .

(ii) Less rapid declines in interfacial tension are evident as the pH increases above zero, indicating lower surface activity of Lix 26. Hence at pH 3,30, where HL is neutral (  $pK_{int} \approx 10,2$  -estimated in this work, Section 3.11.2.4 ;  $pK_a(H_2L^+) \sim 0^{(65)}$  ), ligand is least surface active.

Figure (111) shows plots of interfacial tension versus  $\log[\text{Lix 26}]$  at a number of aqueous phase pH's. A family of curves with varying gradients in the linear region is obtained with the most prominent decreases in interfacial tension occurring for  $pH < 0$  and  $pH > 11,0$ . Table (59) summarises the values of the gradients of these curves in the linear region, the values of  $\Gamma$  calculated from Equation (133) and the molecular coverage of the interface in molecules  $m^{-2}$ . The apparent interfacial area of the Lix 26 molecule at the pH of the measurement is also included in the table.



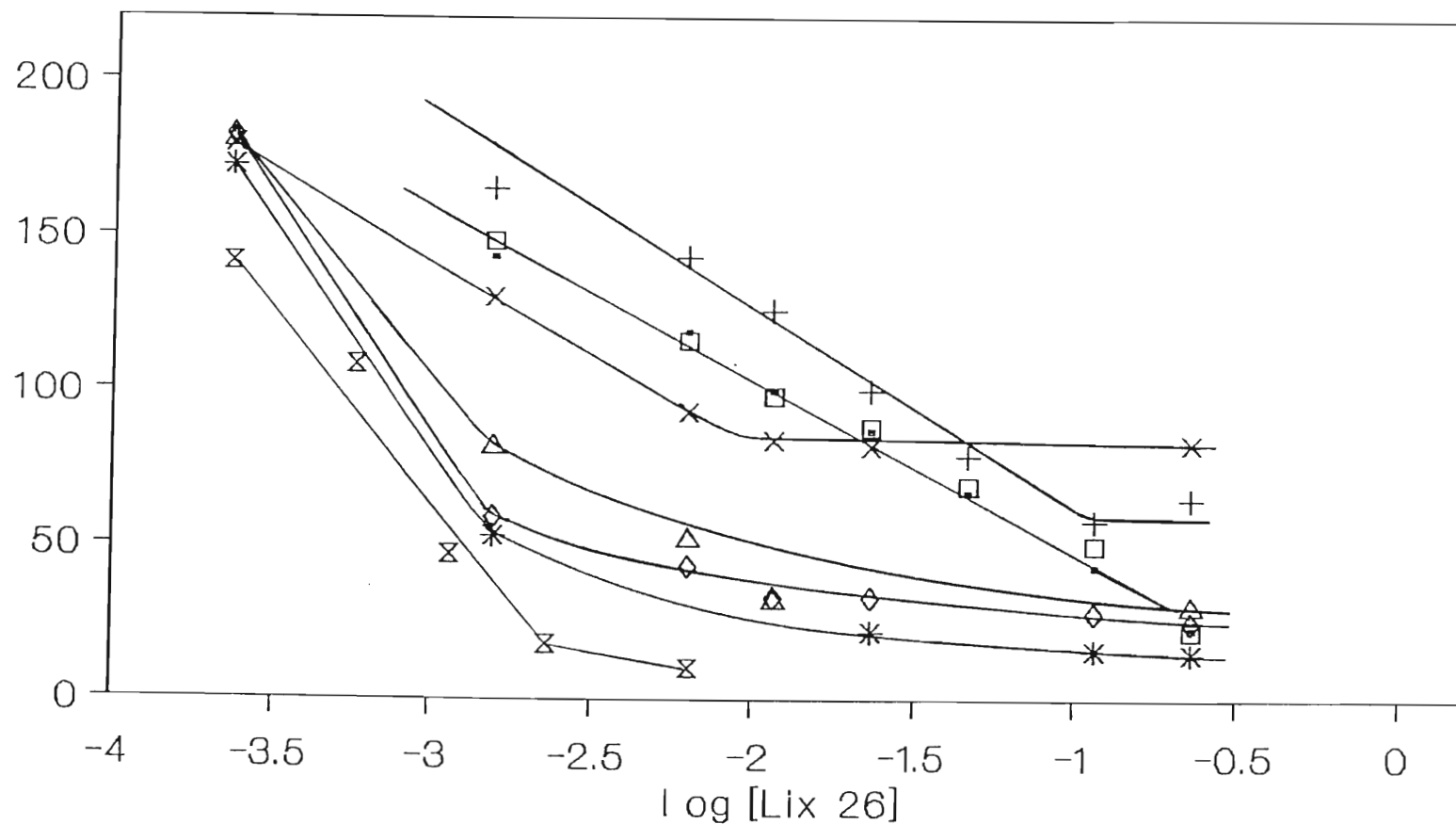
$\gamma$  / (Nm<sup>-1</sup> × 10<sup>-3</sup>)



$\square$  pH 1.90     $+$  pH 3.30     $*$  pH 12.20     $\diamond$  1.5 M  $\text{H}_2\text{SO}_4$

[Lix 26] corrected for active-constituent purity

Figure (110). Interfacial tension between organic phases containing Lix 26 and aqueous phases at various pH's versus the concentration of active-constituent corrected Lix 26 in AR toluene. Ionic strength of aqueous phases was maintained at 0,5 M with  $\text{Na}_2\text{SO}_4$ . Data recorded at 21°C.



• pH 1.90      + pH 3.30      \* pH 12.20      □ pH 1.75  
 x pH 10.00    ◇ pH 12.00    △ pH 11.00    ⊗ pH -0.21

[Lix 26] corrected for active-constituent purity

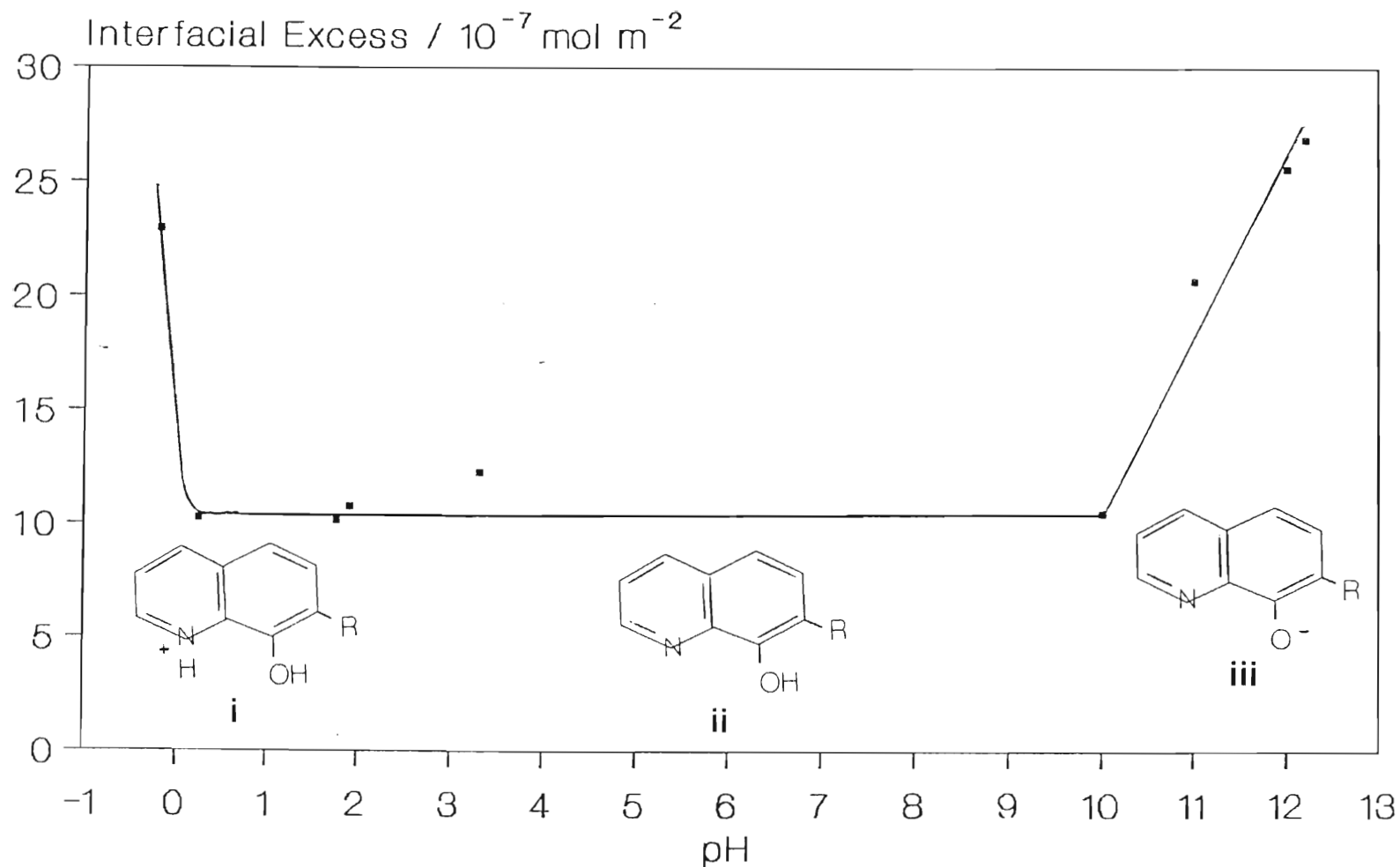
Figure (111). Interfacial tension between organic phases containing Lix 26 and aqueous phases at various pH's, versus log[Lix 26] (corrected for active-constituent purity). Organic phases : Lix 26 in AR toluene; Aqueous phases : various pH's obtained by addition of NaOH or H<sub>2</sub>SO<sub>4</sub> to a solution of constant ionic strength (0,5 M Na<sub>2</sub>SO<sub>4</sub>). Data recorded at 21°C.

| pH    | -(gradient) / Nm <sup>-1</sup> | Γ (Surface Excess) /mol m <sup>-2</sup> | Molecules Lix 26 per unit area of interface /molecules m <sup>-2</sup> | Area per molecule at the interface / Å <sup>2</sup> |
|-------|--------------------------------|---|--|---|
| -0,21 | 1,29 x 10 <sup>-2</sup>        | 2,29 x 10 <sup>-6</sup>                 | 1,38 x 10 <sup>18</sup>  | 72,4  |
| 0,24  | 5,77 x 10 <sup>-3</sup>        | 1,02 x 10 <sup>-6</sup>                 | 6,17 x 10 <sup>17</sup>  | 162,1   |
| 1,75  | 5,71 x 10 <sup>-3</sup>        | 1,01 x 10 <sup>-6</sup>                 | 6,10 x 10 <sup>17</sup>  | 163,9   |
| 1,90  | 6,05 x 10 <sup>-3</sup>        | 1,08 x 10 <sup>-6</sup>                 | 6,47 x 10 <sup>17</sup>  | 154,5   |
| 3,30  | 6,91 x 10 <sup>-3</sup>        | 1,23 x 10 <sup>-6</sup>                 | 7,39 x 10 <sup>17</sup>  | 135,3   |
| 10,00 | 5,89 x 10 <sup>-3</sup>        | 1,05 x 10 <sup>-6</sup>                 | 6,30 x 10 <sup>17</sup>  | 158,7   |
| 11,00 | 1,17 x 10 <sup>-2</sup>        | 2,07 x 10 <sup>-6</sup>                 | 1,25 x 10 <sup>18</sup>  | 80,0  |
| 12,00 | 1,44 x 10 <sup>-2</sup>        | 2,56 x 10 <sup>-6</sup>                 | 1,54 x 10 <sup>18</sup>  | 64,9  |
| 12,20 | 1,51 x 10 <sup>-2</sup>        | 2,69 x 10 <sup>-6</sup>                 | 1,62 x 10 <sup>18</sup>  | 61,8  |

Table (59). Interfacial excess,  $\Gamma$ , and apparent interfacial area of Lix 26 in toluene as a function of aqueous pH.

An indication of the change in the surface activity of Lix 26 which occurs when the aqueous phase pH is altered is given by plotting  $\Gamma$  vs pH. Figure (112) shows such a plot and it consists of three distinct regions: (i)  $\text{pH} \leq 0$  where Lix 26 exists as  $\text{H}_2\text{L}^+$  at the interface and is therefore highly surface active, (ii) a plateau region in which  $\Gamma$  is essentially constant at approximately  $1 \times 10^{-6} \text{ mol m}^{-2}$  and (iii) a second region of high surface activity ( $\text{pH} > 10,0$ ) where the ligand molecule is deprotonated in the form  $\text{L}^-$ . These regions of interfacial activity are also evident in the plots of interfacial tension versus  $\log[\text{Lix 26}]$  of Figure(111)- for regions (i) and (iii) above, the interfacial tension decreases abruptly with concentration of Lix 26 and levels off to a constant (and small) value, whereas for region (ii), the decreases in interfacial tension are more gradual and attain a higher limit of interfacial tension for the concentration range studied than those of regions (i) and (iii). At  $\text{pH } 10,0$ , the surface behaviour for  $\log[\text{Lix 26}] > -1,6$  is curious (Figure (111)), in that it suggests constant interfacial activity and therefore constant interfacial occupancy - this is probably associated with physico-chemical events which occur at values of pH close to the  $\text{pK}_a^{\text{int}}$ , approximately 10,14, and is the topic of discussion in the next section (Section 3.11.2.4).

Although the region of  $\text{pH} > 10$  is of little interest to the solvent extraction of germanium, interfacial tension measurements can be used to calculate an approximate value of  $\text{pK}_a^{\text{int}}$  - the apparent dissociation constant of the active extractant at the interface, (dealt with in the next section),



Structures (a), (b) and (c) correspond to the protonated, neutral and deprotonated forms of the ligand respectively

**Figure (112).** Interfacial excess ( $\Gamma$ ) (defined in Equation (133)) calculated from the gradients of the  $\gamma_c$  versus  $\log[\text{Lix 26}]$  plots of Figure (110) as a function of the aqueous phase pH. Aqueous phase conditions as for Figure (111) apply.

which is suggested by Figure (112) to be in the region of pH 10 - 11. In an analogous manner, interfacial protonation of Lix 26 is estimated to occur in the region of inflexion shown in Figure (112) at approximately pH = 0.

Regarding the change in apparent interfacial area of the Lix 26 molecule with varying pH (see Table (59)), it appears that the orientation of the charged species'  $H_2L^+$  or  $L^-$  at the interface gives an area of 60-80  $\text{\AA}^2$  per molecule, whereas the neutral species i.e. at pH 1-10, has an area in the range 130-160  $\text{\AA}^2$  per molecule. Alchemy, predicts the surface area per molecule to be approximately 125,5  $\text{\AA}^2$  which is therefore in reasonable agreement with the area calculated from interfacial tension measurements in the aqueous phase at a pH for which the Lix 26 species is neutral. The low values of interfacial molecular area at very low and high pH require explanation. Consider, for example, the position at high pH where the 8-hydroxyquinoline group is deprotonated.

Figure (113a) shows the neutral ligand and the 'thickness' of the part of the molecule which is most surface-active, while Figure (113b) shows the deprotonated species obtained by rotating (a) about the y-axis thus positioning the quinoline moiety in a flat plane. Since toluene cannot accommodate the charged portion of the molecule, it is likely that rearrangement occurs at the interface and results in the molecule adopting the most stable conformation which is the resultant of two energy terms: (i) the repulsion between adjacent molecules at the interface and (ii) the desire for the phenolic  $O^-$  to be in the aqueous phase. A similar rationale applies to the occupancy of the interface by the

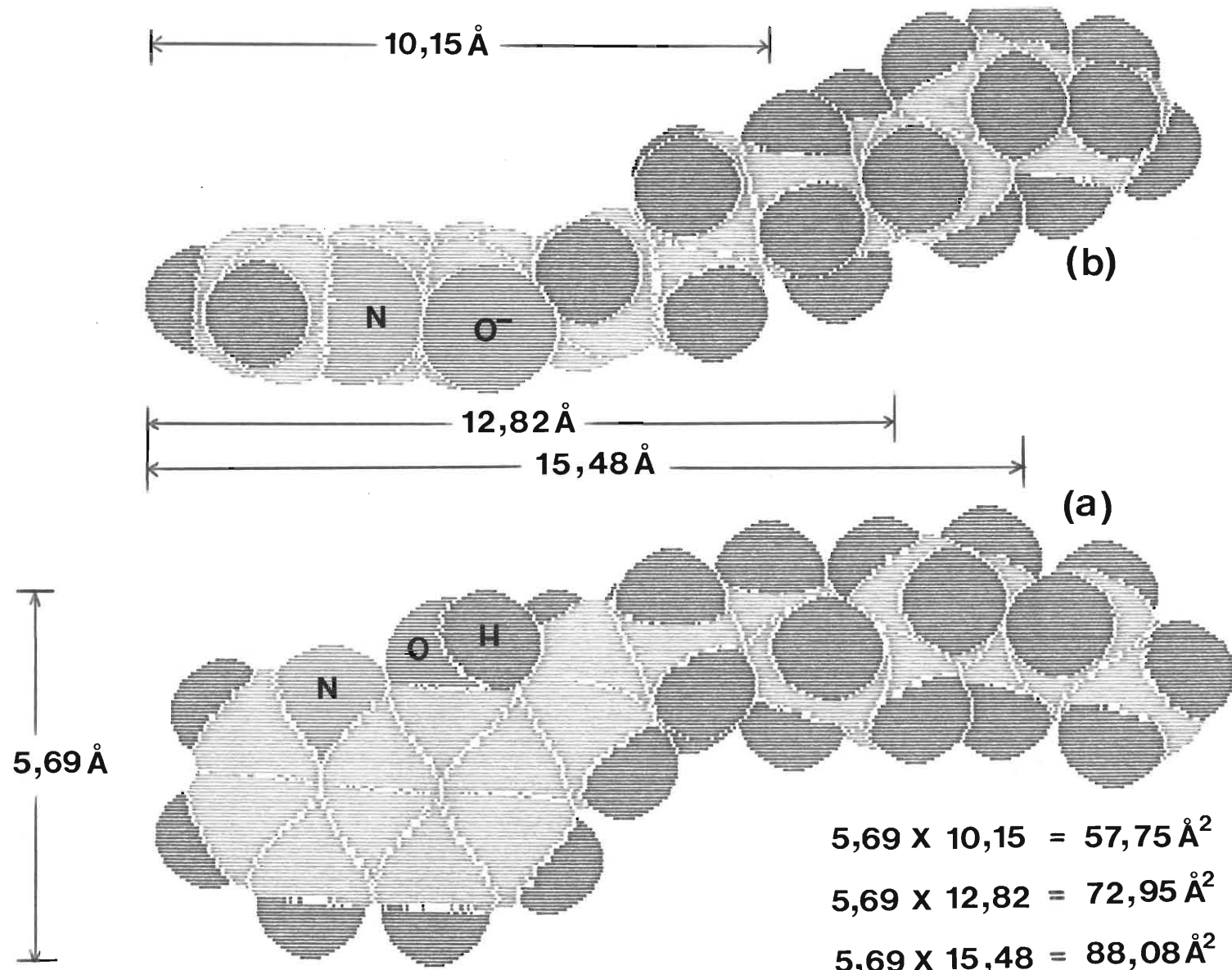


Figure (113). Alchemy-minimized structures of (a) protonated and (b) deprotonated Lix 26, showing approximate interfacial area of the molecule.

protonated form of the ligand. Although it is difficult to give an exact quantitative justification for the area of the molecule to decrease to 60-80 Å<sup>2</sup> under these conditions, a reasonable qualitative estimation is represented in Figure (113b). Using the dimensions which have been mapped out on the figure and assuming that the molecule roughly occupies a rectangle of these dimensions, it is possible to conceive of the molecule occupying an interfacial area in the region of 57-88 Å<sup>2</sup>. One of the difficulties which is implicit in this estimation is in deciding at which point of the 7-alkyl side chain of the molecule the C and H atoms do not occupy surface area at the interface.

There would be an apparent increase in reactivity of Lix 26 at pH < 0 which would be associated with the lower area occupied by the molecule at the interface resulting in increased packing (and therefore increased availability- assuming H<sub>2</sub>L<sup>+</sup> to be the species which reacts with germanium), however it must be reiterated that measurements of interfacial tension at static equilibrium have uncertain applicability to the situation prevailing at a droplet surface in a vigorously-stirred system.

#### 3.11.2.4. The Estimation of the Apparent Interfacial Acid Dissociation Constant $K_a^{int}$ .

The acid dissociation constant of an extractant molecule at an aqueous/organic interface,  $K_a^{int}$ , can be generally defined as follows:



$$K_a^{int} = \frac{[L^-]_{int} [H^+]_{int}}{[HL]_{int}} \quad (134)$$

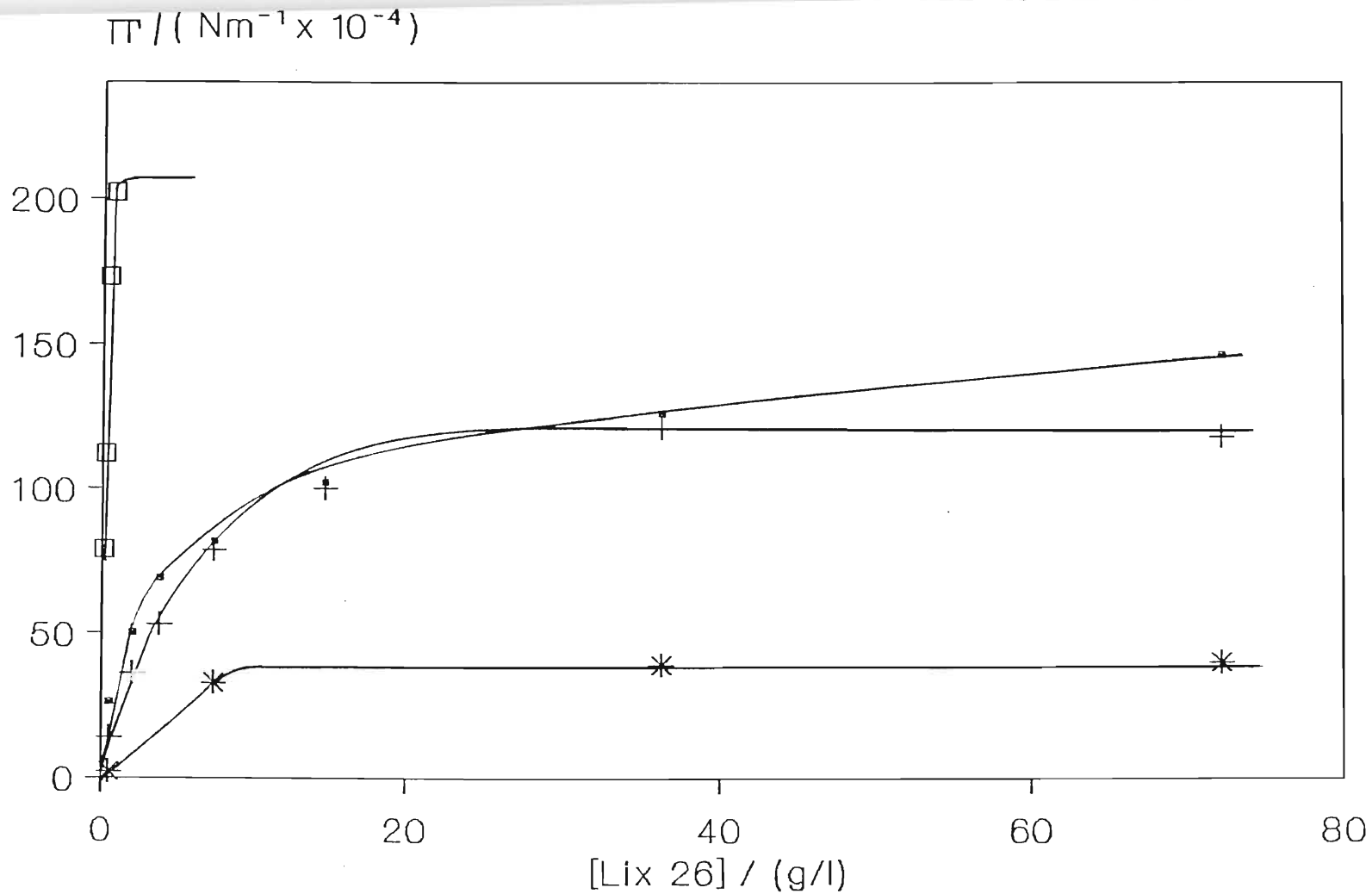
where 'int' denotes species at the phase boundary.

If it is assumed that  $[H^+]_{int} = [H^+]_{aq}$  (bulk phase hydrogen ion concentration), then we can rewrite (134) thus<sup>(233)</sup>:

$$K_a^{int} = \frac{[L^-]_{int} [H^+]}{[HL]_{int}} \quad (135)$$

Since protonation/deprotonation is an interfacial event,  $K_a^{int}$  is used for the acid dissociation constant.

To evaluate  $K_a^{int}$ , the pH dependence of the interfacial tension is examined using very dilute solutions of ligand and determining the interfacial pressure,  $\Pi$ , calculated from  $\Pi = \gamma_0 - \gamma$  where  $\gamma_0$  and  $\gamma$  refer to the interfacial tension in the absence and presence of Lix 26 respectively. Figure (114) shows plots of  $\Pi$  versus  $[Lix\ 26]$  over a wide range of concentration and at three values of pH and illustrates another means by which the concentration of ligand required to completely saturate the interface can be estimated, since such plots become linear when there is no further population of the interface by the ligand—for example at pH 1,90 this occurs at  $[Lix\ 26] \approx 5,0$  g/l. At very low concentration, such plots yield a family of straight lines of the type  $\Pi = m[HL]_{org}$ , where  $[HL]_{org}$  is the bulk organic concentration of ligand and  $m$  is the gradient with units of  $Nm^{-1} dm^3 mol^{-1}$ . The general



◻ pH 1.90    + pH 3.30    \* pH 12.20    ◻ 1.5 M  $\text{H}_2\text{SO}_4$

[Lix 26] corrected for active-constituent purity

Figure (114). The interfacial pressure,  $\Pi$ , between solutions of Lix 26 in toluene and aqueous phases of various pH, as a function of [Lix 26], corrected for active constituent purity. Interfacial pressure is the difference in interfacial tension between the phases which is caused by adsorption of amphiphilic molecules at the phase boundary.

definition of the Gibbs Adsorption Isotherm is given by Equation (136):

$$\Gamma = - \frac{C}{RT} \left( \frac{d\gamma}{dC} \right)_T \quad (136)$$

where all symbols are as previously defined.  $C$  in Equation (136) is the bulk organic concentration of ligand,  $[HL]_{org}$ , and substituting  $\Pi$  for  $\gamma$  and noting that  $-(\gamma_0 - \gamma)$  is the lowering of interfacial tension gives:

$$\Gamma = \frac{[HL]_{org}}{RT} \frac{d\Pi}{d[HL]_{org}} \quad (137)$$

The interfacial excess,  $\Gamma$ , is given by:

$$\Gamma = \frac{n_1^s}{S} + \frac{n_2^s}{S} + \dots + \frac{n_i^s}{S} \quad (138)$$

where :  $n_i^s$  = number of molecules of species  $i$  in the interface

$S$  = the surface area

and therefore, since at any  $pH > pK_a^{int}$  the only species which occupy the interface are  $HL$  and  $L^-$  then,

$$[HL]_{int} + [L^-]_{int} = \frac{[HL]_{org}}{RT} \cdot \frac{d\Pi}{d[HL]_{org}} \quad (139)$$

The distribution coefficient between the interface and the organic phase is given by:

$$D_{int} = \frac{[HL]_{int}}{[HL]_{org}} \quad (140)$$

Multiplying both sides of Equation (135) by Equation (140) gives:

$$K_a^{int} D_{int} = \frac{[L^-]_{int}[H^+]}{[HL]_{int}} \cdot \frac{[HL]_{int}}{[HL]_{org}} \quad (141)$$

and therefore:

$$\frac{D_{int} K_a^{int}}{[H^+]} = \frac{[L^-]_{int}}{[HL]_{org}} \quad (142)$$

Solving Equation (139) for  $d\Pi/d[HL]_{org}$  gives:

$$\frac{d\Pi}{d[HL]_{org}} = m = RT \frac{[HL]_{int}}{[HL]_{org}} + RT \frac{[L^-]_{int}}{[HL]_{org}} \quad (143)$$

Inserting Equations (135) and (140) into (143) gives finally:

$$m = RT D_{int} + \frac{RT D_{int} K_a^{int}}{[H^+]} \quad (144)$$

Examination of Equation (144) shows that the first term is independent of  $[H^+]$ , hence when  $[H^+]$  is high as at low pH,  $RT D_{int} K_a^{int}/[H^+] \rightarrow 0$  and  $m = m_a = RT D_{int}$ . Thus, taking the logarithm of (144) and inserting  $m_a$  for the first term gives:

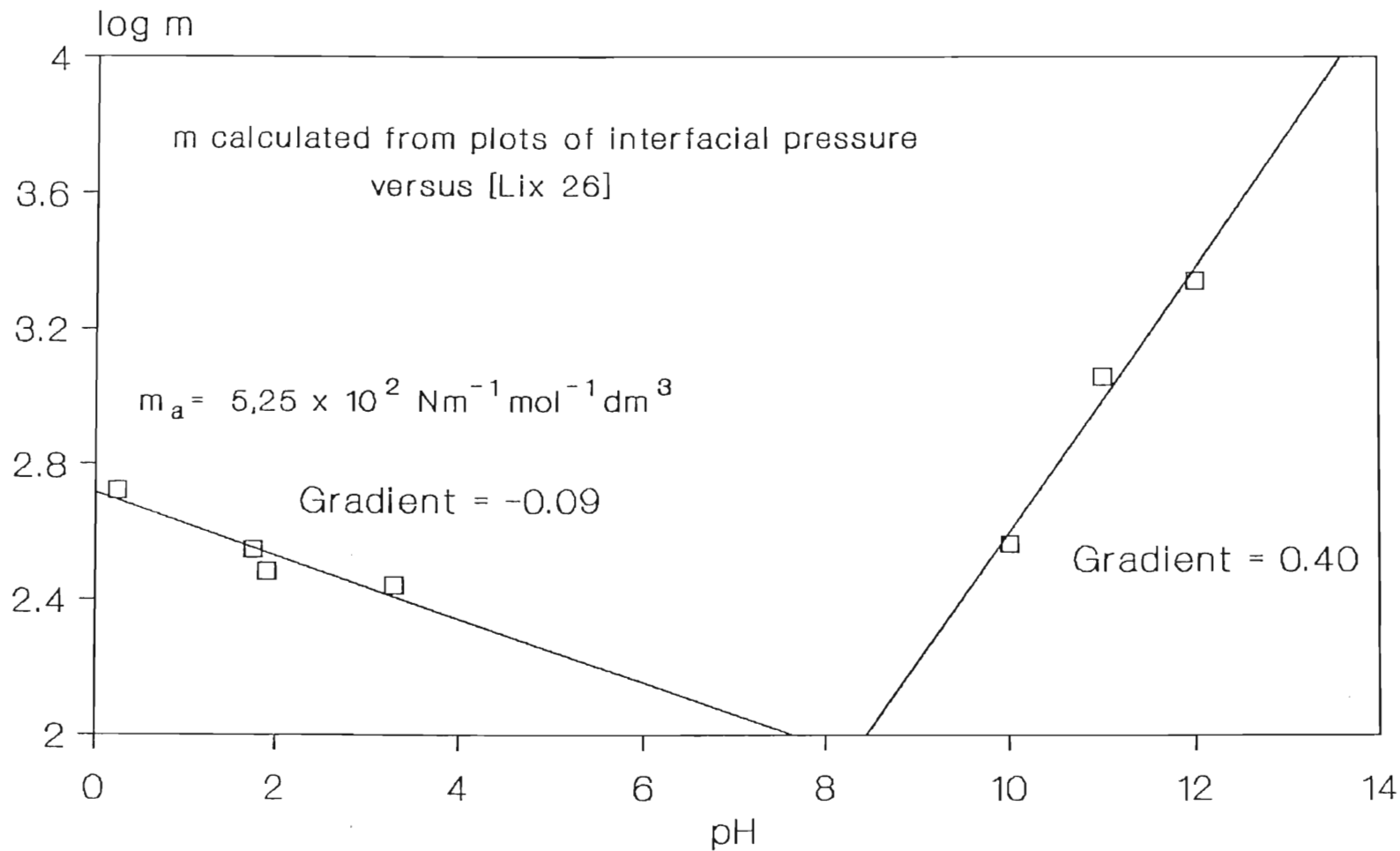
$$\log(m - m_a) = pH + \log RT D_{int} K_a^{int} \quad (145)$$

Equation (145) suggests that in the acidic region,  $\log m$  is constant, whereas in an alkaline medium  $\log (m-m_a)$  tends to increase with pH. Figure (115) shows a plot of  $\log m$  versus pH for the regions 0,24 - 3,30 and 10,0 - 12,0. Although  $\log m$  is not constant at low pH (probably as a result of the error associated with calculating the value of  $m$  over too few experimental points and partly because at pH close to 0, the ligand begins to protonate - this is evident from the deviation from linearity at pH 0,24 in Figure (115)), it does however show little change over the range studied

(gradient = -0,09) and a value of

$m_a = 5,25 \times 10^2 \text{ Nm}^{-1} \text{ mol}^{-1} \text{ dm}^3$  is calculated. At high pH,  $m$  increases linearly with pH with a gradient of 0,40. From the observed value of  $m_a = 5,25 \times 10^{-1} \text{ Nm}^{-1} \text{ mol}^{-1} \text{ dm}^3$ ,  $D_{\text{int}}$  can be calculated from  $m_a = RTD_{\text{int}}$  giving  $D_{\text{int}} = 2,15 \times 10^{-7} \text{ m}$  at 21°C. The value of  $K_a^{\text{int}}$  can now be calculated by selecting any pH along the straight line plot of Figure (115) and interpolating for a value of  $m$ . For example, at pH = 10,50,  $\log m = 2,73$ , hence  $m = 5,37 \times 10^{-1} \text{ Nm}^{-1} \text{ mol}^{-1} \text{ dm}^3$  and  $\log (m-m_a) = 1,08$ .

Solving Equation (145) for  $K_a^{\text{int}}$  at 21°C using the value of  $D_{\text{int}}$  above gives  $\text{p}K_a^{\text{int}} \approx 10,14$ . The apparent interfacial dissociation constant is therefore  $7,24 \times 10^{-11} \text{ M}$ . This value of  $\text{p}K_a$  compares closely with the bulk value of  $10,40 \pm 0,05$  measured by Bag and Freiser<sup>(91)</sup> for Kelex 100 and is slightly higher than the value of  $9,66 \pm 0,03$  for 8-hydroxyquinoline<sup>(90)</sup> (which is expected because the 7-alkyl group of the Lix 26 exerts an inductive effect on the ortho 8-hydroxy group rendering it a weaker acid). This value of  $\text{p}K_a^{\text{int}}$  means that at pH 12, for example, approximately 99% of the Lix 26 is adsorbed at the interface in the dissociated form. This



m : gradient of the plot  $\Pi = m [\text{HL}]$  (e.g. from Figure 113) obtained at low ligand (i.e. the linear portion) concentration

Figure (115). Plot of  $\log m$ , where  $m$  is the gradient of the straight line plots of  $\Pi = m[\text{HL}]$  obtained at very low Lix 26 concentration, versus the pH of the aqueous phase for which interfacial tension measurements were made.

observation has implications in the description of the processes occurring during stripping at high pH.

Thus far, the Gibbs Adsorption Isotherm has been utilised to facilitate a thermodynamic treatment of surface tension measurements, however there are a number of other isotherms which provide descriptions of monolayer adsorption of solute molecules at an interface and one of these is described below.

### 3.11.2.5. Application of the Langmuir Isotherm to Interfacial Pressure Data for Lix 26/Toluene Systems

Examination of the plots of interfacial pressure versus Lix 26 concentration in Figure (114) shows a form of dependence reflecting the increasing difficulty that surface-active molecules have in populating the interface as saturation of the interface is approached. This behaviour is somewhat analogous to the adsorption of a monolayer of gas onto a solid support. Consequently, it seems plausible that the Langmuir Isotherm may be used to characterize the interfacial properties of extractants spread as a monolayer film at the aqueous/organic interface.

The conventional Langmuir Adsorption Isotherm may be written in the form given in Equation (146)<sup>(234)</sup>:

$$\frac{P}{V} = \frac{1}{bV_m} + \frac{P}{V_m} \quad (146)$$

where P is the gas pressure,  $V_m$  is the amount of gas adsorbed per gram of solid at the monolayer point, V is the amount of gas adsorbed per gram of solid and b is a function of a number of constants and the temperature viz.<sup>(234)</sup>

$$b = NA^2 \Gamma_o \sqrt{1/(2\pi RM)} \cdot e^{Q/RT} \quad (147)$$

where : N : Avogadro's Number

A : Area of an adsorbate molecule

$\Gamma_o$  : Time of stay of a molecule in the vicinity of the surface assuming no attractive forces between the molecule and the solid surface

R : Gas constant

M : Molar mass of the adsorbate

Q : Energy of adsorption

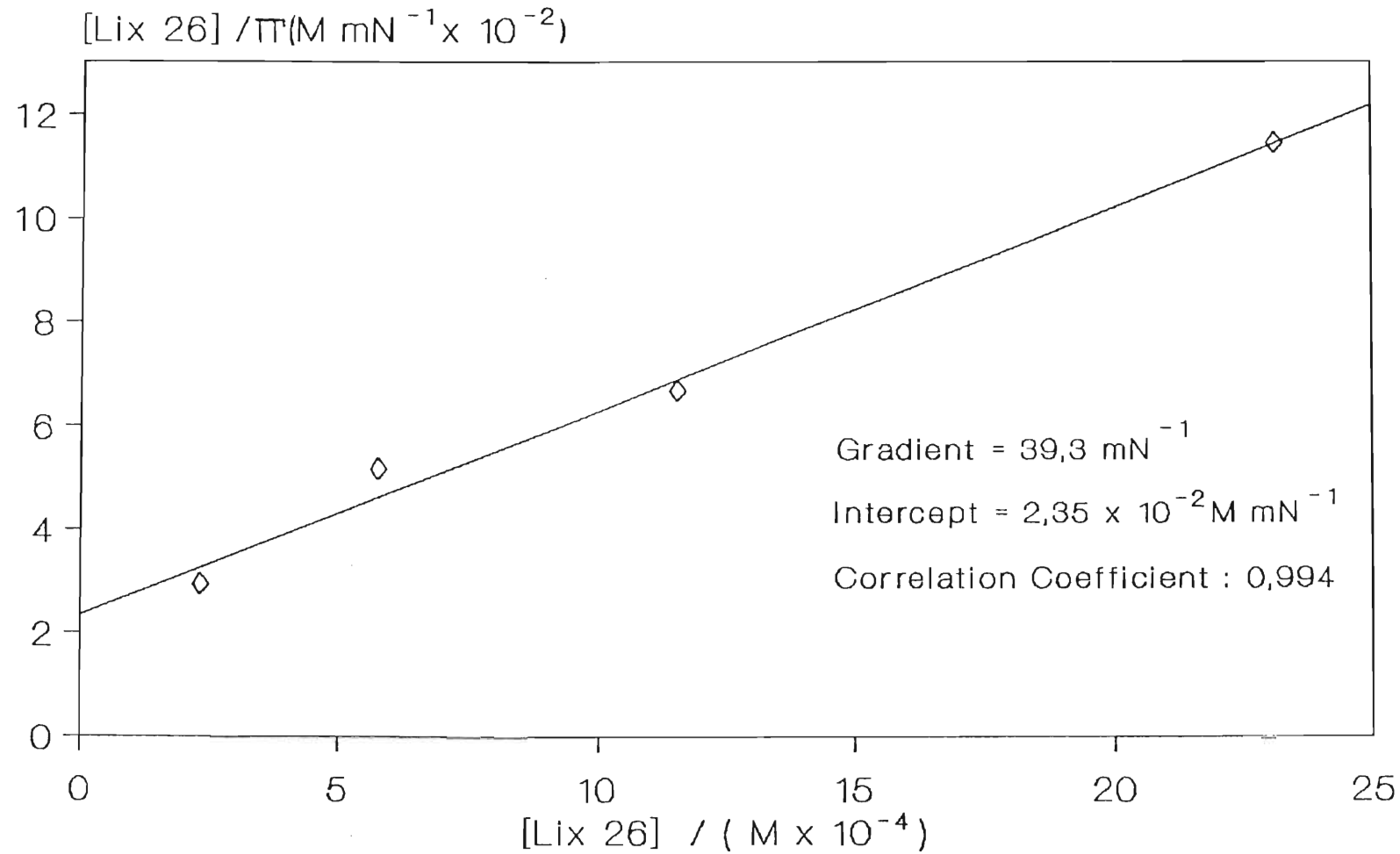
Equation (148) gives a form of Equation (146) appropriate to the adsorption of extractant molecules from a bulk organic phase onto an organic/aqueous interface<sup>(184)</sup> :

$$\frac{c}{\Pi} = \frac{1}{pq} + \frac{c}{q} \quad (148)$$

where c is the bulk organic concentration of extractant,  $\Pi$  is the interfacial pressure ( $\gamma_o - \gamma$ ) in  $\text{Nm}^{-1}$  and p and q have physical meanings analogous to b and  $V_m$  for liquid interface adsorption, i.e. q is an indication of the number of extractant molecules adsorbed as a monolayer at the interface and the change in p with pH indicates the deviation of (147) from ideality as the attractive forces associated with the interface vary.

The form of Equation (148) shows that, if the Langmuir Adsorption Isotherm is a relevant representation of surface coverage by extractant, a plot of  $c/\Pi$  versus c should give a linear plot with gradient  $1/q$  and intercept  $1/pq$ . Figures (116) - (118) show such plots for Lix 26 at values of pH of -0,21, 1,75 and 10,00 respectively. The linear form of





**Langmuir type Isotherm** :  $\frac{c}{\Pi} = \frac{1}{pq} + \frac{c}{q}$     c : concentration of Lix 26 in toluene,  $\Pi$  : interfacial pressure, p, q : constants

Figure (116). Langmuir-type isotherm (Equation (148)) obtained from interfacial tension data for Lix 26 solutions of various concentration and an aqueous phase 1,5 M in H<sub>2</sub>SO<sub>4</sub> (approximate pH = -0,21). Data recorded at 21°C.

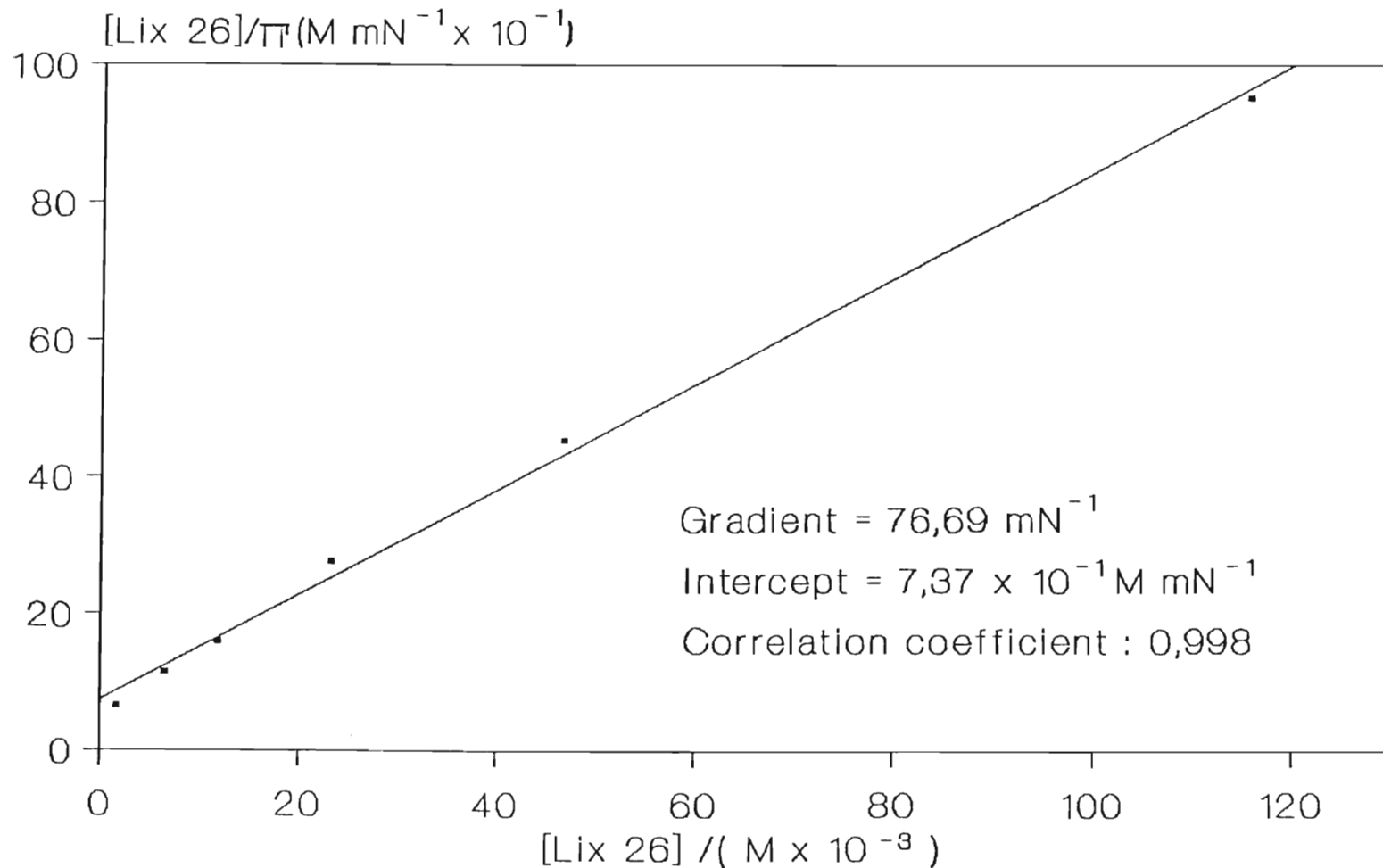
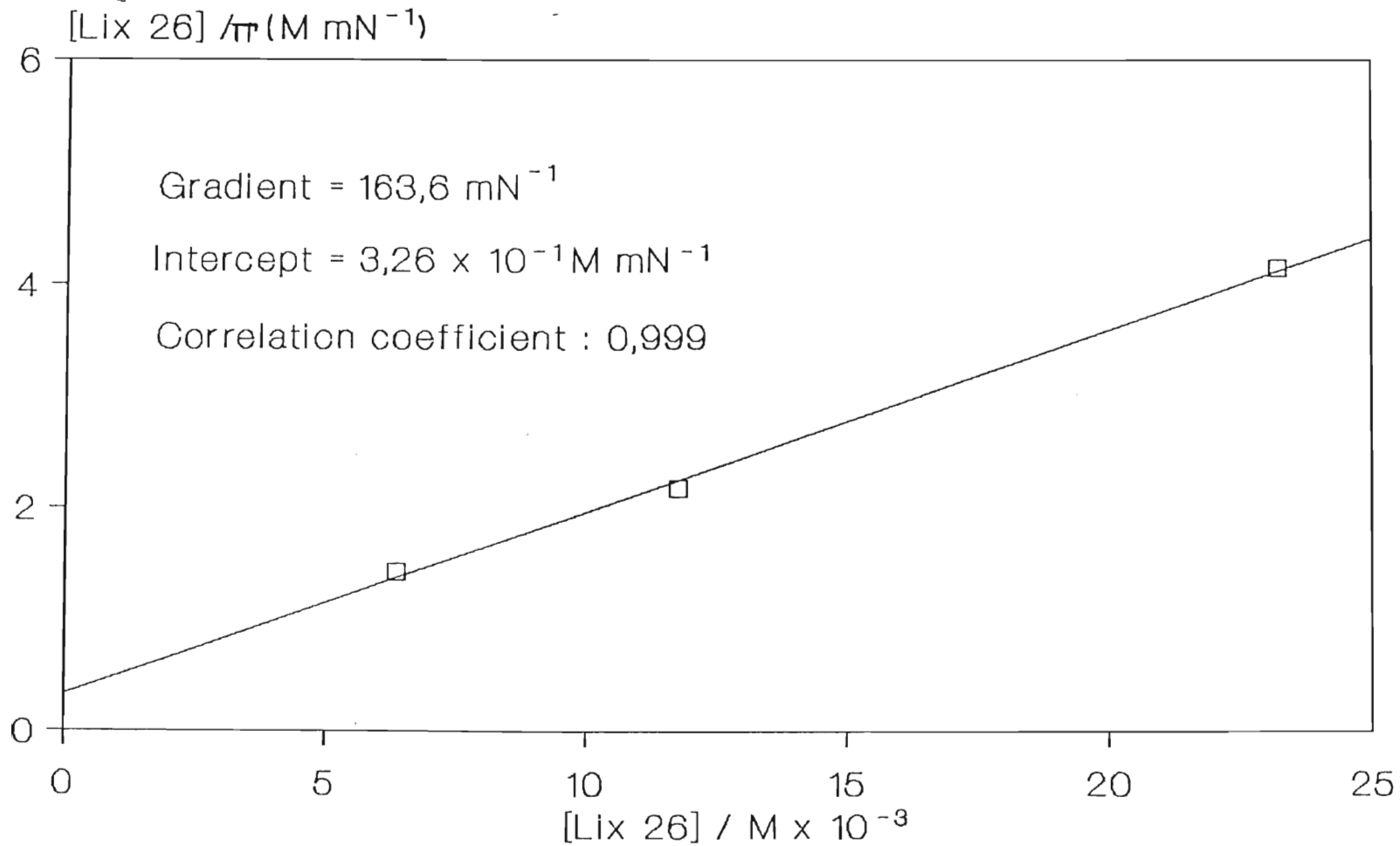


Figure (117). Langmuir-type isotherm obtained from interfacial tension data for Lix 26 solutions of various concentration and an aqueous phase of pH 1,75. Data recorded at 21°C.



**Figure (118).** Langmuir-type isotherm obtained from interfacial tension data for Lix 26 solutions of various concentration and an aqueous phase of pH 10,00. Data recorded at 21°C.

these plots demonstrates that, in principle, the Langmuir isotherm is no less valid in application to a liquid/liquid interface than a gas/solid system. Values of  $p$  and  $q$  calculated from these data are given in Table (60).

| pH    | $p / \text{mol}^{-1} \text{ m}^3 \times 10^{-3}$ | $q / \text{Nm}^{-1}$  | Correlation coefficient |
|-------|--|-----------------------|-------------------------|
| -0,21 | 1672,0   | $2,55 \times 10^{-2}$ | 0,994                   |
| 1,75  | 104,1  | $1,30 \times 10^{-2}$ | 0,998                   |
| 10,00 | 502,7  | $6,11 \times 10^{-3}$ | 0,999                   |

Table (60). Values of the constants  $p$  and  $q$  in Equation (148) calculated from Langmuir-type plots of interfacial pressure data for Lix 26 in toluene.

The decreasing value of  $q$  in Table (60) is associated with a decrease in the number of molecules of Lix 26 in the interfacial monolayer while the fluctuation in the value of  $p$  correlates, on a qualitative level, with the difference in attractive forces experienced by a Lix 26 molecule during its length of stay at the interface, i.e. if some attractive forces, e.g. between the charged  $\text{H}_2\text{L}^+$  molecule and the species in the aqueous medium if  $\text{pH} < 0$ , are present at the interface, then according to Frenkel<sup>(235)</sup>, the average time of stay,  $\Gamma$ , (N.B. this use of the symbol  $\Gamma$  is not the Interfacial excess as previously defined), of the molecule at the interface (or on the surface for gas/solid adsorption) is:

$$\Gamma = \Gamma_0 e^{(Q/RT)} \quad (149)$$

and hence  $\ln(\Gamma - \Gamma_0) = Q/RT$ . Therefore at constant temperature,  $(\Gamma - \Gamma_0)$  is a function of the difference in energy between a monolayer of neutral HL molecules at the interface which experiences attractive forces and a monolayer which does not.<sup>2</sup> Inspection of this equation shows that if the interaction energy is constant (which would occur if the pH of the aqueous phase, ionic strength and [HL] were kept constant) then  $\ln(\Gamma - \Gamma_0)$  is proportional to  $1/T$  - hence as the temperature of an aqueous/organic mixture in contact is increased, the energy of attraction between HL and aqueous species at the interface decreases and conversely, as the temperature is decreased, the energy of attraction increases. This implies that as the temperature increases, molecules spend less time at the interface (i.e.  $\Gamma - \Gamma_0$  is large) and this is manifest by the observed decrease in germanium extraction rate reported in Section 3.9.2 and the rationale that ligand availability is responsible for the apparent negative activation energy.

Examination of Equation (147) shows that the term  $\Gamma_0 e^{Q/RT}$

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<sup>2</sup> In the case of this study, the ideal situation in which non-interaction between ligand molecules and the aqueous medium does not exist because molecules of HL possess polar moieties viz -OH and =N- which are surface-active. However it is envisioned that  $\Gamma_0$  is an estimate of the time spent at the interface by the form of HL (neutral) which experiences the lowest possible interaction-  $H_2L^+$  and  $L^-$  would experience greater attraction at the interface.

incorporates all of the adjustable parameters since  $N$ ,  $A$ ,  $R$  and  $M$  are constant if the media are the same and the ligand is present in the same ionic form (i.e. the aqueous phase pH is constant). Since  $p$ -the constant obtained from the Langmuir treatment of liquid-liquid absorption, is equivalent to  $b$  for gas/solid adsorption, then solving Equation (147) for  $p$  ( $\approx b$ ) =  $1672 \times 10^3 \text{ mol}^{-1} \text{ m}^3$  with  $A = 72,4 \times 10^{-20} \text{ m}^2$  (from interfacial tension measurements - see Table (59)) for  $\text{pH} = -0,21$  gives:

$$\Gamma_o e^{Q_1/RT} = 490 \quad (\text{pH}=-0,21) \quad (150)$$

where  $Q_1$  is the interaction energy applicable to ligand in its protonated form  $\text{H}_2\text{L}^+$  at the liquid-liquid interface.

Similar treatment for  $\text{pH} 1,75$  ( $A = 163,9 \times 10^{-20} \text{ m}^2$ ,  $p = 104,1 \times 10^3 \text{ mol}^{-1} \text{ m}^3$ ) and  $\text{pH} 10,00$  ( $A = 158,7 \times 10^{-20} \text{ m}^2$ ,  $p = 502,7 \times 10^3 \text{ mol}^{-1} \text{ m}^3$ ) gives:

$$\Gamma_o e^{Q_2/RT} = 13 \quad (\text{pH}=1,75) \quad (151)$$

$$\Gamma_o e^{Q_3/RT} = 67 \quad (\text{pH}=10,00) \quad (152)$$

Inspection of Equations (150) to (152) shows that at constant temperature  $Q_1 > Q_3 > Q_2$  i.e. the interaction energy at the phase boundary is high when the ligand is present in its protonated form  $\text{H}_2\text{L}^+$  where Equation (150) applies and in its anionic form  $\text{L}^-$  (at  $\text{pH} 10,00$ ,  $[\text{L}^-] = 0,72[\text{HL}]$  for  $\text{pK}_a^{\text{int}} = 10,14$  i.e. at  $\text{pH} 10,00$  the ligand is 72% deprotonated)

where Equation (152) applies. Unfortunately, the value of  $\Gamma_0$  is not quantifiable and could conceivably be anything from the diffusion-controlled lifetime of a molecule at the interface to some value greater than that at which it reacts with germanium and this puts  $\Gamma_0$  in the approximate range  $1 \times 10^{-3} - 1 \times 10^{-9}$  s (these are mean lifetimes approximated from  $\Gamma_0 = 1/k$ ), thus the evaluation of  $Q_1$ ,  $Q_2$  and  $Q_3$  is not possible, however a ratio of the interaction energies can be determined viz.

$$\begin{array}{ccc} Q_1 & : & Q_2 & : & Q_3 \\ \ln(490) & & \ln(13) & & \ln(67) \\ 6,19 & & 2,56 & & 4,20 \end{array}$$

The interaction energy between  $H_2L^+$  and aqueous species at the interface is therefore approximately 2,4 times the interaction energy experienced by the neutral molecule and this result suggests that the protonated form of the ligand is a highly reactive and more surface-active interfacial species compared with the neutral molecule.

### 3.11.3. The Change in Solution Viscosity With Increasing Ligand Concentration.

In Section 2.4.2.2.6, it was mentioned that the prime reason for diluting an extractant with a diluent was to reduce the viscosity of the as-received material to overcome difficulties associated with their handling. Approximate viscosities of TN 01787, TN 02181 and Lix 26 in their as-received forms are summarised in Table (61) below (measured as described in Section 2.5.3).

| Reagent  | Viscosity / $\text{N s m}^{-2} \times 10^{-3}$ |
|----------|--|
| Toluene  | 0,56   |
| Lix 26   | 3,56   |
| TN 02181 | 3,52   |
| TN 01787 | 3,45   |

Table (61). Viscosities of Lix 26, TN 02181 and TN 01787 and toluene at 25°C. Measurements made with a U-tube Ostwald Viscometer.

$$1 \text{ N s m}^{-2} = 1 \text{ kg s}^{-1} \text{ m}^{-1}.$$

Such high viscosities suggest that increasing ligand concentration in the organic phase used for kinetic and equilibrium extraction studies, may result in increased viscosity. Figure (119) shows the relationship between viscosity and the as-received ligand concentration for the three extractants of interest to this work. For all three ligand preparations, the viscosity increases steadily up to approximately 100,0 g/l and then rapidly thereafter. In Section 3.2.1.2, it was suggested that the reason for the tendency towards fractional order behaviour of these three extractants at high ligand concentration is the attainment of a completely saturated interface i.e. further ligand loading results in no observed change in extraction kinetics. In this work, it has been proposed that the rate-determining step in the extraction of germanium by 7-alkylated-8-hydroxyquinoline reagents is the stereochemically-controlled reaction between



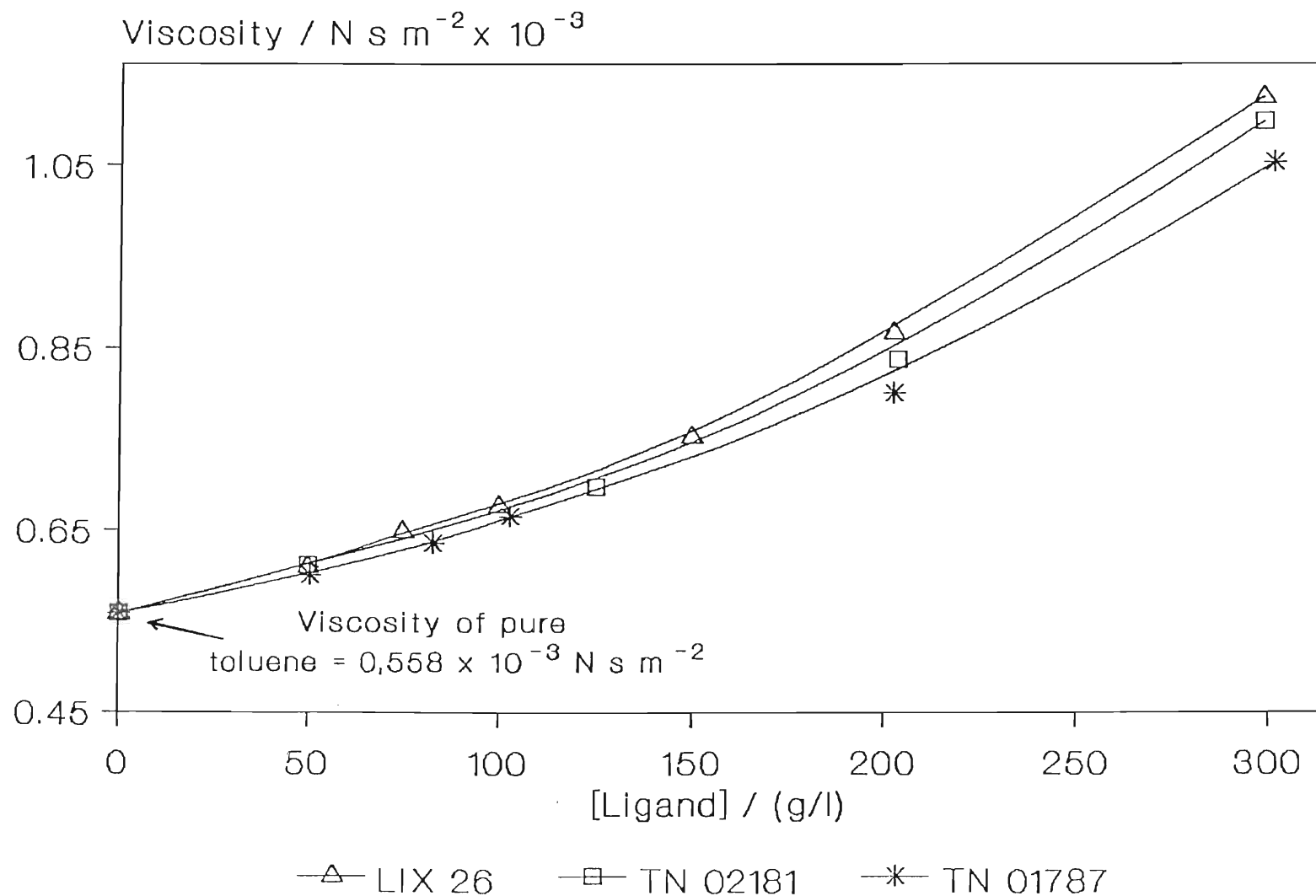
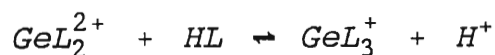


Figure (119). Change in organic solution viscosity of Lix 26, TN 02181 and TN 01787 as a function of the quantity of ligand reagent added to the toluene diluent. All measurements were made at  $25^{\circ}\text{C}$  with a U-tube Ostwald Viscometer.

the intermediate  $\text{GeL}_2^{2+}$  and a molecule of neutral HL at the interface viz.



and thus since the rate of diffusion of reactants and products to and from the interface is much greater than the chemical reaction rates, diffusion effects are unlikely to be rate-limiting, however it is suggested that the increase in viscosity which occurs with high ligand loading of the diluent may contribute to the fractional apparent reaction order with respect to ligand since diffusion of ligand to the interface and products, i.e.  $\text{GeL}_3^+\text{HSO}_4^-$ , away from it are reduced with increasing viscosity. It is therefore proposed that over and above exceeding the maximum interfacial population discussed above, that at some high viscosity limit, the rate-determining step is modified to reflect the slowness of reactant replacement and product diffusion from the interface.

There are very few reported studies of the relationship between the diffusion with reaction of solutes across an organic/aqueous interface and the viscosity of the extractant/diluent solution. This is probably a result of, for the most part, the difficulty of controlling all parameters besides the viscosity in order to attribute any observed change exclusively to the viscosity, however Hughes *et al.*<sup>(158)</sup> observed a linear relationship between the diffusivity (in  $\text{cm}^2 \text{s}^{-1}$ ) of copper in aqueous solution into organic solutions of Lix 63, Lix 64N and Lix 65N in Escaid 100 (a diluent marketed by Esso containing 20 % aromatics, 56,6 % paraffin and 23,4 % naphthenes) and the reciprocal of

the viscosity i.e. diffusion rates of the metal ion decreased with increasing viscosity. Unfortunately the present knowledge of the transfer of solutes across liquid-liquid boundaries is not sufficiently developed to provide a basis for a satisfactory predictive model in terms of viscosity. However all of the models which have been proposed indicate some inverse relationship between solute transfer and organic phase viscosity. The predictability of such models and their limitations have been reviewed by Pratt<sup>(236)</sup>. In addition, it has been noted by Hanson *et al.*<sup>(237)</sup>, that bulk viscosities do not necessarily represent the viscosity in the vicinity of the liquid-liquid interface. Also there is evidence that the organic phase viscosity increases markedly as it becomes loaded with metal<sup>(238)</sup>.

It is apparent from Figure (119) that for the extractant systems studied in this work (all in toluene), the increase in viscosity with increasing [HL] is approximately the same for all three. In Sections 3.1.3 and 3.2.1.2, it was shown that the observed deviation of  $k_f(\text{obs})$  from a linear dependence on  $\log[\text{HL}]$  for all three extractants occurred at approximately 100 g/l in both the Lewis Cell and in the vigorous shaking apparatus (except for TN 02181 in the Lewis Cell, the observed fractional order dependence occurred at a concentration of ~ 75 g/l) and these concentrations correlate with solution viscosities of approximately  $7,0 \times 10^{-3} \text{ N s m}^{-2}$ . This, however, is the change in bulk organic viscosity and as suggested above may or may not represent the viscosity in the vicinity of the liquid-liquid interface. If the viscosity of the reactants and the products of the metal-ligand reaction at the interface are a limiting factor then layers of them may separate bulk ligand

from the interface and hence the diffusion of these species may be significant in the rate equation. The experiments performed in this work have not extended to the unknown physical conditions of such (high ligand concentration) films and therefore it is not possible to postulate an analytical expression to account for this effect.

#### 3.11.4. Correlations Between Dielectric Constant of Organic Media and Extractant Performance.

In Section 3.7.1, the relationship between the dielectric constant of modifier solutions of ligand and the increase in the observed rate of germanium extraction was discussed. Although the mechanism by which these additives enhance the equilibrium and kinetics of extraction is little understood<sup>(208)</sup> it seems likely that they hydrogen-bond to the extractant and improve its interfacial characteristics by rendering it slightly more hydrophilic. Furthermore, modifiers assist the extraction process by lowering the interfacial tension and reducing the tendency toward the formation of stable emulsions and in some cases the formation of a three-phase system<sup>(17,239,240)</sup>. In addition, it is proposed in this work that modifiers improve the receptiveness of the organic medium to the charged  $\text{GeL}_3^+\text{HSO}_4^-$  species and the occurrence of this phenomenon can be supported by trends in the observed changes in the dielectric constant with modifier addition. Remarks have already been made about the broad generalisation required to attribute an increase in observed rates of extraction to a single parameter such as dielectric constant. The addition of a modifier always alters a number of physico-

chemical characteristics of a system besides the dielectric . However the relationship observed between  $\epsilon_c^f$  and  $k_f(\text{obs})$  is remarkable and suggests that a modifier's action can be predictable if all the other related properties e.g. solubility, viscosity, flash-point are satisfactory. In Section 3.7.3, an account was given of the change in germanium extraction characteristics (as percentage extraction at equilibrium) of Lix 26/BDH Distillate solutions containing a varying quantity of n-octanol. It was observed that up to approximately 40-50% by volume, improved extraction was obtained, however at n-octanol > 60% v/v, the percentage extraction decreased. Figure (120) shows the relationship between the relative dielectric constant of the Lix 26 solutions in toluene and the percentage of n-octanol added. If an increase in dielectric constant were the only factor involved in the improved extractability by Lix 26 in the presence of n-octanol, then it might be expected that the plot of Figure (91) would correlate with the increase in  $\epsilon_c^f$  shown by Figure (120). The fact that a reduction in extraction is observed for [n-octanol]  $\geq$  60% v/v illustrates the limitations if this type of generalization and highlights the requirement for experimentation.

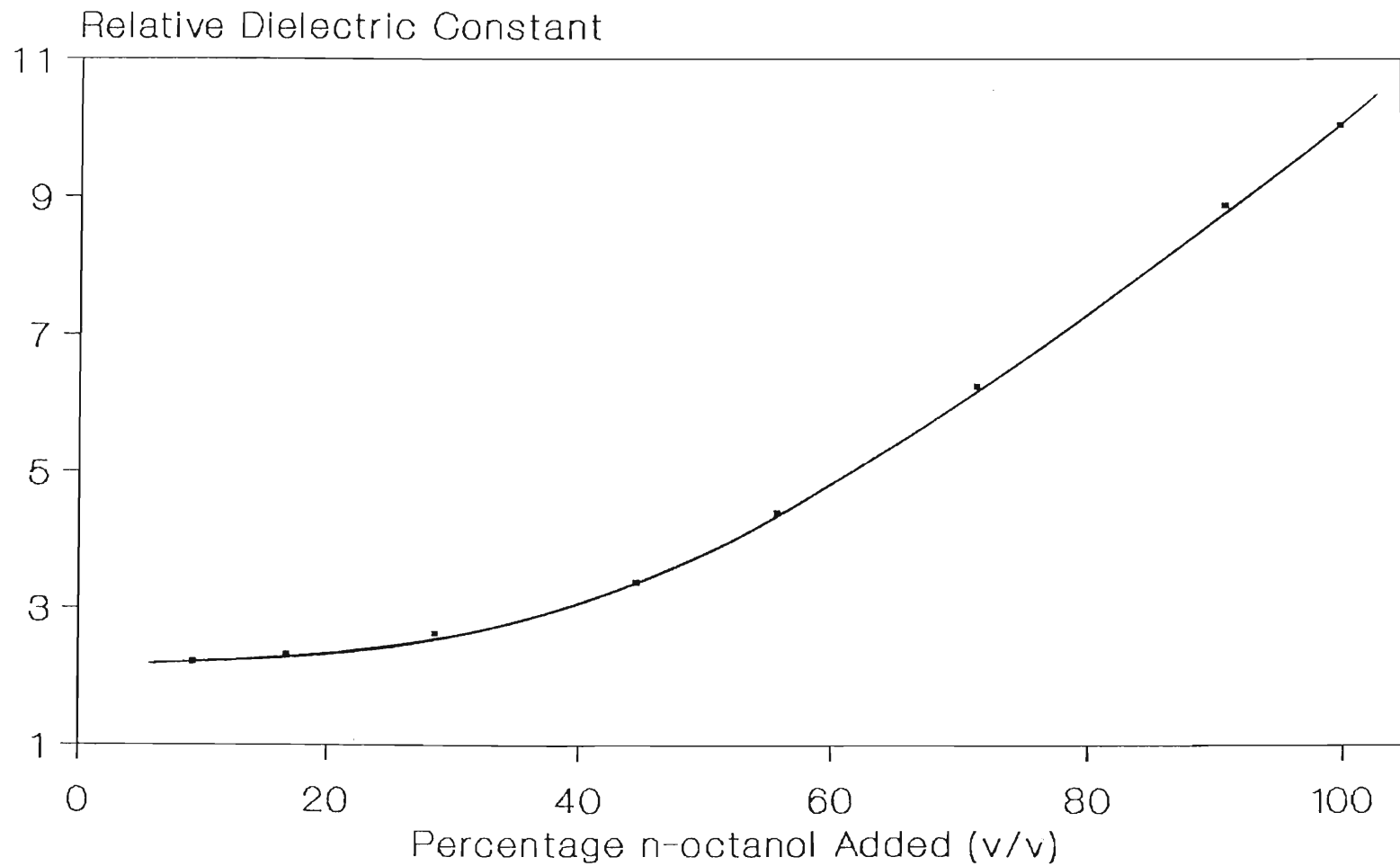


Figure (120). The change in the relative dielectric constant of solutions of Lix 26 in BDH Distillate as a function of the volume percent of n-octanol added. Measurements made with a variable capacitor -see Section 2.5.2.

In the previous section, data relating to the change in solution viscosity with increasing extractant content was discussed and was suggested to be a factor of importance in considering the reasons for the modification of the kinetic behaviour of 7-alkylated-8-hydroxyquinoline reagents at high concentration. An analogous situation applies to the change in dielectric constant. Figure (121) shows the change in  $\epsilon_c^r$  of Lix 26 in toluene with varying ligand concentration. A linear increase in  $\epsilon_c^r$  is evident over the concentration range presented according to the linear equation  $\epsilon_c^r = 2,36 + 2,48 \times 10^{-3}[\text{Lix 26}]$ , where  $\epsilon_c^r$  is the relative dielectric constant at concentration  $c$  (in g/l). Similarly, for TN 01787 and TN 02181 linear equations with slopes  $2,52 \times 10^{-3}$  and  $2,63 \times 10^{-3} \text{ lg}^{-1}$  were obtained. If the suggestion that an increase in dielectric constant of the organic medium favours extraction by improving the compatibility of the solute (in this case  $\text{GeL}_3^+\text{HSO}_4^-$ ) and solvent is correct, then the increase in  $\epsilon_c^r$  with ligand concentration (and of course the constituent impurities such as free 8-hydroxyquinoline) must be a contributing factor to the kinetic enhancements. This of course is hard to separate from the increasing interfacial excess obtained as ligand concentration increases. In this context it is worth recalling that a comparison of the extraction performance of Lix 26 at the same concentration in different diluents (Section 3.6), showed toluene, with  $\epsilon_c^r = 2,37$  to be a superior medium to the other diluents with  $\epsilon_c^r < 2,10$ . Thus, apparently even small differences in medium dielectric impact upon extraction characteristics- this observation is not without precedent<sup>(207)</sup>.

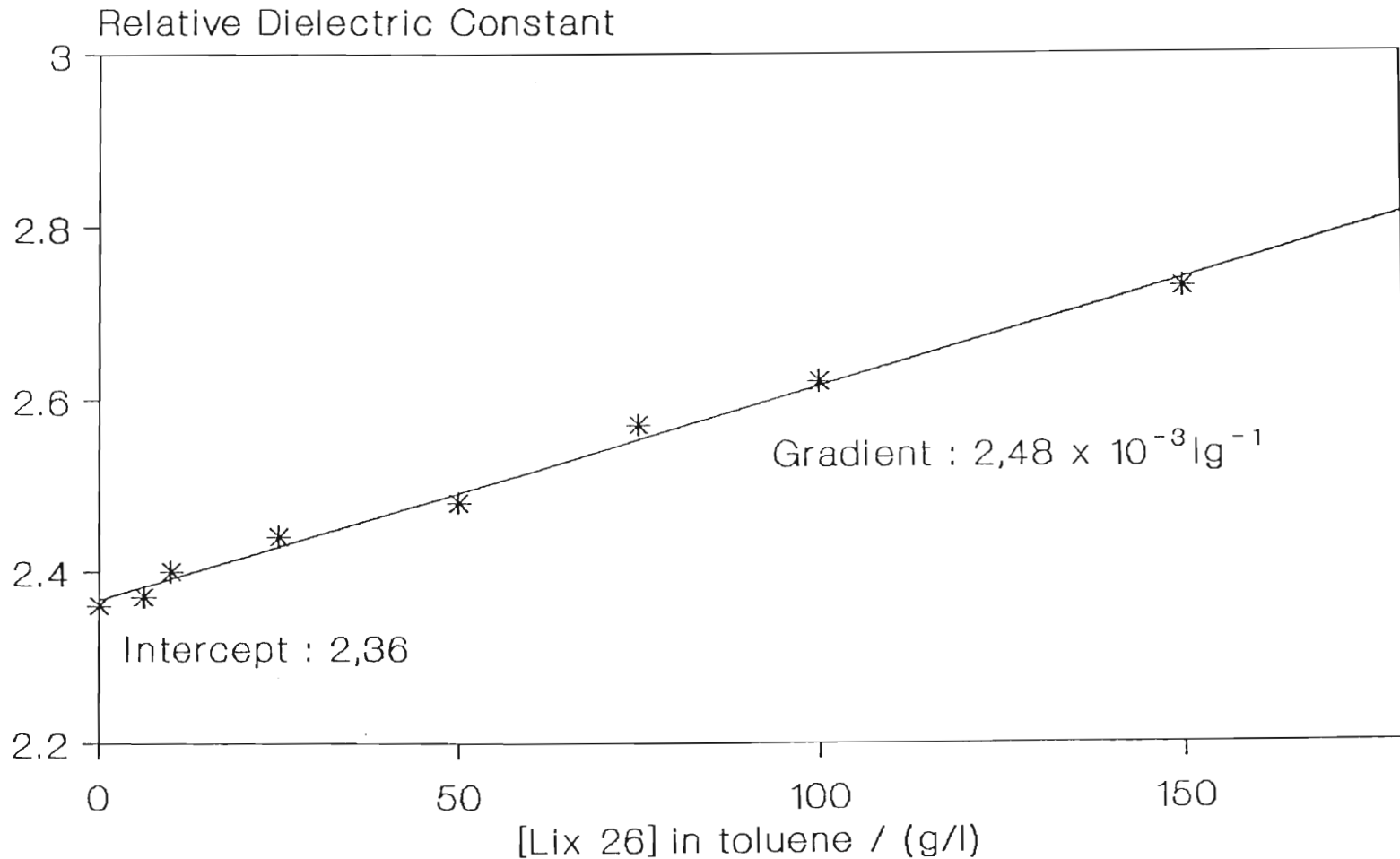
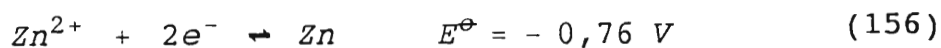
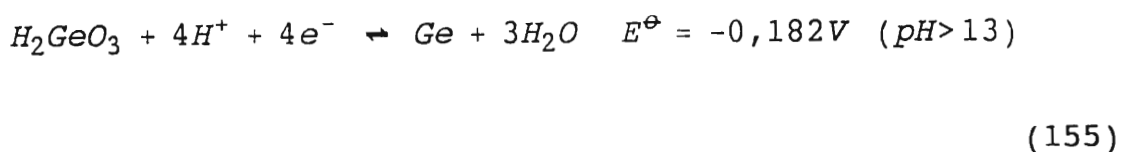
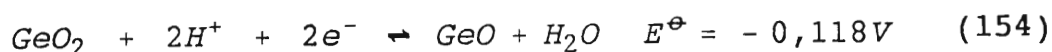
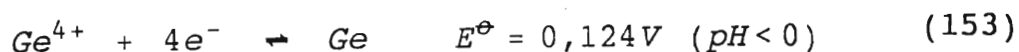


Figure (121). The change in the relative dielectric constant of Lix 26 in AR toluene as a function of the Lix 26 concentration added. A linear increase in  $\epsilon_c^r$  is indicated according to the relation  $\epsilon_c^r = 2,36 + 2,48 \times 10^{-3} [\text{Lix 26}]$  where [Lix 26] is the concentration in g/l of the as-received commercial material.



3.12. The Selectivity for Germanium by 7-Alkylated-8-hydroxyquinoline Extractants from Aqueous Feed Solutions Containing  $Zn^{2+}$ .

In Chapter 1 and in Section 2.4.2.2.10, mention was made of the economic importance of the removal of germanium from zinc-containing acidic leach liquors. The electrolysis of zinc can only be achieved with a good yield when germanium has been completely eliminated from the electrolyte. A comparison of the standard reduction potentials of  $Ge^{4+}$  species in solution (Equations (153) to (155) below<sup>(156)</sup>), with that of  $Zn^{2+}$  (Equation (156)), shows that germanium is plated out at the expense of the zinc no matter what the pH of the zinc-containing aqueous phase.



Besides its occurrence in zinc-containing ores (mainly sphalerite,  $ZnS$ ), germanium is also found in combination with a number of other metals in coals and beneficiation of the germanium from this source would rely upon a quantitative method for its separation from these other metals, of which  $Zn^{2+}$  is usually a major constituent (Table 3), particularly if the coal is sourced from a zinc smelter (spent coal or

'fume'). One economic set-back which should be mentioned is that although the development of a separation process for the pretreatment of zinc electrowinning electrolytes to remove soluble germanium is intrinsically attractive, the volumes of zinc-containing liquors that would have to be treated would make the process uneconomic. Nevertheless, it will be shown in this section that the 7-alkylated-8-hydroxyquinoline reagents are specific for germanium in aqueous solution and this is of potential value to germanium-in-coal beneficiation.

Since zinc is the major contaminant in germanium-containing leach liquors for both of the above situations, the problem of separating the germanium could be handled either:

- (i) By a zinc extraction:- the alkyl-substituted dithizones<sup>(74,241)</sup> are particularly efficient in extracting zinc or,
- (ii) By a solvent extraction process which selectively removes the germanium from the leach liquor.

The second of these two options is more desirable since the process could yield a loaded organic containing only germanium which would therefore require no further purification processes. The question is then, are the reagents of interest to this work specific to germanium over zinc or can chemical conditions be controlled to enforce some type of selectivity?

Stary<sup>(198)</sup> has reported the extraction of zinc by 8-hydroxyquinoline into a chloroform solution of the reagent as the complex  $Zn(Ox)_2 \cdot 2HOx$  (Ox : oxinate anion, HOx : 8-hydroxyquinoline) and obtained quantitative extraction at pH 4-5. The complex however, was destroyed at higher pH values

and it is suggested by the author that this is a result of the formation of  $\text{Zn}(\text{Ox})_2 \cdot 2\text{H}_2\text{O}$  which is insoluble in chloroform. Rao and Ramesh<sup>(68)</sup> determined the distribution of  $\text{Zn}^{2+}$  between aqueous phases of various pH and an organic phase of methyl isobutyl ketone (MIBK) containing Lix 26. Their data is reproduced in Figure (122) and suggests that quantitative extraction of zinc can be obtained at a pH of approximately 7,0, however it is also apparent that no zinc is extracted below  $\text{pH} \sim 4,0$ . This is thus a pH region of considerable interest for the separation of germanium from zinc-containing electrolytes.

Cote and Bauer<sup>(53)</sup> produced a plot analogous to Figure (122) for the distribution of zinc ( $5,0 \times 10^{-4}$  M) between aqueous phases of varying pH and a kerosene solution of Kelex 100 (5 g/l). Similarly, no extraction of zinc was observed by these workers for  $\text{pH} < 5,0$ .

It is apparent from the data of the aforementioned authors that zinc is extracted efficiently by 7-alkylated-8-hydroxyquinoline derivatives over a narrow range of pH, viz. 4,2 - 7,2. In order to explain the origin of this pH dependence and additionally to recommend a pH at which germanium may be quantitatively and selectively separated from zinc, it is necessary to analyse the speciation of zinc in aqueous solution. The speciation program Haltafall<sup>(242)</sup> was used to speciate a  $1 \times 10^{-2}$  M solution of zinc (as  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ).

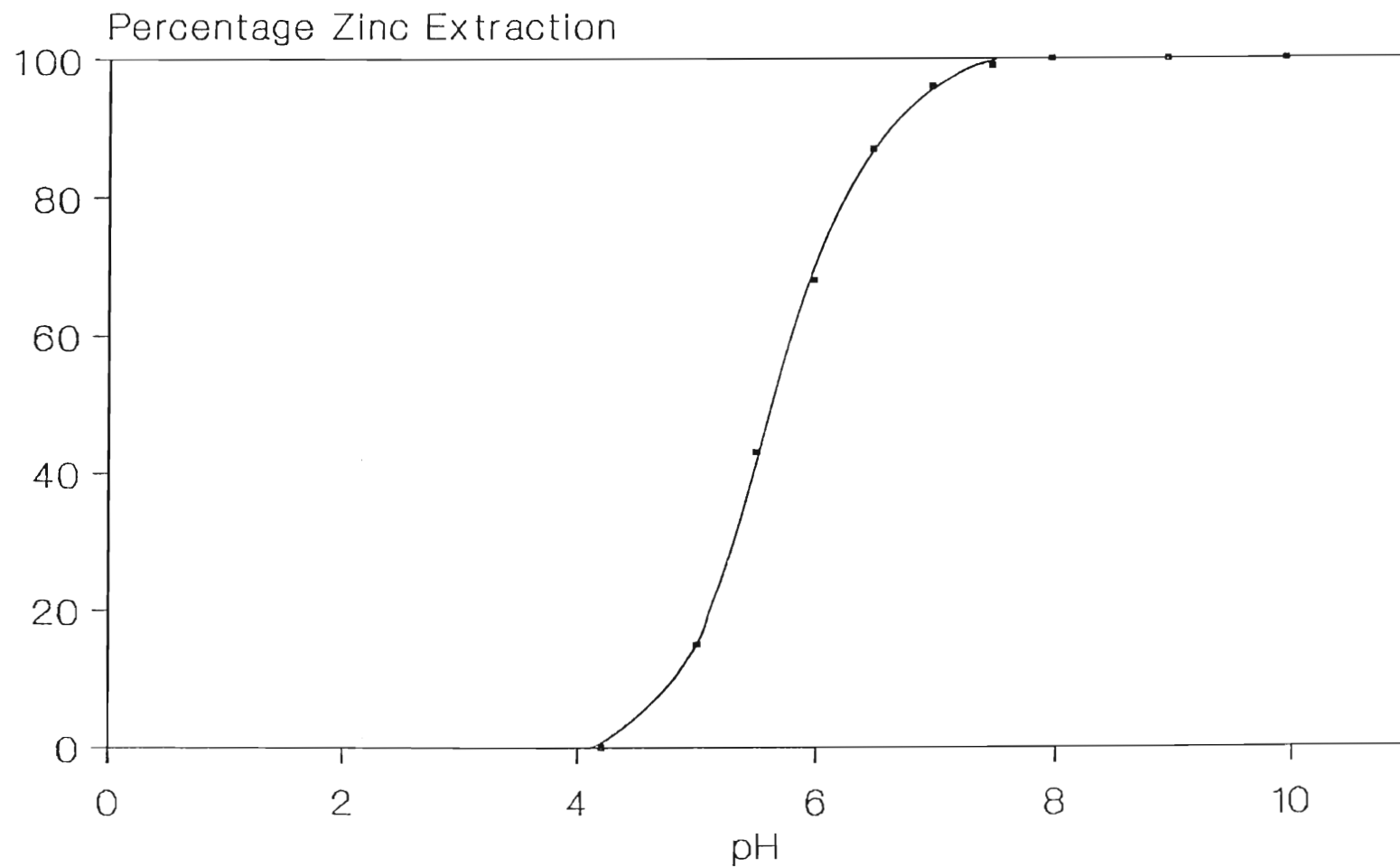
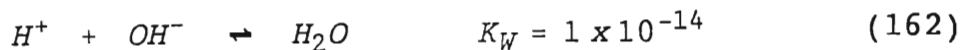
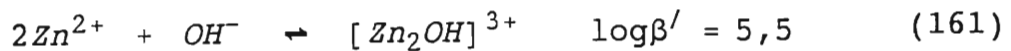
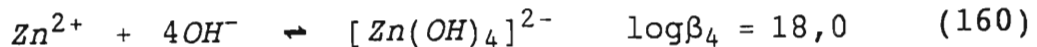
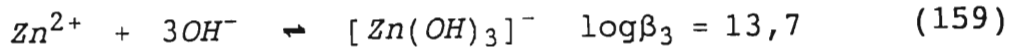
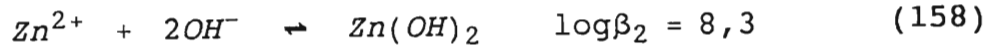
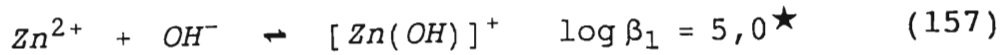


Figure (122). The percentage extraction of  $Zn^{2+}$  by Lix 26 in methyl-isobutyl-ketone as a function of aqueous phase pH, after Rao and Ramesh<sup>(68)</sup>.

The following equilibria and formation constants were utilised for input to the program<sup>(251)</sup>:



Note: Values of  $\beta$  quoted at 25°C, ionic strength = 3,0 M, except  $\star$  for which ionic strength is quoted as zero (by extrapolation).

Figure (123) shows the zinc speciation for an initial zinc concentration of  $1,0 \times 10^{-2}$  M. It is clear from the plot that  $\text{Zn}^{2+}$  predominates for  $\text{pH} < 7$  and no aqueous insoluble  $\text{Zn}(\text{OH})_2$  is formed until a  $\text{pH}$  of  $\sim 7,5$ . Cationic zinc cannot therefore be quantitatively removed from solution by a solvent extraction process at any  $\text{pH}$  higher than this value. The plot

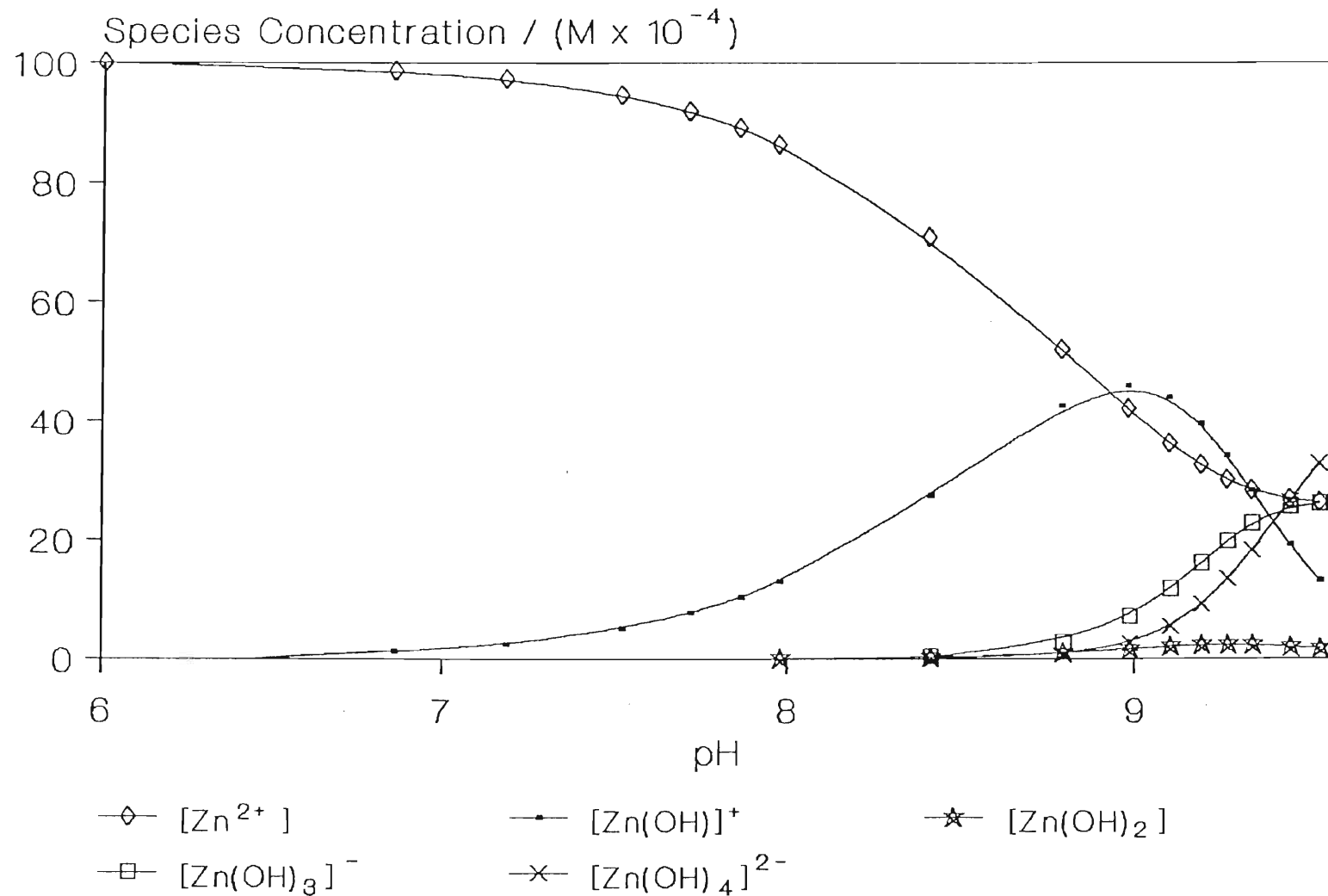


Figure (123). The distribution of zinc species in aqueous solution as a function of aqueous phase pH. The distribution shown was calculated by the speciation program Haltafall<sup>(242)</sup> using the values of formation constants given in the text and an initial  $Zn^{2+}$  concentration of  $1 \times 10^{-2}$  M.

also demonstrates that at the pH most suitable for the complete extraction of germanium i.e.  $\text{pH} < 1$ , zinc is present in solution as  $\text{Zn}^{2+}$ , at which pH, according to the work of the authors detailed above, the metal ion is not extracted by 8-hydroxyquinoline or the 7-alkylated-8-hydroxyquinoline reagents.

An investigation was initiated in this laboratory to determine (i) whether TN 01787/02181 or Lix 26 extracted any zinc at all from an aqueous solution of 1,5 M  $\text{H}_2\text{SO}_4$ , (ii) whether any extraction occurred at the higher pH of 2,5 and (iii) the effect of the presence of zinc in equimolar and 10-fold molar excess in an aqueous phase containing germanium, on the kinetics and equilibrium extraction of germanium by Lix 26. Experimental details of these investigations were given in Table (23).

Over a period of 24 hours, no zinc was extracted by 50 g/l solutions of all three reagents in toluene from an aqueous phase 1,5 M in  $\text{H}_2\text{SO}_4$ . Similarly at pH 2,5 and for the same shaking time, no zinc was removed from the aqueous phase by Lix 26. Figure (124) shows the percentage of germanium extracted from aqueous solutions containing no zinc and a ten-fold stoichiometric excess of  $\text{Zn}^{2+}$ . Neither the germanium extraction kinetics ( $k_f(\text{obs}) \sim 7,6 \times 10^{-4} \text{ s}^{-1}$ ), nor the equilibrium percentage extraction ( $\sim 97,5\%$ ) were affected by the zinc and no extraction of  $\text{Zn}^{2+}$  by the reagent was observed. A 1:1 Zn:Ge aqueous solution produced a plot co-linear with the plots of Figure (124). (The plot is excluded for simplicity.)

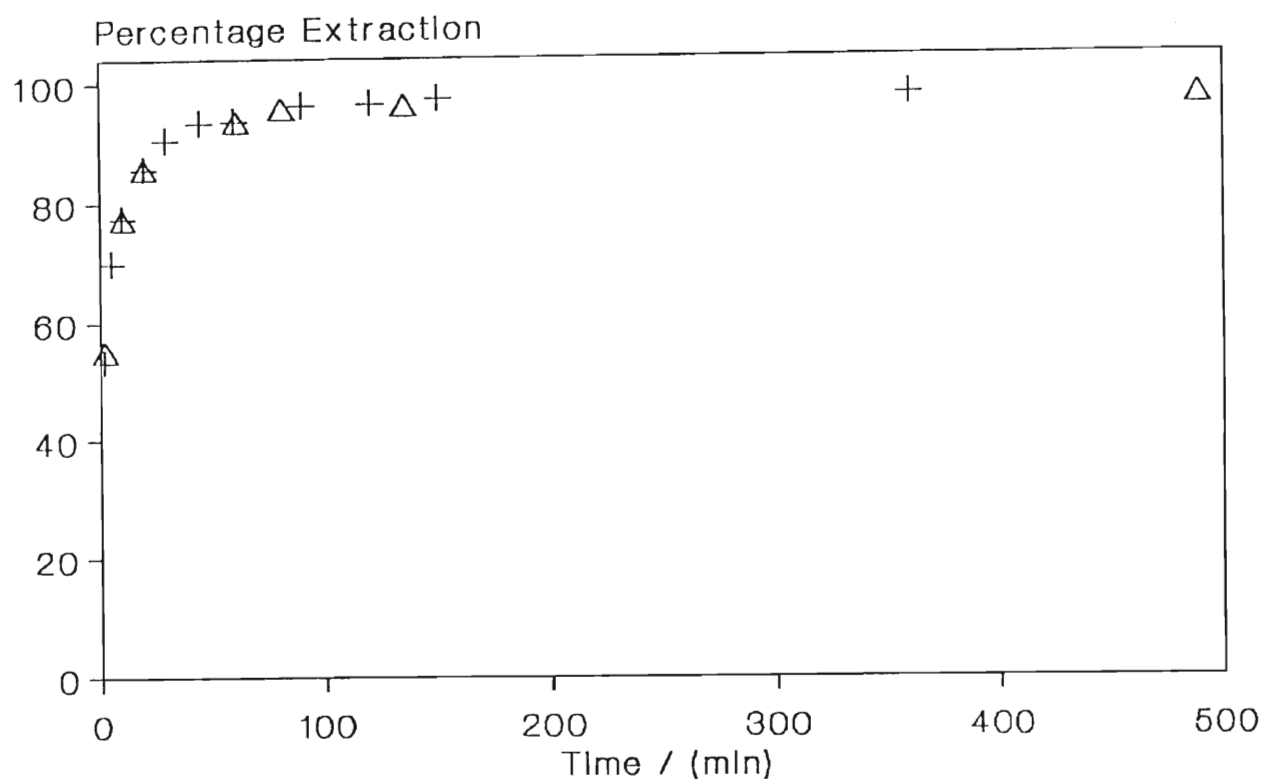


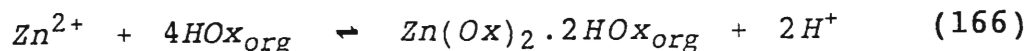
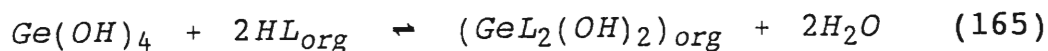
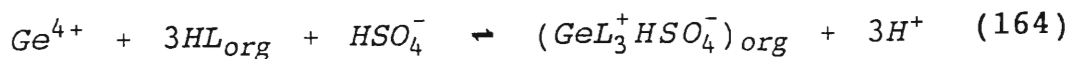
Figure (124). The percentage of germanium extracted from aqueous solution by 50 g/l solutions of Lix 26 in toluene as a function of time for various aqueous phase composition. The triangles show percentage extraction data for which the aqueous phase contained only germanium, whereas the crosses indicate germanium extraction data in which the aqueous phase contained a 10-fold stoichiometric excess of zinc compared with germanium.  $[\text{Ge}]_{\text{aq}} : 8,95 \times 10^{-3} \text{ M}$ ;  $[\text{Zn}^{2+}] : 8,77 \times 10^{-2} \text{ M}$ . All solutions were 1,5 M in  $\text{H}_2\text{SO}_4$ .



An obvious question which arises from these data is the origin of the selectivity of germanium(IV) over zinc(II) by these reagents. In most cases the answer to this type of selectivity lies either in a difference in affinity for the metal ions by the ligand (which can be attributed to ionic radius, charge, the presence of vacant orbitals which can accept electron pairs etc.), which is therefore a kinetic effect or there are thermodynamic (i.e. equilibrium constants) grounds for the justification of the observed selectivity. The literature contains a plethora of studies which aspire to answering this paradigm with a view to proposing some general trend or linear free-energy relation which allows some speculation of the complexation characteristics of ligands for various metal ions. A particular example of the extent to which reagents demonstrate selectivity for one metal-ion over another is the study reported by Fleming<sup>(250)</sup>, who concluded the origin of the selectivity of Kelex 100 for  $\text{Cu}^{2+}$  over  $\text{Fe}^{3+}$  to be chemically-controlled by virtue of the slow reaction between  $\text{Fe}^{3+}$  and the ligand.

For the results obtained in this work, a kinetic rationale which would explain the origin of the selectivity seems highly unlikely since no zinc is extracted at all. Some evidence

however is provided by the equilibria summarised below:



HL : Kelex 100, HOx : 8-hydroxyquinoline

Values of formation constants for these three processes are as follows:

| Equation | log K                         |
|----------|-------------------------------|
| 164      | 6,44 ± 0,35 <sup>(65)</sup>   |
| 165      | 2,24 ± 0,09 <sup>(65)</sup>   |
| 166      | -2,41 ± 0,03 <sup>(198)</sup> |

Table (62). Values of formation constants for Equations (164) to (166), all at 25°C.

The most interesting comparison is between the values of log K for Equations (165) and (166), in that whilst extraction of germanium is thermodynamically very favourable, extraction of zinc by 8-hydroxyquinoline is not- i.e. the stability of the germanium-Kelex 100 complex is approximately 4,5 log units greater than the stability of the zinc-8-hydroxyquinoline complex. It is proposed therefore that the selectivity of germanium over zinc is related to the low thermodynamic stability of the species  $\text{Zn}(\text{Ox})_2 \cdot 2\text{HOx}$ , particularly at low pH

which favours the left-hand-side of Equation (166).

### 3.13. The Visualization of Metal-Chelate Structures, Stereochemical Effects and the Determination of Minimum Energy Conformations by Alchemy

During the last two decades a number of studies have been reported which attempt to give some understanding of the relationship between ligand structure and metal-chelate formation efficacy. The most significant studies use NMR<sup>(177,243)</sup>, Infrared<sup>(244-246)</sup>, Raman<sup>(244)</sup> and UV/VIS<sup>(245)</sup> spectroscopic techniques to assist in explaining the nature of intermediates and chelate products formed during solvent extraction. Additionally methods such as ESR<sup>(247)</sup> and X-Ray Scattering<sup>(248)</sup> have been utilised to determine the coordination mode of organic molecules in metal-ion/extractant complexes.

Unfortunately, there is very little information vis-à-vis the size, shape and orientation of extractant molecules and this is presumably related to the effort which has been required to build libraries of relevant and accurate data pertaining to bond lengths and strengths, energies of interaction, force constants etc. and the availability of appropriate computer software to utilise this information in the prediction of stable molecular conformations.

The use of computer models to predict structures relating to extractant molecules is currently producing exciting

results<sup>(178-180)</sup> and in this work the molecular modelling program Alchemy has been used as a tool to conduct empirical energy calculations upon the ligands and germanium-ligand-chelate structures in order to facilitate the visualization of the stereochemical aspects and to determine energies and molecular areas as they apply to the solvent extraction of germanium. Thus the sections which follow detail comparisons of the structures and energies of the ligands concerned in this work with a view to proposing qualitative reasons for their difference in extraction efficacy and to provide details relating to the nature of the rate-determining step and the formulation of a chelation mechanism.

### 3.13.1. Minimum Energy Conformations, Structural Differences and Geometrical Areas of TN 01787, TN 02181, Lix 26 and Some Ligand Reagent Impurities.

As the title above suggests, this section of the work is primarily aimed at presenting a dimensional and stereochemical awareness of the active ligand molecules under investigation in this work.

Figure (125a) shows the spacefill structure of 8-hydroxyquinoline with the metal chelation sites indicated (O and N). Figure (125b-h) show the energy minimized structures of Lix 26 (b), TN 01787 (c), TN 02181 (d-g) and Kelex 100(h). Unlike Lix 26 and TN 01787, the structure of TN 02181 has not been discussed previously. This ligand (or ligand mixture) comprises a number of isomeric species for which the total carbon content of the  $\beta$ -unsaturated side chain is C<sub>12</sub>.

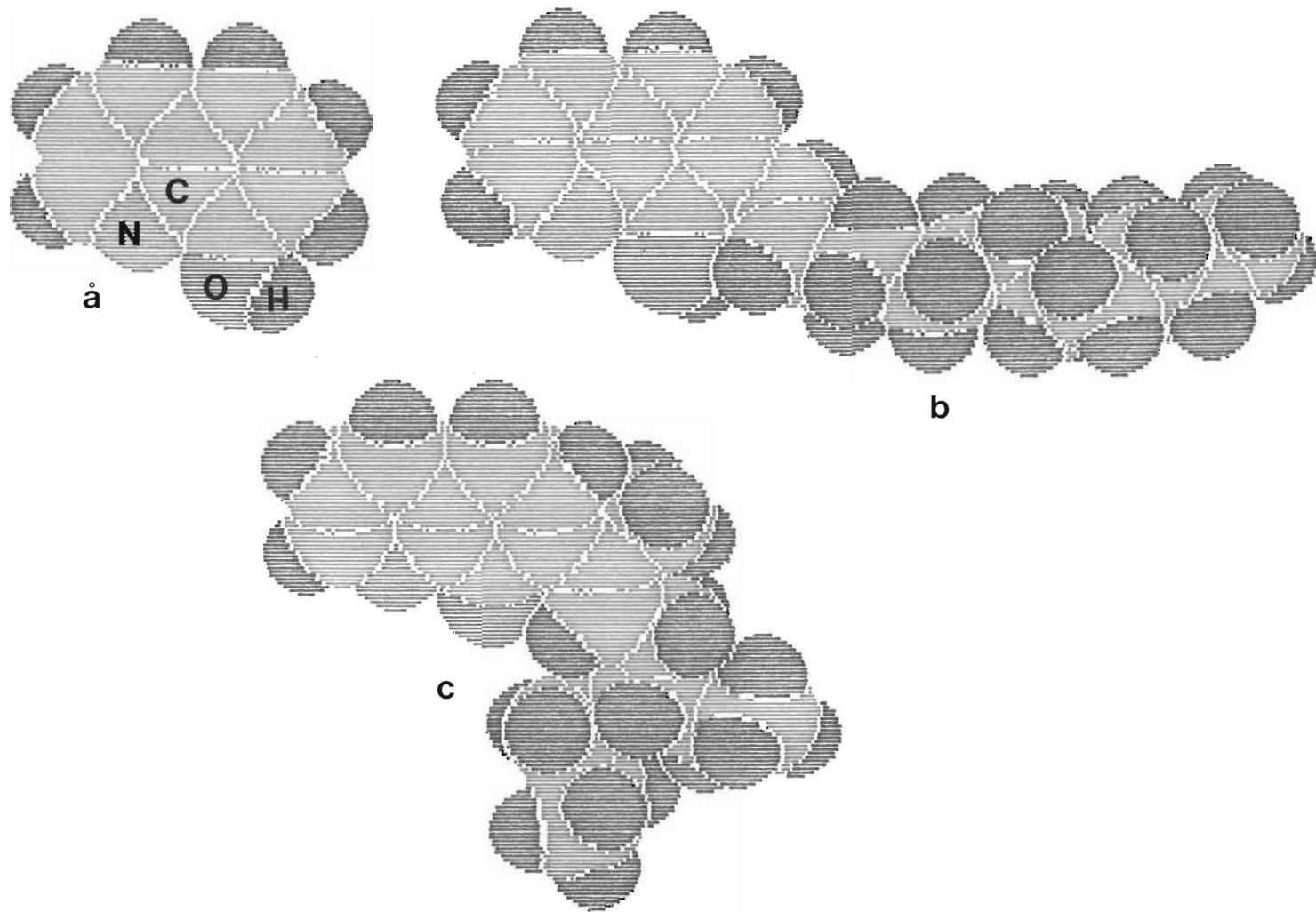


Figure (125). Spacefill Alchemy-minimized structures of (a) 8-hydroxyquinoline, (b) Lix 26 and (c) TN 01787. The colour codes for C, H, O and N are shown in (a).

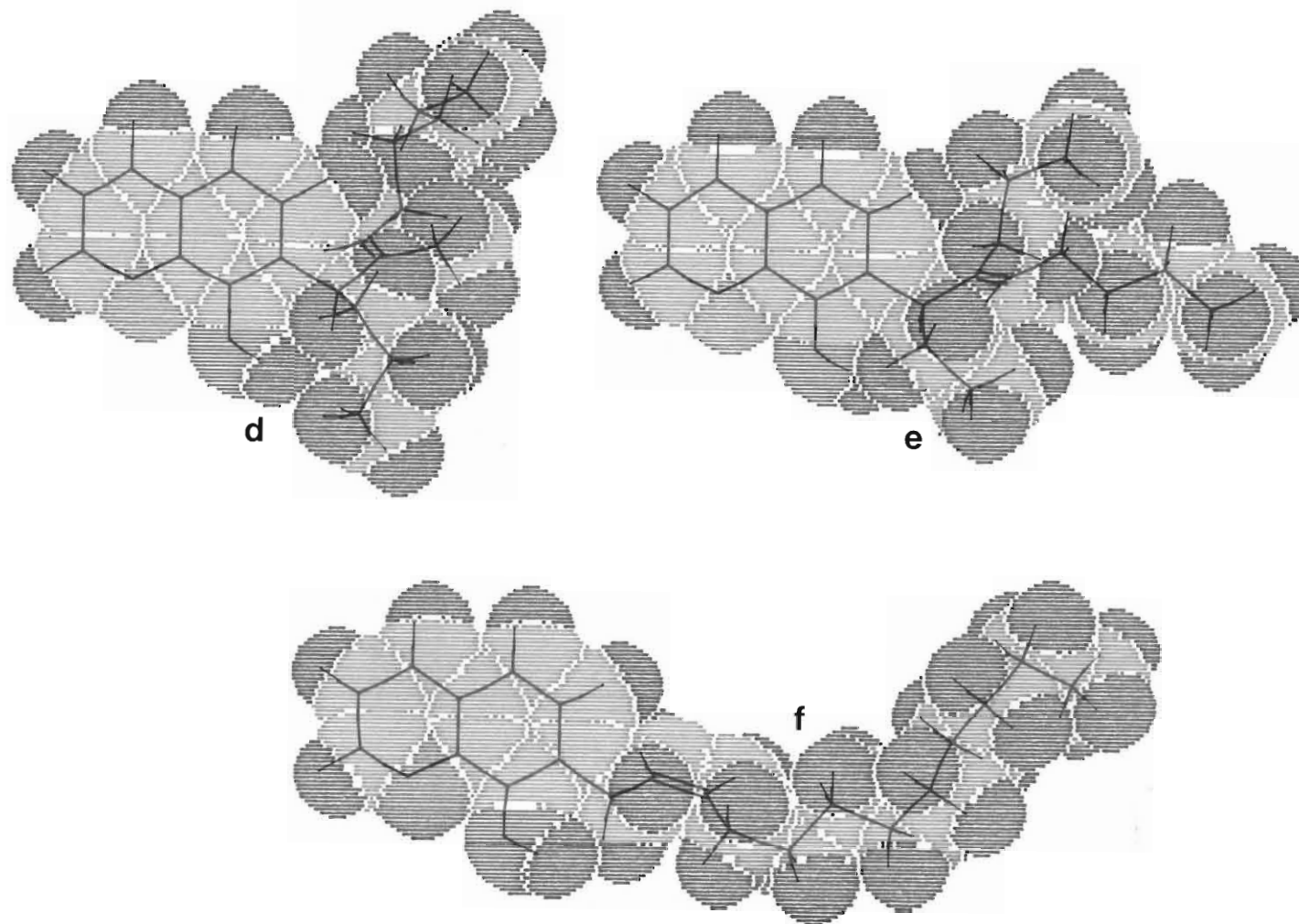


Figure (125). Spacefill Alchemy-minimized structures of (d) TN 02181A, (e) TN 02181B and (f) TN 02181C. The overlay illustrates the diversity of the shapes of the isomers of the extractant.

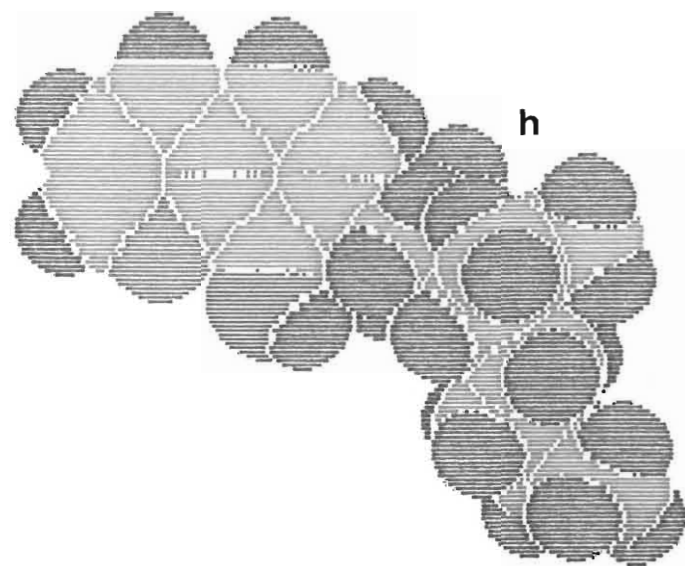
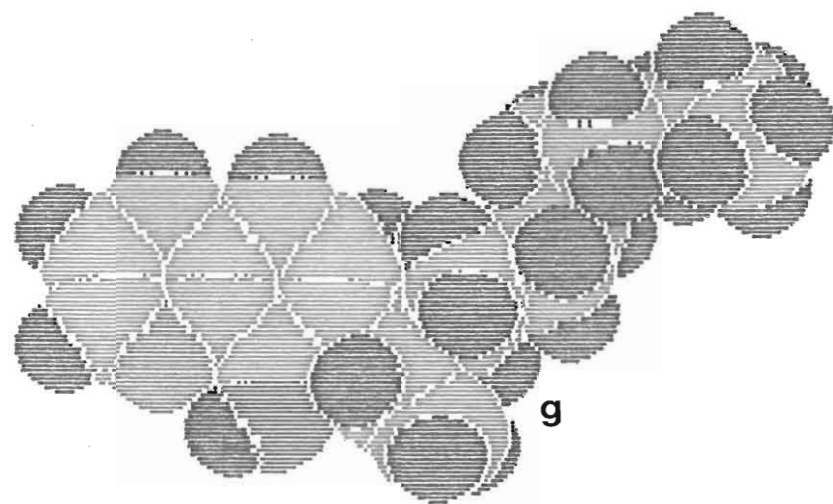
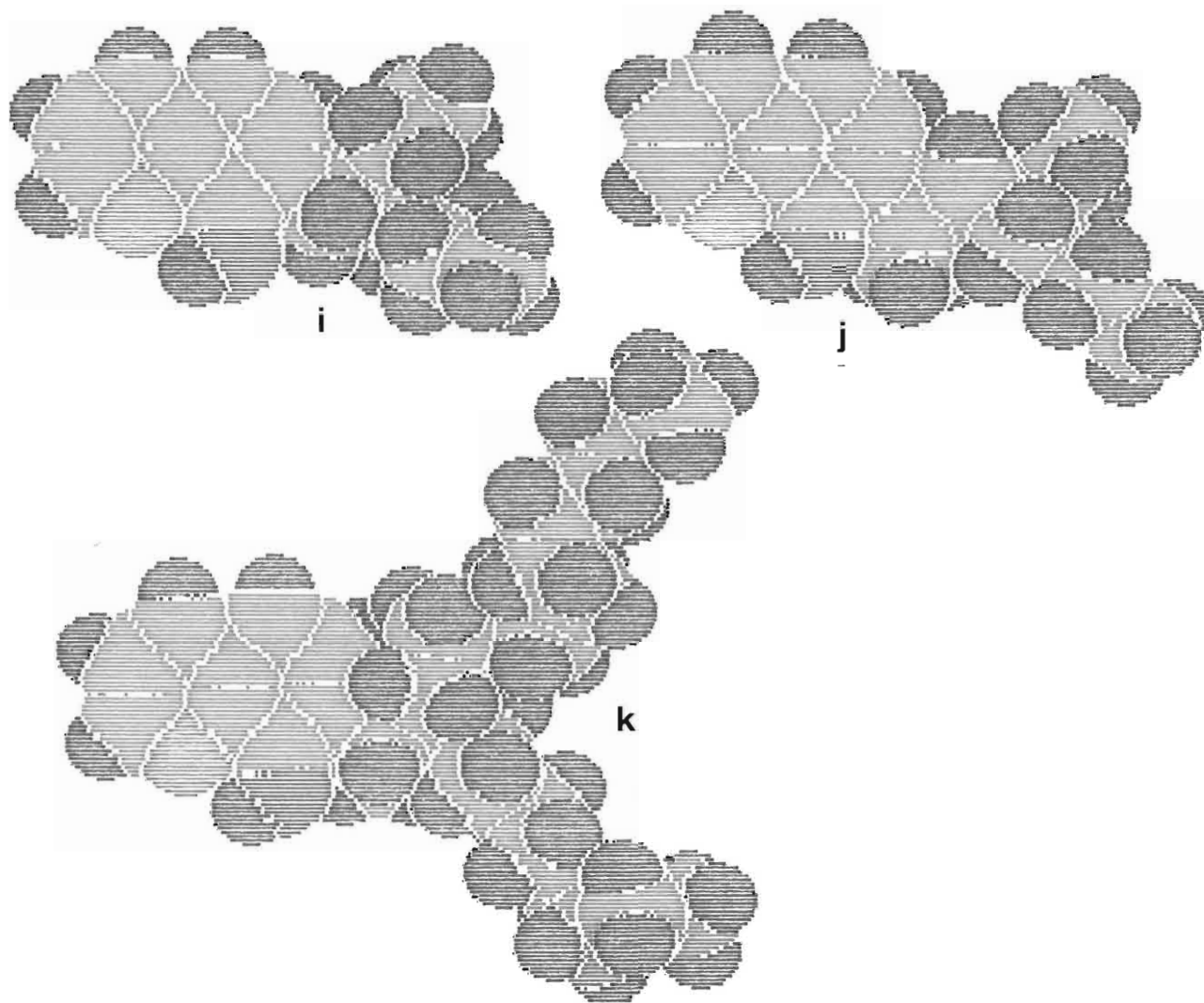


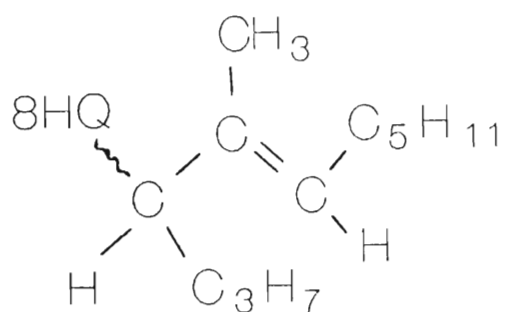
Figure (125). Spacefill Alchemy-minimized structures of (g) TN 02181D and (h) Kelex 100.



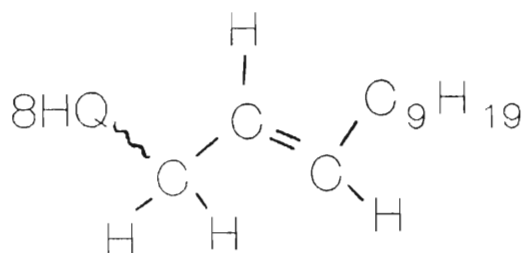
**Figure (125).** Spacefill Alchemy-minimized structures of (i) Impurity 4, (j) Impurity 5 and (k) Impurity 8, (see Table (6)).



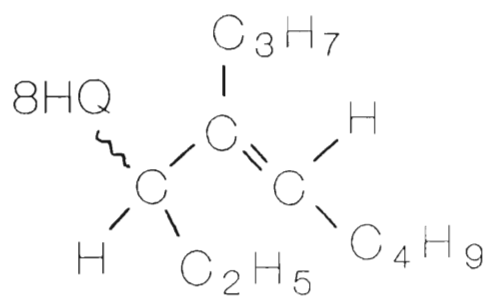
In order to gain some appreciation of the diversity of sizes and shapes which may occur for a side chain of  $C_{12}H_{23}$ , the extremes of a close-packed (Figure 125d), expanded (Figure 125f) and two intermediate structures (Figures 125e and 125g) were considered. For clarity, these side chains are shown below in Figure (126).



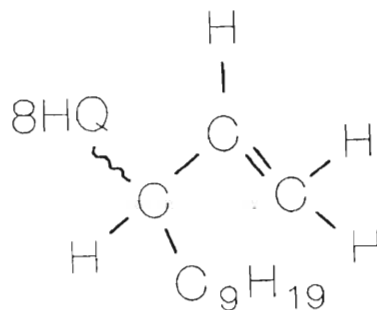
TN 02181A (d)



TN 02181C (f)



TN 02181B (e)



TN 02181D (g)

Figure (126). Some of the possible structures of TN 02181. Numbers in brackets refer to the spacefill structures of Figure (125).

Values of the total energy, bond stretching, angle bending, torsional, out-of-plane and Van der Waals energy terms for these molecules in their lowest energy i.e. most stable, conformations as determined by the minimization routine of Alchemy, are given in Table (63).

Examination of the values in Table (63) show that the major contribution to the total energy comes from the Van der Waals energy term which for all of the molecules modelled is negative and results in a negative total energy (except for TN 01787). Since the minimization routine obtains the most stable conformation by reducing all energy terms as far as possible within the constraints of the bond flexibilities, it can be assumed that the more negative an energy term, the greater the contribution to overall stability. Thus, for example Kelex 100 with a total energy of  $-41 \text{ kJ mol}^{-1}$  is more stable per se than Lix 26 with a total energy of  $-7,95 \text{ kJ mol}^{-1}$ . Most of the difference in energy is reflected by the Van der Waals term indicating greater non-attractive or less attractive atom-atom interactions for Lix 26 than for Kelex 100. Although the relative stabilities of the monomer molecules are thermodynamically important, a better indication of size and structure effects upon germanium extraction is portrayed by the energy terms of the  $\text{GeL}_3^+$  chelates and these are discussed in the next section (Section 3.13.2).

The final column of Table (63) gives approximate areas for the extractant molecules. These were calculated by orienting the molecules in a flat plane with the chelate site facing into the plane, and rotating the molecule until the minimum number of atoms of the 7-alkyl-side chain were colinear with the

| Molecule           | $E_{\text{total}}$ | Bond Stretching | Angle Bending | Torsional | Out-of-plane | Van der Waals | Area / Å <sup>2</sup> |
|--------------------|--------------------|-----------------|---------------|-----------|--------------|---------------|-----------------------|
| 8-hydroxyquinoline | -4,18              | 0,42            | 0,84          | 0         | 0            | -5,44         |                       |
| Lix 26             | -7,95              | 0,84            | 5,44          | 20,08     | 0            | -34,31        | 125,5                 |
| TN 01787           | 2,51               | 1,26            | 4,60          | 32,22     | 0            | -35,56        | 77,4                  |
| TN 02181A          | -9,20              | 1,26            | 9,20          | 24,27     | 0            | -43,93        | 68,7                  |
| TN 02181B          | -10,05             | 1,67            | 9,62          | 17,57     | 0            | -38,91        | 87,1                  |
| TN 02181C          | -3,35              | 0,84            | 4,18          | 16,32     | 0            | -24,69        | 105,6                 |
| TN 02181D          | -13,38             | 1,26            | 6,28          | 12,13     | 0            | -33,05        | 95,7                  |
| Kelex 100          | -41,00             | 0,84            | 3,77          | 8,79      | 0            | -54,40        | 86,3                  |
| Impurity 4         | -25,53             | 0,84            | 7,11          | 9,20      | 0            | -42,68        |                       |
| Impurity 5         | -2,50              | 1,26            | 3,77          | 11,72     | 0            | -19,25        |                       |
| Impurity 8         | -59,84             | -1,26           | 7,95          | 28,45     | 0            | -94,98        |                       |

Table (63). Energy terms for the minimum energy conformations of extractant molecules and some impurities.  $E_{\text{total}} = E_{\text{b.s}} + E_{\text{a.b}} + E_{\text{tors}} + E_{\text{oop}} + E_{\text{vdw}}$ . Units are all kJ mol<sup>-1</sup>. Refer to Table (6) for the structures of impurities 4,5 and 8.

plane. In so doing the plane is imagined as a flat interface and the surface active molecule is placed upon it in such a way that the plane incorporates the minimum possible of the 7-alkyl-side chain- it is envisioned that the polar nature of the interface in reality would reject as far as possible, the highly hydrophobic alkyl group of the ligand. The approximate interfacial area was then calculated using the Alchemy program by assuming that the molecule occupied a rectangular area enclosing the entire 8-hydroxyquinoline moiety and the portion of the 7-alkyl group lying at the planar surface. In this way portions of the molecule which bend away from the plane (and are therefore not strictly at the interface but more in the organic medium) are not included in the estimation. The error inherent in this estimation process is therefore associated with deciding to what extent an atom is resident at the interface and if it should be rejected. Some indication of the extent to which the final result is affected by such judgements was given in Section 3.11.2.3.

Comparison of the areas indicated in Table (63) shows that Lix 26 (Figure 125b) has the largest area while TN 02181A (Figure 125d) has the smallest area. The difference between Lix 26 and TN 02181C lies in the position of unsaturation-the energy minimized conformation of Lix 26 gives a linear structure to the alkyl chain backbone whereas for TN 02181C, the  $C_9H_{19}$  group is bent upwards and away from the point of unsaturation.

The possible variations in structure pertaining to TN 02181 are given by Figures (125d-g) and the overlay of d-f (showing

clearly the difference in the stereochemistry of these three isomers). A number of conformations, ranging in area from approximately 69-106 Å<sup>2</sup> are possible and it is likely that they have different interfacial activities. GC/MS data (Section 2.2.2.3) suggests that structure A (Figure 125d) is present in significant quantity compared with any other isomers and this could be one reason for the faster extraction kinetics observed for the TN 02181 reagent. In the shaking apparatus (Section 3.2.1.4), the order of germanium extraction efficacy at low ligand concentration is Kelex 100 < TN 01787 < Lix 26 < TN 02181. If physical size of the ligand however, is the only criterion for interfacial activity then it might be expected that Lix 26 would be the worst extractant which it is not. There are obviously other considerations which dictate the order given above and some suggestions are presented in Section 3.13.3.

Figures (125i-k) show the spacefill structures of impurities 4,5 and 8 of Table (6). While the furoquinoline derivatives present as impurities in 7-alkylated-8-hydroxyquinoline reagents would not be expected to extract metal ions, these three molecules possess active sites for germanium attachment and would therefore be expected to complex metal-ion to some degree. By virtue of its bulk, however, impurity 8 is probably relatively inactive compared with the other two impurities and the active ligands.

### 3.13.2. Size and Structure Relationships of the Tri-ligand Chelates of Germanium.

At low pH, germanium extracts into an appropriate diluent as

the ion-association complex  $\text{GeL}_3^+\text{HSO}_4^-$ . It has been shown in this work that the chelation reaction occurs entirely at the aqueous/organic interface and it has also been proposed that the attachment of the third ligand to the intermediate  $\text{GeL}_2^{2+}$  is, on stereochemical grounds, the rate-determining step. A pictorial representation of this reaction is shown in Figure (127). The Figure shows the stereochemical and chemical constraints which are imposed upon the third incoming ligand molecule to the vacant  $\text{sp}^3\text{d}^2$  orbitals (highlighted in green) of the central germanium (IV) atom. Stereochemically, the incoming ligand molecule of approximate thickness  $3,5 \text{ \AA}$ , is presented with a region of approximately  $6,2 \text{ \AA}$  through which to enter and chemically orient with the germanium orbitals. Chemically, the greatest constraint which applies to the reaction is that the hydrophobic groups of the incoming ligand and the  $\text{GeL}_2^{2+}$  intermediate must remain solubilized by the organic phase while the central region, which is charged, must be accommodated at the interface (and probably planar with it) - this limits the rotational flexibility of the  $\text{GeL}_2^{2+}$  intermediate and therefore reduces the accessibility of the reactive face of the molecule to the third ligand. Moreover the attachment of the third ligand necessitates rearrangement of the two molecules already chelated at the germanium atom, resulting in large differences in the normal  $\text{sp}^3\text{d}^2$  bond angle of  $90^\circ$ , (Figure 128) and therefore considerable increases in the bond stretching and angle bending energies (Table 64).

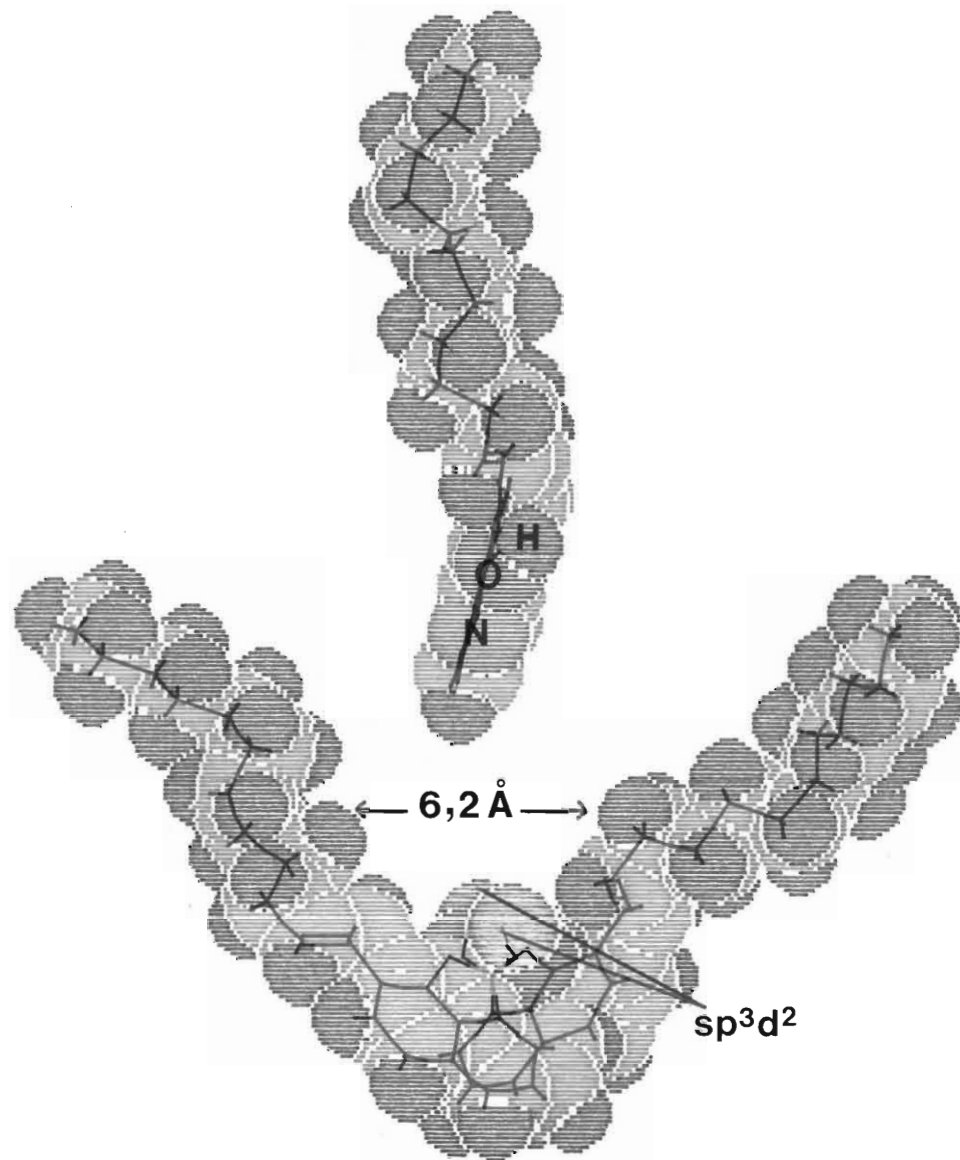
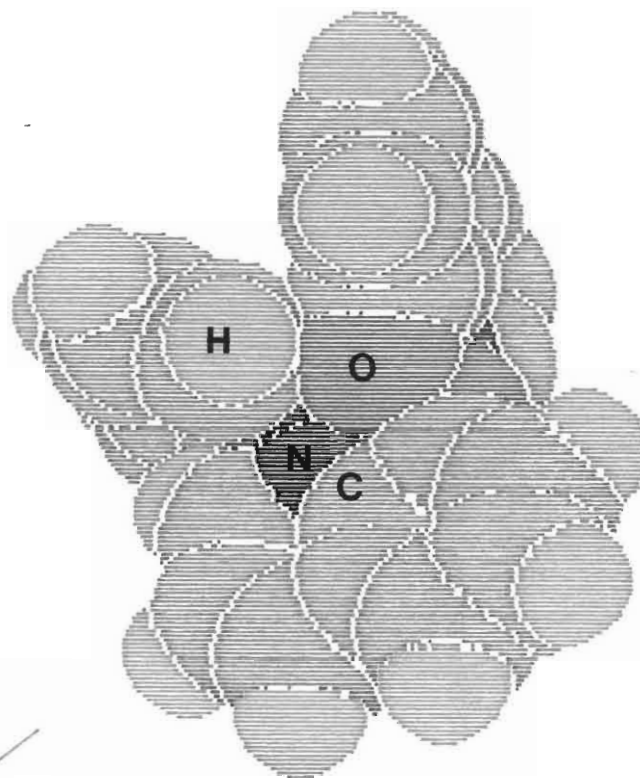
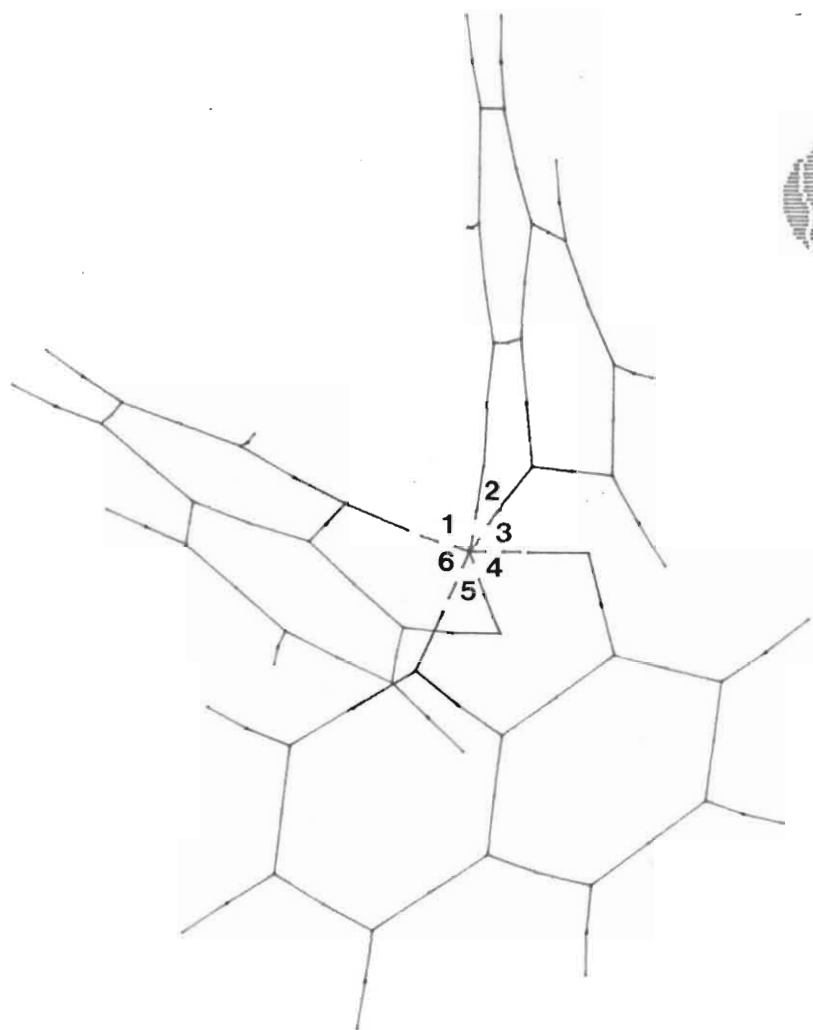


Figure (127). Size, structure pictorial representation of the rate-determining step in the chelation of germanium by Lix 26.



1.  $87,6^\circ$
2.  $98,2^\circ$
3.  $89,5^\circ$
4.  $97,6^\circ$
5.  $76,7^\circ$
6.  $88,2^\circ$

Figure (128). Alchemy-minimized structure representation of germanium chelated to three 8-hydroxyquinoline moieties (meridionally coordinated), showing the deviation from the  $sp^3d^2$  bond angle of  $90^\circ$ .



| Molecule            | $E_{\text{total}}$ | Bond<br>Stretching | Angle<br>Bending | Torsional | Out-of-<br>Plane | Van der<br>Waals |
|---------------------|--------------------|--------------------|------------------|-----------|------------------|------------------|
| $\text{GeL}_2^{2+}$ | 1361,9             | 212,1              | 1129,7           | 39,3      | 1,7              | -20,9            |
| $\text{GeL}_3^+$    | 1497,1             | 315,1              | 1297,0           | 60,7      | 3,8              | -179,5           |

Table (64). Energy terms determined by Alchemy for germanium complexed with two and three Lix 26 ligands. Units  $\text{kJ mol}^{-1}$ .

It must be noted here that the Alchemy program cannot accommodate the introduction of ionic charges on atoms nor counterions required for electro-neutrality and thus the figures quoted in Table (64) reflect the energies in the absence of ionic interactions resulting from the monovalent and bivalent cationic charge, however it is reasonable to assume that in this case the relative difference in energy between these two species resulting from this phenomenon is lessened by the delocalisation of the charge over the 8-hydroxyquinoline molecules bound to the germanium atom. Spacefill structures of the extractable  $\text{GeL}_3^+\text{HSO}_4^-$  species formed with, for example Lix 26 and TN 02181A are shown in Figures (129) and (130) respectively. These two structures were chosen for pictorial presentation because they differ significantly in surface area (cf.  $267 \text{ \AA}^2$  for  $\text{Ge}(\text{TN 02181A})_3^+$  versus  $648 \text{ \AA}^2$  for  $\text{Ge}(\text{Lix 26})_3^+$ ). For both structures the germanium atom is completely enclosed by a non-polar sheath and the 7-alkyl groups generally orient on one side of a plane drawn through the chelation centre. For the two structures shown, the nitrogen and oxygen donor atoms of the 8-

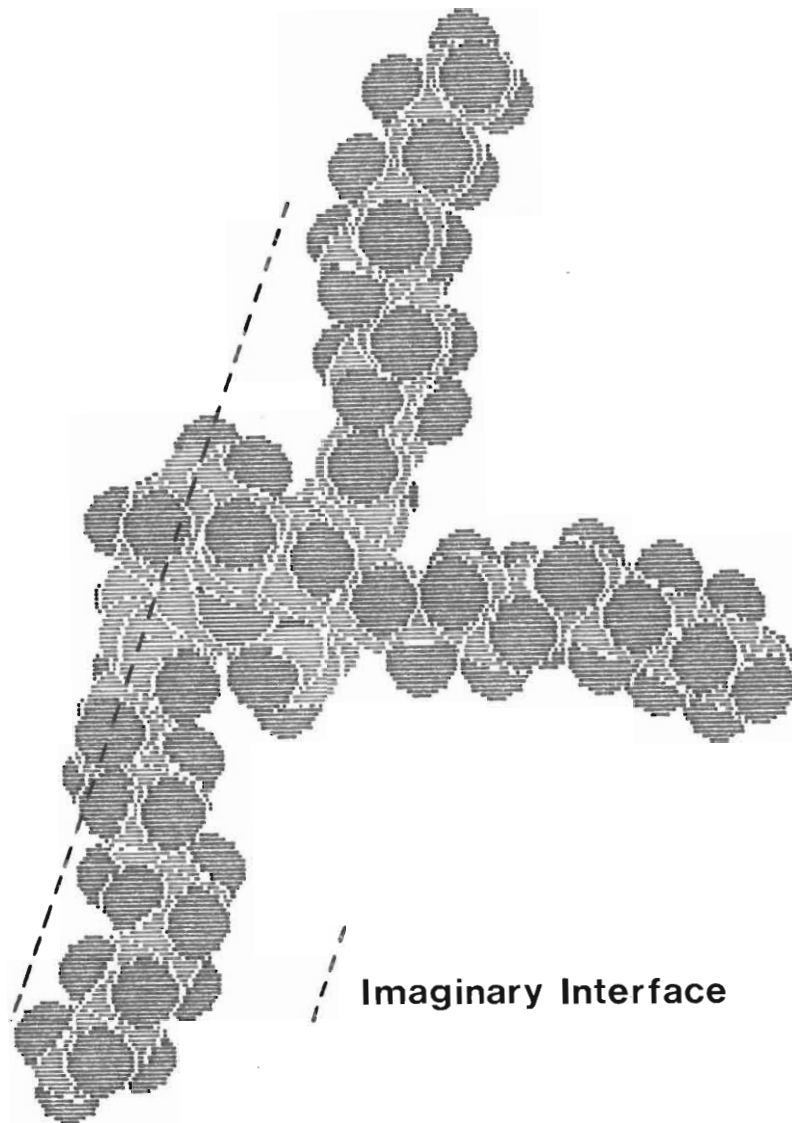
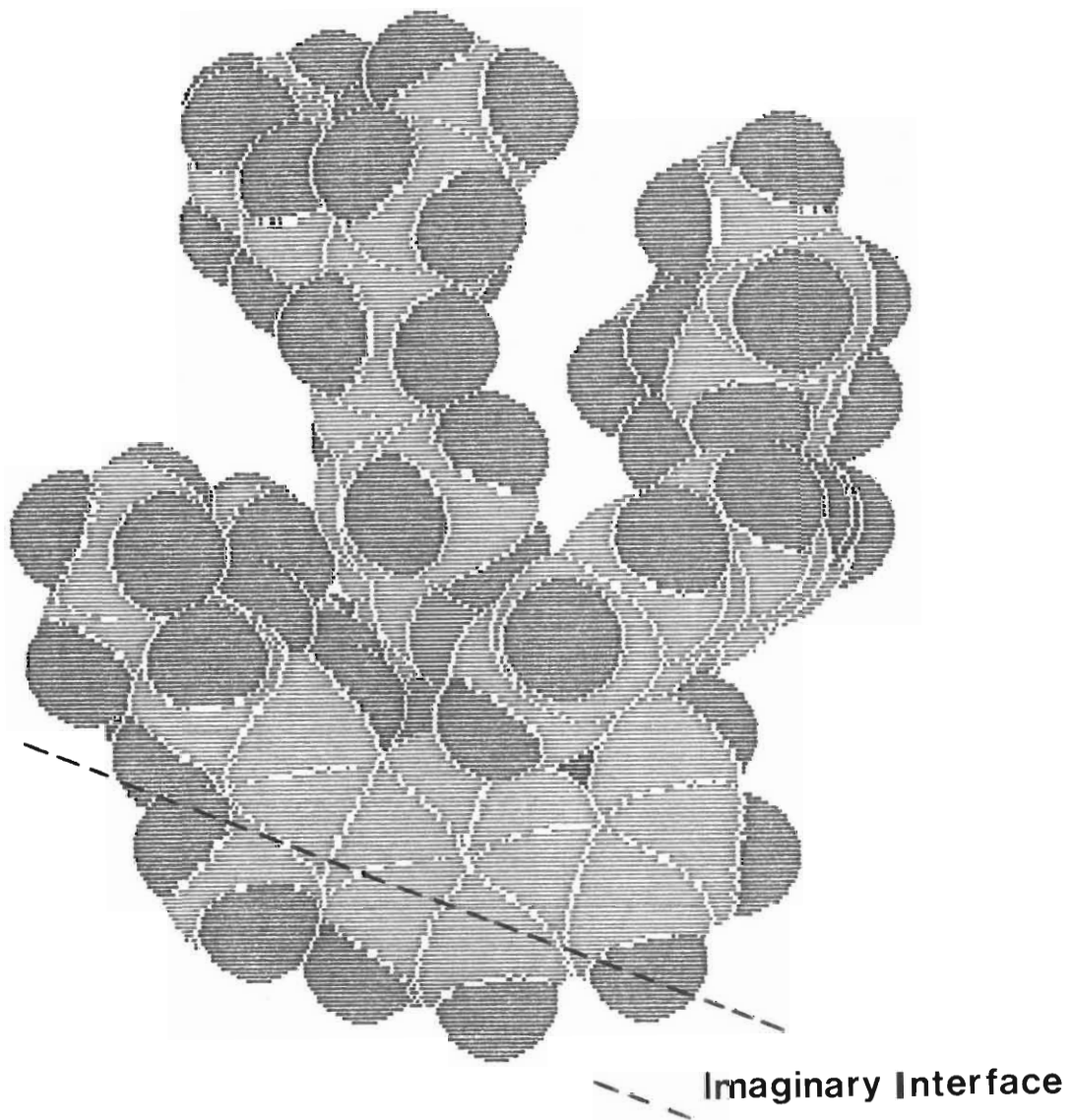


Figure (129). Alchemy-minimized structure of germanium bound to three molecules of Lix 26.



**Figure (130).** Alchemy-minimized structure of germanium bound to three molecules of TN 02181A.

hydroxyquinoline molecules have been meridionally coordinated with the central germanium atom. A question which arises therefore is whether energy differences exist if the ligands complex the metal ion in a facial arrangement- any large differences would indicate a stereochemical preference and would have to be accounted for in the rate equation and the holistic kinetic model. The results of the two modes of orientation are shown in Figure (131), energies calculated via Alchemy for Lix 26 and TN 02181A are summarised in Table (65).

The data in Table (65) suggests that there are no significant energy differences between the two modes of coordination both for extended (as in Lix 26) and compressed (TN 02181A) systems and it is therefore probable that both forms are produced equally at random. There is however, a substantial difference in the physical size (Figure (131) and the final column of Table (65)) of the two Lix 26 forms which probably affects their relative rates of diffusion from the interface.

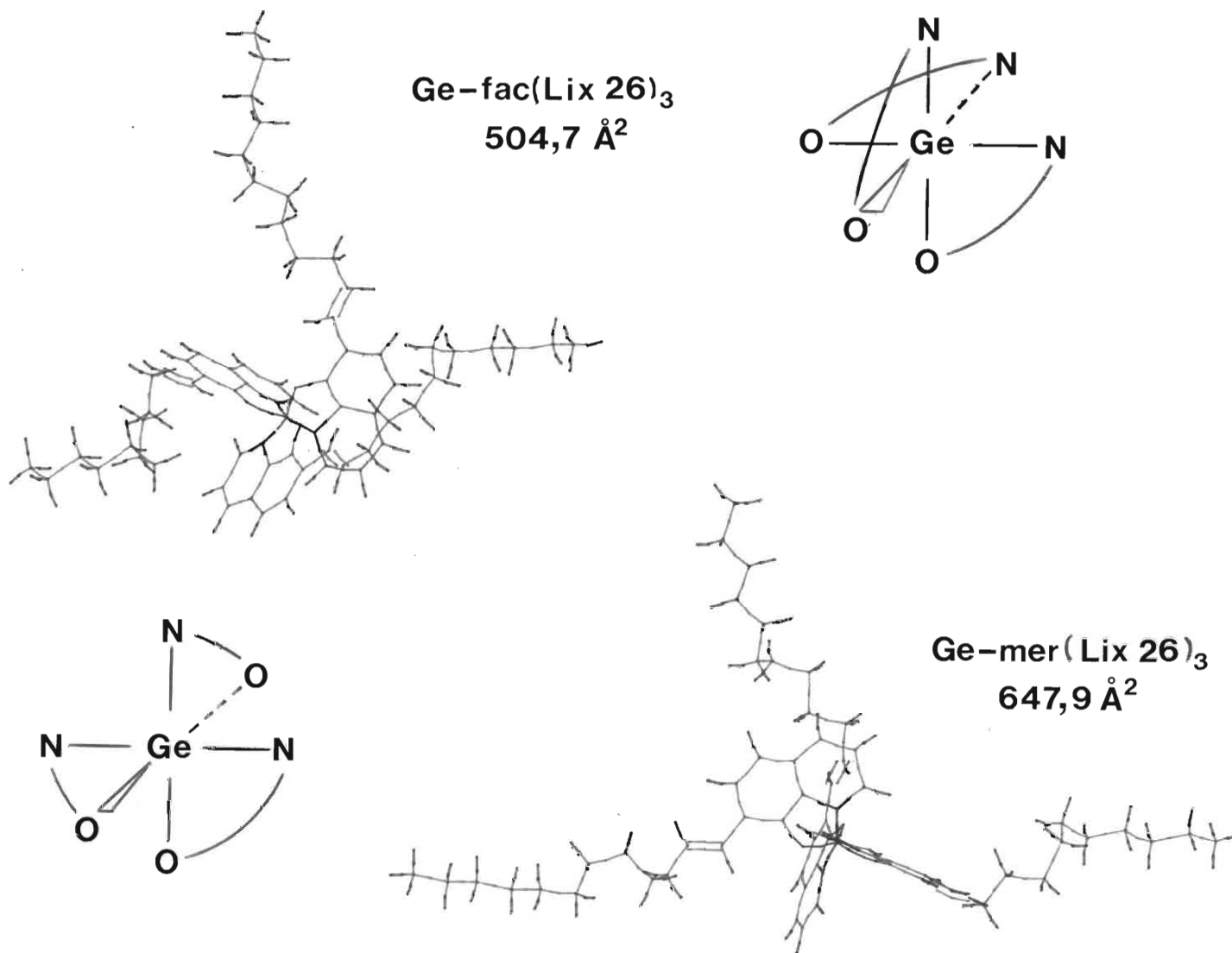


Figure (131). The difference in the conformation of the Alchemy-minimized tri-ligand chelates of germanium with Lix 26 coordinated in the facial and meridional arrangements.

| Molecule                 | $E_{\text{total}}$ | Bond Stretching | Angle Bending | Torsional | Out-of-Plane | Van der Waals | Area / $\text{\AA}^2$ |
|--------------------------|--------------------|-----------------|---------------|-----------|--------------|---------------|-----------------------|
| Ge-fac(Lix 26) $_3^+$    | 1510,4             | 317,1           | 1338,9        | 54,8      | 1,7          | -202,1        | 504,7                 |
| Ge-mer(Lix 26) $_3^+$    | 1497,1             | 315,1           | 1297,0        | 60,7      | 3,8          | -179,5        | 647,9                 |
| Ge-fac(TN 02181A) $_3^+$ | 1680,6             | 365,7           | 1297,0        | 97,9      | 14,6         | -94,6         | 262,4                 |
| Ge-mer(TN 02181A) $_3^+$ | 1644,5             | 339,3           | 1255,2        | 32,6      | 5,0          | 12,6          | 267,1                 |

Table (65). Minimum energies determined by Alchemy for facial and meridionally coordinated Lix 26 and TN 02181A in the  $\text{GeL}_3^+$  complex. All units  $\text{kJ mol}^{-1}$ . See Figure (131) for pictorial representation of the structures.

A full set of Alchemy-minimized energies for all the possible  $\text{GeL}_3^+$  species of interest to this work, including the impurities previously mentioned and Kelex 100, are given in Table (66). The data presented in the table do not reveal any trends in structure which may explain the reaction order  $\text{Kelex 100} < \text{TN 01787} < \text{Lix 26} < \text{TN 02181}$  for the ligands in the vigorous shaker at low concentration. Indeed, the total energies of the tri-ligand chelates are dominated by the angle bending term generated at the Ge-N and Ge-O bonding sites (see value of angle bending term for 8-hydroxyquinoline in Table (66)). The major difference between the total energies of the tri-ligand chelates (approximately  $200 \text{ kJ mol}^{-1}$  between the most stable i.e. Kelex 100 and the least stable i.e. TN 02181C which is a significant difference considering that the ligand monomers all have total energies in the range  $-60$  to  $+2 \text{ kJ mol}^{-1}$ ), is attributable to the difference in the Van der Waals' energy term. One trend which does emerge from the data lies in the values of this term:  $\alpha$ -unsaturated (Lix 26 and TN 01787) and saturated (Kelex 100) ligands have low (highly negative) Van der Waals energies whilst the  $\beta$ -unsaturated TN 02181 forms have only slightly negative or positive Van der Waals energies. The difference can be ascribed to the degrees of rotational freedom associated with the 7-alkyl chains; compare for example  $\text{Ge}-(\text{TN 01787})_3^+$  and  $\text{Ge}-(\text{TN 02181A})_3^+$  of Figure (132) where for the former the  $\alpha$ -unsaturation does not restrict the  $\text{C}_8\text{H}_{17}$  group attached at the  $\beta$  carbon atom thus allowing the minimization routine greater levity in performing structural changes than exists for TN 02181A where the  $\beta$ -unsaturation has the effect of 'pulling' the alkyl chain

| L in GeL <sub>3</sub> <sup>+</sup> | E <sub>total</sub> | Bond Stretching | Angle Bending | Torsional | Out-of-Plane | Van der Waals | Area / Å <sup>2</sup> |
|------------------------------------|--------------------|-----------------|---------------|-----------|--------------|---------------|-----------------------|
| Lix 26                             | 1497,1             | 315,1           | 1297,0        | 60,7      | 3,8          | -179,5        | 647,9                 |
| TN 01787                           | 1530,0             | 307,5           | 1297,0        | 63,6      | 3,7          | -141,8        | 411,5                 |
| TN 02181A                          | 1644,5             | 339,3           | 1255,2        | 32,6      | 5,0          | 12,6          | 267,1                 |
| TN 02181B                          | 1666,9             | 338,9           | 1297,0        | 34,7      | 4,2          | -7,9          | 235,0                 |
| TN 02181C                          | 1677,7             | 344,3           | 1255,2        | 29,7      | 4,6          | 43,9          | 475,2                 |
| TN 02181D                          | 1646,9             | 340,6           | 1255,2        | 31,0      | 5,0          | 15,1          | 498,0                 |
| Kelex 100                          | 1517,9             | 363,6           | 1297,0        | 84,5      | 10,9         | -238,1        | 361,1                 |
| Impurity 4                         | 1498,2             | 350,2           | 1297,0        | 71,5      | 4,6          | -225,1        | 240,6                 |
| Impurity 5                         | 1498,7             | 312,1           | 1297,0        | 53,6      | 4,2          | -168,2        | 254,1                 |
| Impurity 8                         | 1576,5             | 313,8           | 1255,2        | 39,3      | 2,9          | -34,7         | 604,6                 |
| 8-hydroxyquinoline                 | 1637,5             | 319,2           | 1255,2        | 23,4      | 4,6          | 35,1          | 116,3                 |

Table (66). Minimum total energies and values of the parameters minimized by Alchemy. Units kJ mol<sup>-1</sup>. Figure (132) shows the structures of Lix 26, TN 01787, TN 02181A and Kelex 100 for L in the extractable complex GeL<sub>3</sub><sup>+</sup>.



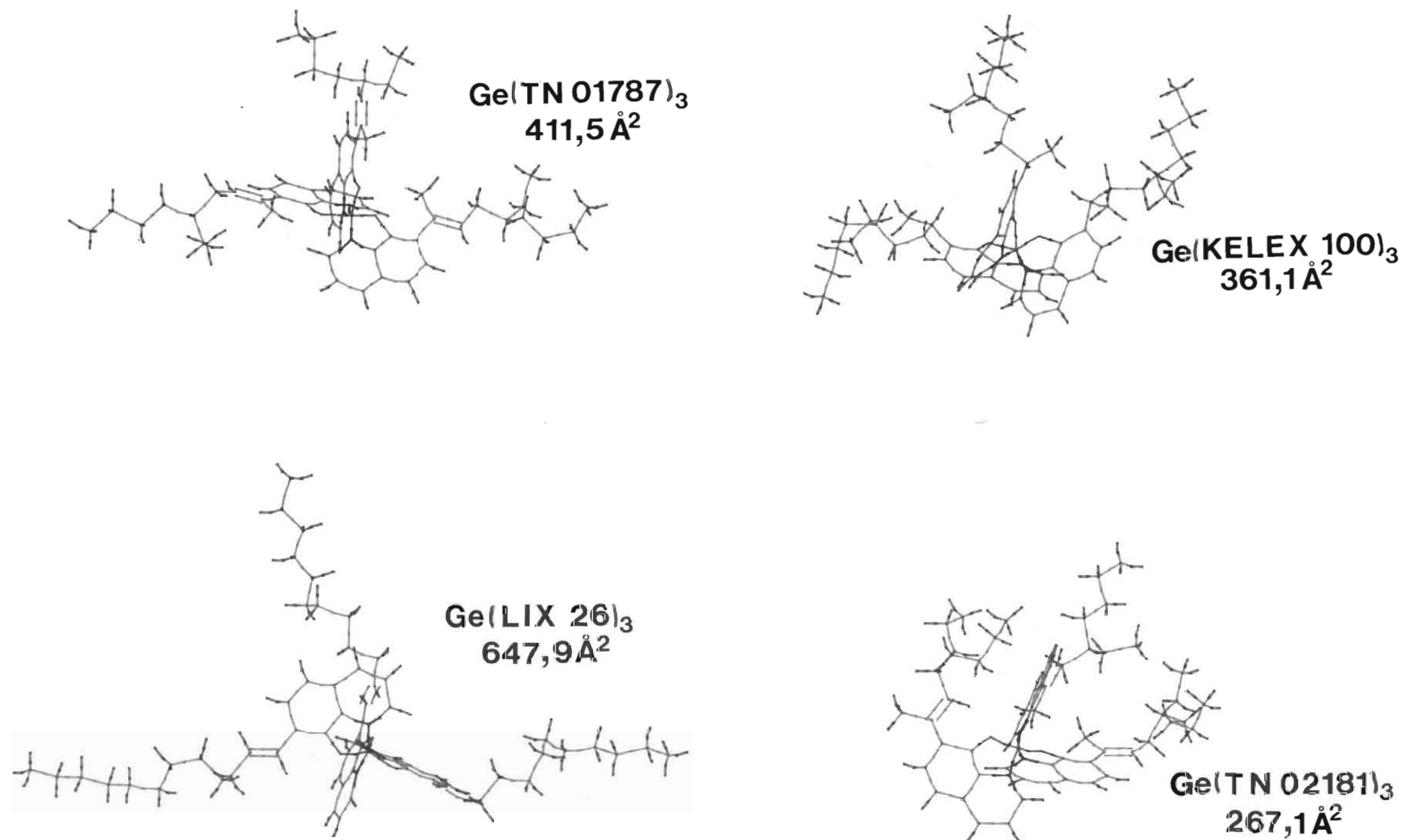


Figure (132). A visual representation of the difference in the most stable conformations of the tri-ligand chelates of germanium with TN 01787, Kelex 100, Lix 26 and TN 02181 (isomer A). Interfacial areas are included.

towards the central region, particularly if it is branched. The approximate surface areas given in Table (66) likewise show no correlation to the order of extraction efficacy, except the smallest most compact structure,  $(\text{Ge}-(\text{TN } 02181\text{A})_3^+)$  is also the most efficient ligand.

### 3.14. The Chelation of Germanium-Hydroxy Species by 7-Alkylated-8-hydroxyquinoline Derivatives at Low pH.

Under typical solvent extraction conditions, 7-alkylated-8-hydroxyquinoline molecules may be regarded as being unionised and intramolecularly hydrogen-bonded (Section 3.11.1), except under conditions of very low pH (i.e.  $\text{pH} \sim 0$ ) where the tertiary amine group protonates forming  $\text{H}_2\text{L}^+$  which is proposed in this work to be the reactive species during the fast initial reaction regime (Section 3.4.6, hypothesis 3). It is reasonable to suppose that the first step in the coordination of an germanium-hydroxy species to a ligand molecule involves some type of reaction with either the lone pair of the aromatic nitrogen or one of the lone pairs of the  $\text{sp}^3$ -hybridised phenolic oxygen. The possibility that the reaction proceeds via simple ionisation of the phenolic hydrogen and subsequent coordination of the metal-hydroxy species can be excluded in view of the high acidity of the aqueous phase (e.g.  $\text{pH} = -0,21$  for 1,5 M  $\text{H}_2\text{SO}_4$ ). It is suggested that the formation of the mono-ligand complex  $\text{GeL}^{3+}$  is in some way analogous to the series of events which result in the chelation of  $\text{Cu}^{2+}$  by hydroxyaryloximes proposed by Price and

Tumilty<sup>(249)</sup> and follows steps I and II of Figure (133). In this scheme the formation of the  $\text{GeL}^{3+}$  complex involves first the coordination of the phenolic oxygen to the germanium-hydroxy species (coordination of the tertiary amine is proposed to be less likely because this site is involved in hydrogen bonding), followed by an intramolecular inversion which breaks the hydrogen-bonding interaction between the aromatic nitrogen and phenolic hydrogen and facilitates the orientation of the  $\text{sp}^3$  lone pair with a vacant  $\text{sp}^3\text{d}^2$  orbital of germanium. The nitrogen lone pair then coordinates with the metal. During these series of reactions (steps I and II in Figure (133)), the germanium ion must lose the moiety occupying two of its  $\text{sp}^3\text{d}^2$  orbitals.

It must be noted that the reactions described above occur in the interfacial region and therefore the attachment of the second and third ligand molecules (Step III in Figure (133)), become successively more stereochemically difficult, with respect to the intramolecular inversion proposed for step I- this is in addition to the stereochemical demands placed upon the ligand and the chemical restrictions applicable to the intermediate chelate which were discussed in Section 3.12.2. This further stereochemical constraint adds additional support to the suggestion that the chelation of the third ligand is rate-determining.

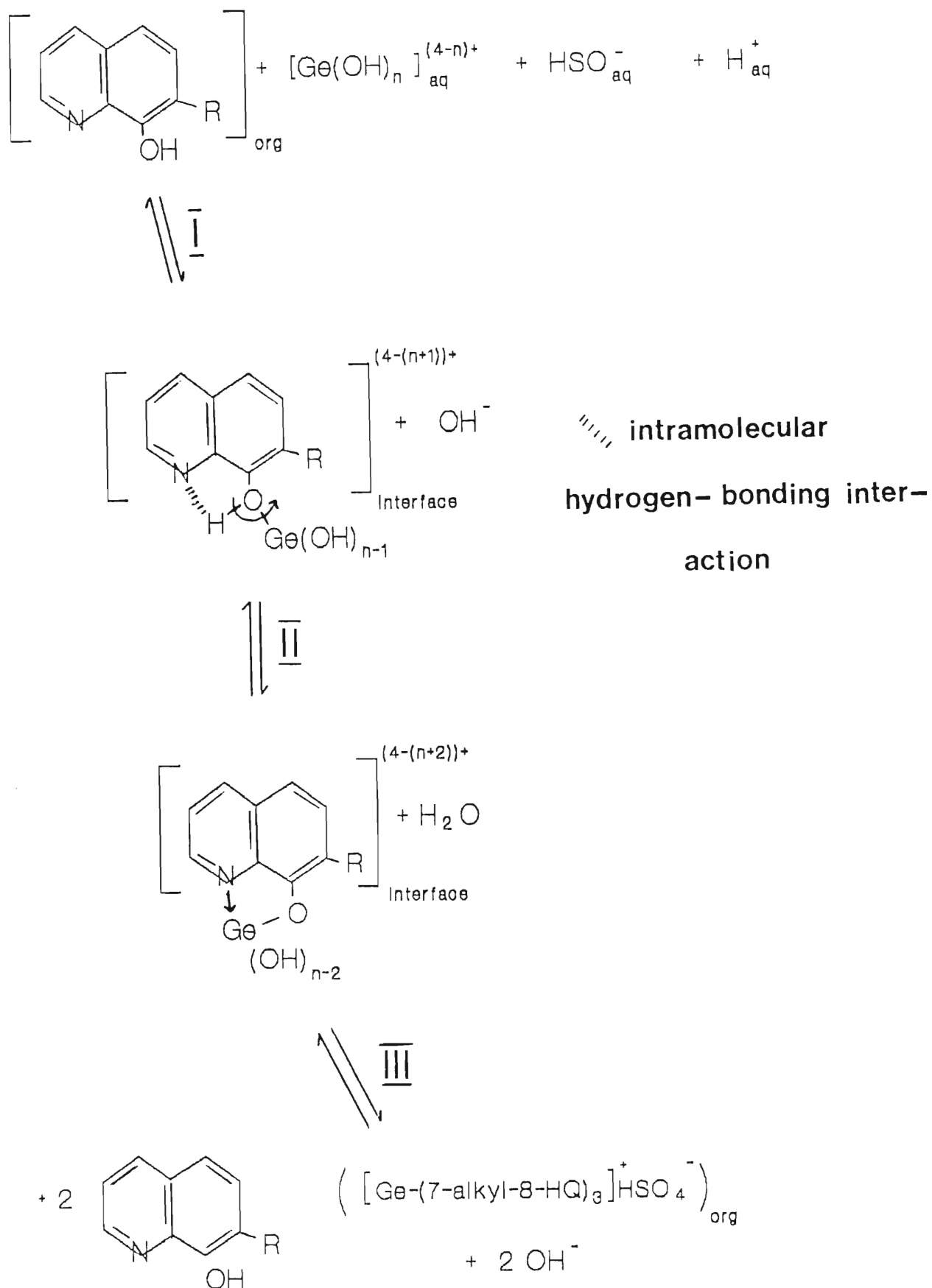


Figure (133). Proposed reaction scheme for the chelation of germanium hydroxy species by 7-alkyl-8-hydroxyquinoline.

One final note regarding this mechanism which is important to point out relates to the speciation of germanium in aqueous solution as discussed in Section 3.4.5 and the ease with which the various hydroxylated germanium species react with the ligand. The process depicted in Step I of the scheme of Figure (133), i.e. coordination of the phenolic oxygen to germanium and concomitant loss of  $\text{OH}^-$  is probably accelerated as the value of  $n$  is decreased in the molecular formula since fewer Ge-OH bonds are required to be broken - hence  $\text{Ge}^{4+}$  would be expected to react very quickly,  $\text{Ge}(\text{OH})^{3+}$  at a slower rate and so on. Furthermore, the inversion which occurs during Stage I would be less inhibited, both on steric and energetic grounds by say  $\text{Ge}^{4+}$  as opposed to  $\text{Ge}(\text{OH})_3^+$ .

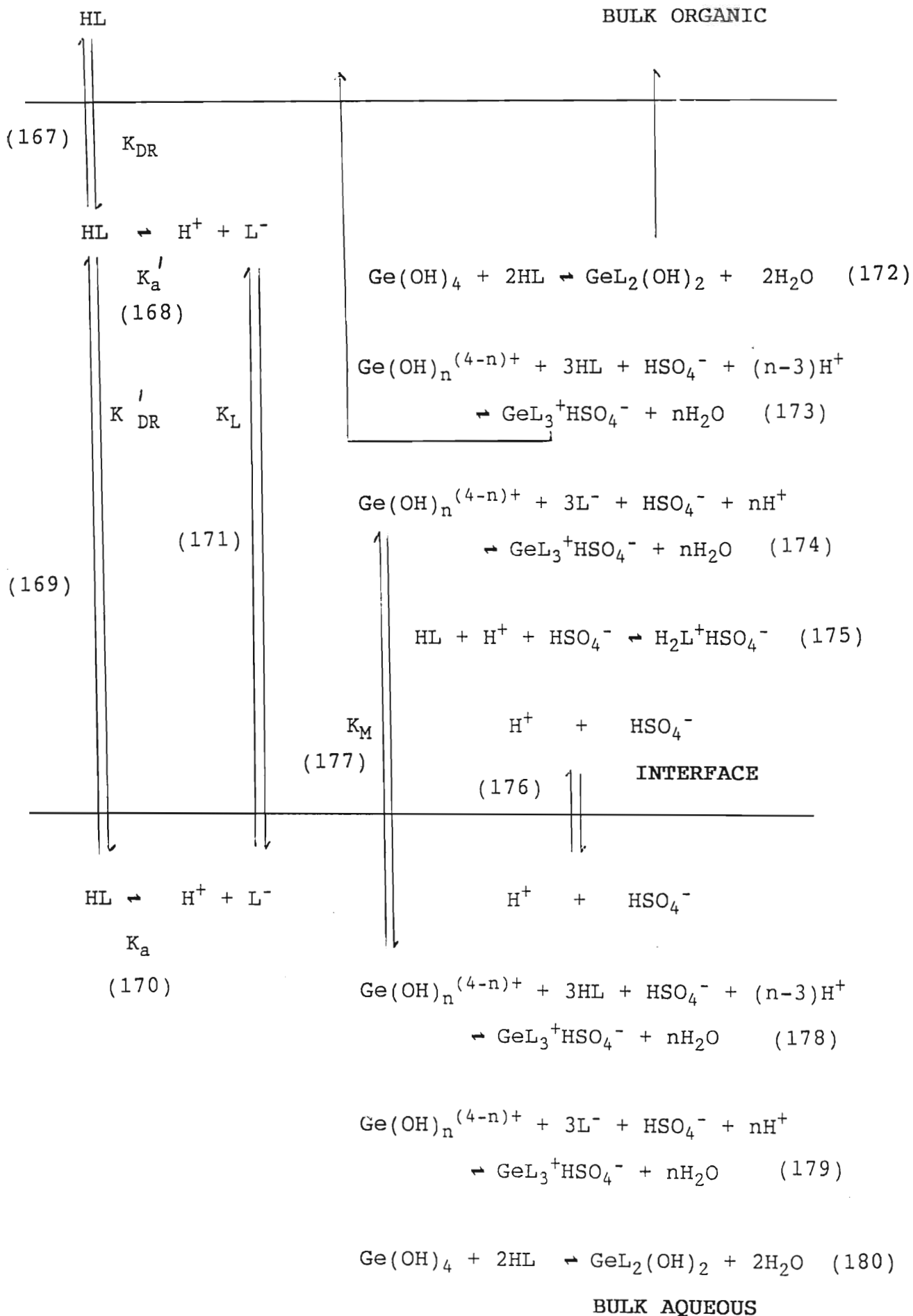
Regarding the acidity of the phenolic proton, an interesting test for the formation of the mono-ligand intermediate as represented here would be the introduction of electronegative substituents or electron donating groups on the phenolic system to assist or hinder ionisation of the phenol group and therefore convert the ligand into a stronger or weaker extractant. Some suggestion for experimental investigation is presented in Chapter 5.

### 3.15. A Proposed Holistic Kinetic Model for Germanium Extraction by Commercial 7-Alkylated-8-hydroxyquinoline Reagents.

In Chapter 1, a general mechanism for the solvent extraction of a metal ion,  $\text{M}^{n+}$ , by a ligand HL, was presented in order to

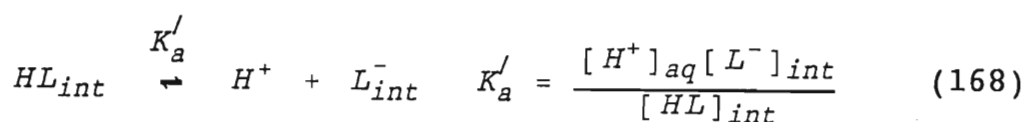
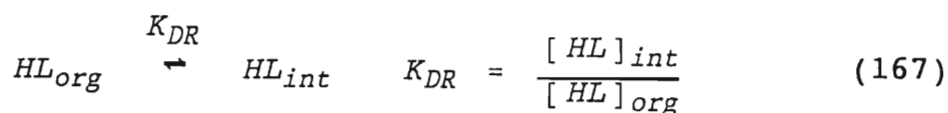
illustrate the principles of solvent extraction and to highlight the importance of the interfacial reaction zone and the significance of the aqueous phase pH in determining what combination of mechanisms is operative during chelate formation. The model which was discussed however was rudimentary and it is the intention in this section to propose an overall model for germanium extraction by 7-alkylated-8-hydroxyquinoline derivatives, to point out the factors which have an effect upon the observed extraction kinetics, propose optimum reaction conditions and to propose a rationale pertaining to the nature of the predominant reactions occurring and to identify processes which are neither rate-determining nor likely to influence the observed kinetics to any great extent.

Consider the kinetic-equilibrium model of Figure (134). The scheme partitions the two-phase reaction mixture into three discrete regions, (i) the bulk organic phase which comprises the ligand, HL, and its constituent impurities and any solvents, plus a diluent and (often) a modifier, (ii) the bulk aqueous phase which is immiscible with the organic phase and which contains dissolved germanium in various hydroxylated forms depending upon the selected pH, a quantity of acid and in some cases a background electrolyte to maintain ionic strength and (iii) an interfacial zone which can be imagined as a region of uncertain thickness but possessing large surface area in vigorously-stirred systems.

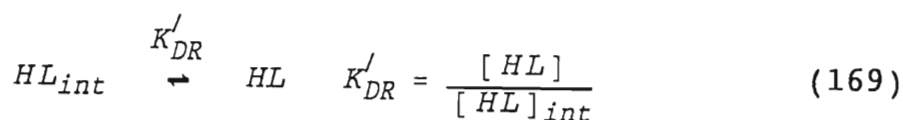


The model allows for four distinct concurrent reaction pathways: (a) reaction between metal ion and neutral ligand in the interface, (b) reaction between metal ion and ligand anion in the interface, (c) metal ion complexation by neutral ligand in the aqueous phase and (d) reaction of metal ion with ligand anion in the aqueous phase. Polarity incompatibility precludes the bulk organic phase as a possible site for any reaction involving ligand and germanium species. The following processes are therefore envisaged to occur:

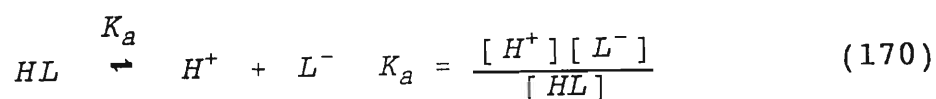
(i) Ligand distributes from the bulk organic phase to the interface where some dissociates into ligand anion. These processes are summarised by Equations (167) and (168) respectively:



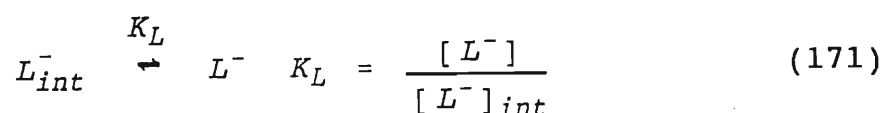
Following these steps, some interfacially adsorbed ligand distributes to the aqueous phase where it dissociates in an analogous manner i.e.







An equilibrium is also established between ligand anion at the interface and that formed via Equation (170) and is represented as Equation (171) viz.



(ii) At low pH ( $\leq 2$ ), extraction of germanium as the tri-ligand chelate  $GeL_3^+HSO_4^-$  could occur via processes (173) and (174), however given the approximate value of  $K_a^{int} = 7,24 \times 10^{-11}$  M (Section 3.11.2.4), and inserting  $[H^+] = 1,62$  M (for 1,5 M  $H_2SO_4$ ) gives, from Equation (168):

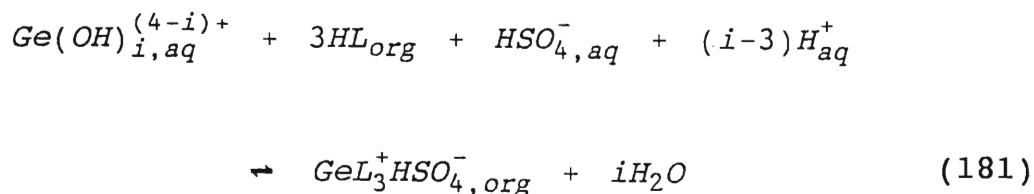
$$\frac{[L^-]_{int}}{[HL]_{int}} = 4,47 \times 10^{-11}$$

For Lix 26, measurements of interfacial tension show that for  $[Lix\ 26] \geq 1,10$  g/l at a static interface (Section 3.11.2.2), the interface is completely saturated with ligand. Assuming this value to be indicative of  $[HL]_{int}$ , but noting the caveat already pointed out regarding the adoption of interfacial tension data for vigorously-stirred systems, allows for the estimation of a value for  $[L^-]_{int} = 1,6 \times 10^{-13}$  M, which suggests that extraction of germanium via Equation (174) is insignificant.

The reaction of germanium(IV) with neutral HL and L<sup>-</sup> in the aqueous phase via Equations (178) and (179) respectively, is unlikely to contribute significantly to the overall germanium extraction rate. The solubility of 7-alkylated-8-hydroxyquinoline extractants is typically  $\leq 1 \times 10^{-3}$  g/l<sup>(183)</sup>, giving  $K_{DR}' \sim 10^{4,70}$  i.e. <0,002 % of the ligand distributes to the aqueous phase.

At 'high' pH (>2), the only reactions which can possibly result in the transfer of germanium across the phase boundary are (172) and (180), both of which describe the formation and extraction of a bi-ligand chelate which, by virtue of its exposed hydroxyl groups (Section 3.4.6 and Figure (71)), extracts at a much slower rate than the tri-ligand species. Again, the low expected concentration of neutral ligand which transfers to the aqueous medium, reduces the importance of Equation (180) compared with Equation (172).

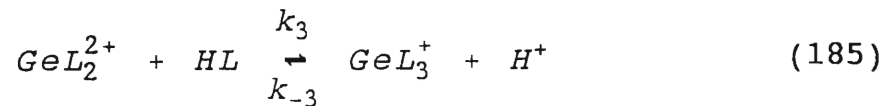
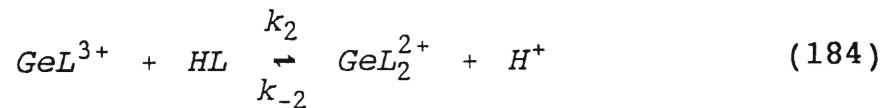
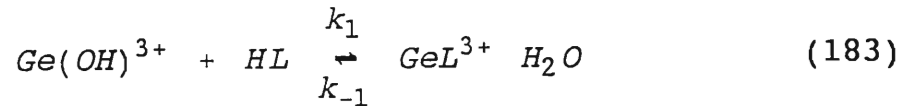
For pH < 1, germanium is thought to extract as  $GeL_3^+HSO_4^-$  according to the general equation:



The total rate of germanium extraction is given by the summation:

$$-\frac{d[Ge]_{tot}}{dt} = \sum_{i=0}^{i=4} k_i [Ge(OH)_i]^{(4-i)+} [HL]^x \quad (182)$$

$k_i$  : observed rate constant for the  $i^{th}$  species.  
Consider for example the extraction of  $Ge(OH)^{3+}$  which occurs via Equations (183) to (185):



For Equation (183),  $K_1 = [GeL^{3+}] / ([HL] \cdot [Ge(OH)^{3+}])$  and from (184),  $K_2 = [GeL_2^{2+}][H^+] / ([GeL^{3+}][HL])$ . The observed rate of germanium extraction, assuming negligible back reaction ( $k_{-3}$  small) is given by:

$$Rate_1 = -\frac{d[Ge(OH)^{3+}]}{dt} = k_3 [GeL_2^{2+}] [HL] \quad (186)$$

Solving for  $[GeL_2^{2+}]$  from  $K_1$  and  $K_2$  defined above gives:

$$Rate_1 = \frac{k_3 K_1 K_2 [HL]_{org}^3 [Ge(OH)^{3+}]}{[H^+]} \quad (187)$$

and since  $[HL]_{org} = [HL]_{int} / K_{DR}$  from Equation (167):

$$\text{Rate}_1 = \frac{k_3 K_1 K_2 [HL]_{int}^3 [Ge(OH)^{3+}]}{K_{DR}^3 [H^+]} \quad (188)$$

Equation (188) represents the rate at which  $Ge(OH)^{3+}$  is removed from aqueous solution by the ligand HL in terms of the interfacial concentration of HL, the aqueous phase hydrogen-ion concentration and the distribution coefficient for ligand to the interface from the bulk organic. A similar analysis for  $Ge^{4+}$  yields Equation (189):

$$\text{Rate}_0 = \frac{k_3 K_2 K_1' [HL]_{int}^3 [Ge^{4+}]}{K_{DR}^3 [H^+]^2} \quad (189)$$

where  $K_1' = [GeL^{3+}][H^+]/[Ge^{4+}][HL]$ .

Unlike Equations (188) and (189), species for which  $i \geq 2$  in Equation (182) do not have a term in  $[H^+]$ .

Since the total observed rate of extraction is given by the sum of the rates of extraction of all the possible germanium species i.e.

$$\text{Rate}_{total} = \text{Rate}_0 + \text{Rate}_1 + \dots + \text{Rate}_4 \quad (190)$$

then  $\text{Rate}_{total}$  is proportional to  $(1 + [H^+])/[H^+]^2$ , i.e.  $(1/[H^+]^2 + 1/[H^+])$ . It might therefore be expected that at low pH, orders with respect to  $[H^+]$  may vary from zero to inverse two. For the ligand reagents concerned in this work, orders with respect to  $[H^+]$  at low pH were observed to (a) change during the germanium extraction reaction and (b) were not confined to the range 0 to -2 suggested above. In particular, orders with respect to  $[H^+]$  of inverse 2,83 for Lix 26 in the initial fast reaction

regime and 2,73 for TN 01787 in the slower 'equilibrium' reaction regime have been determined in this work. It is suggested that a complex mixed-order circumstance is associated with the effect of  $[H^+]$  upon the rate of germanium extraction and this is proposed to be related to the diverse reactions which produce and consume hydrogen ions during extraction. As stated above, rate equations for which  $i \geq 2$  do not have a term in  $[H^+]$  - this is observed in practice since for this pH range, germanium is only present as  $Ge(OH)_2^{2+}$ ,  $Ge(OH)_3^+$  and  $Ge(OH)_4$  and shows a tendency to zeroth order in  $[H^+]$ .

(iii) The only reaction which 'opposes' Equation (173) in the scheme is the uptake of sulphuric acid by ligand, (Equation (175)), forming  $H_2L^+HSO_4^-$  which occurs very rapidly after phase contact (Section 3.4.6). It is proposed in this work that this species is reactive during the initial fast reaction regime until it is depleted, whence the reaction mechanism involves ligand monomer. *Inter alia* the formation of this protonated ligand species reduces the interfacial tension (Section 3.11.2.2) considerably and therefore probably enhances the mass transfer characteristics of the interface (but not the rate since the rate-determining step is reaction-controlled).

(iv) Implicit in the scheme of Figure (134) but not depicted is the reaction between  $GeL_3^+$  cation species and  $HSO_4^-$  counterions, provided via Equation (176). In Section 3.5, a kinetic treatment of the formation of the ion-association complex  $GeL_3^+HSO_4^-$  was discussed as a means for explaining a decrease in observed rate with

increasing ionic strength.

In essence then the locale of the extraction reaction(s) is the interface - a result which is substantiated in this work via the measurement of observed rates of germanium extraction with changing interfacial area in a reaction assembly (Lewis Cell) designed to maintain a quiescent interface and reduce all sources of turbulence. At very low pH then, the only processes summarised in Figure (134) which need to be considered are (167) and (177)-representing the diffusion of ligand and germanium to and from the interfacial region, Equations (173), (175) and (176) in which the ligand extracts germanium (IV) or an hydrogen ion and a counter-ion for electroneutrality and finally the diffusion of chelated germanium away from the interfacial zone and into the bulk organic (indicated by the arrows from the chelate products in Figure (134)).

On good stereochemical grounds, it has been proposed that the rate-limiting step in germanium extraction is the formation of  $\text{GeL}_3^+$  from the bi-ligand intermediate  $\text{GeL}_2^{2+}$  (either by reaction with neutral HL or with  $\text{H}_2\text{L}^+\text{HSO}_4^-$ ). It is recalled (Section 3.1.3) that a kinetic analysis invoking the steady-state approximation for the species  $\text{GeL}^{3+}$  and  $\text{GeL}_2^{2+}$  for the slow 'equilibrium' germanium extraction regime yielded:

$$\text{Rate} = \frac{k_1 k_2 k_3 [\text{Ge}] [\text{HL}]^3}{(k_{-2} [\text{H}^+] + k_3 [\text{HL}]) (k_{-1} [\text{H}^+] + k_2 [\text{HL}])}$$

which, assuming the extent of back reaction to be negligible, simplifies to:

$$\text{Rate} = k_f(\text{obs})[\text{Ge}][\text{HL}]^3$$

implying that plots of  $\log k_f(\text{obs})$  versus  $\log [\text{HL}]$  should be linear with a slope of approximately 3. In practice this was observed for Lix 26 and TN 01787 with apparent reaction orders with respect to ligand of 2,7 and 3,1 respectively, however an order of 1,1 was obtained for TN 02181 (suggestions for this latter behaviour were presented in Section 3.4.6). TN 02181 is therefore the most efficient reagent for germanium extraction and illustrates that the mechanism is a function of a number of physical and chemical parameters. It is also worth noting that the order of reaction was observed to change with time: for Lix 26 and TN 01787, fast initial (i.e. in the first 2-5 minutes of reaction) kinetics were observed with apparent reaction orders of 2,1 and 1,8 respectively and these orders can be rationalized by invoking a rate-determining step involving reaction of the  $\text{GeL}_2^{2+}$  intermediate and  $\text{H}_2\text{L}^+\text{HSO}_4^-$ . No change between initial and slower 'equilibrium' kinetics was observed for TN 02181. The differences in behaviour of these three ligands must be related to their structures- apparently the  $\beta$ -unsaturation is propitious to extraction, however it is not obvious why there should be such a vast difference in efficacy. The fast initial rates observed for these reagents compared with the 'equilibrium periods' are probably related both to the aqueous phase speciation of germanium:- higher hydroxy species are proposed to extract at a slower rate than non-hydroxylated or partially hydroxylated Ge(IV) and to the protonated ligand/ $\text{GeL}_2^{2+}$  reaction.

At very high ligand concentration, all of the reagents studied in this work were observed to tend towards a fractional order dependence in ligand. This is probably a result of two influences: (i) the interface is completely saturated with ligand and further ligand merely increases the bulk organic concentration and (ii) the solution viscosity increases rapidly with increasing ligand concentration and this could result in a necessity to introduce diffusion effects into the rate equation. For the ligand reagents reported in this work, concentrations of the as-received material in excess of 75 g/l do not improve germanium extraction characteristics.

There are a number of parameters which have been investigated in this work which either benefit or retard the rate of germanium extraction but which have not been included in the model. The following results must therefore be borne in mind in considering optimum operating conditions:

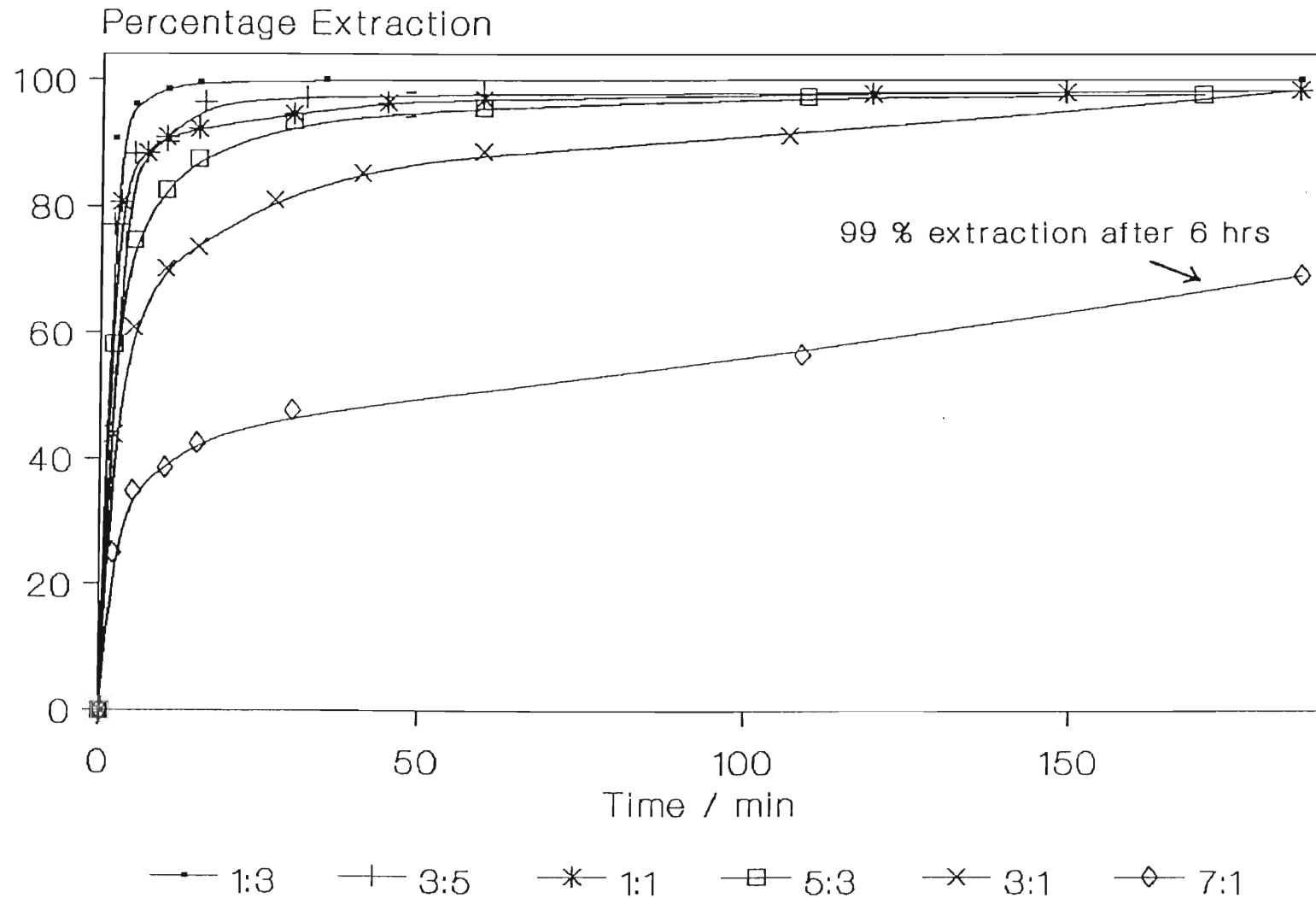
- (i) Increasing the ionic strength ( $I$ ) above approximately 2,0 M reduces the observed rate constant in an approximately linear fashion according to the relation  $\log k_f(\text{obs}) = -3,26 - 0,17 I$ . This may be of importance in situations where salt concentrations are high e.g. a leach liquor.
- (ii) The addition of an appropriate modifier (usually an aqueous insoluble alcohol) can greatly enhance the kinetics of germanium extraction and improve equilibrium yields. The choice of a suitable diluent is also consequential to the performance of the ligand.
- (iii) An increase in the operating temperature reduces the yields and the kinetics of germanium extraction. This is attributed to the lower available concentration of



ligand which is present at the interface with increasing temperature. For the conditions prevailing in the AKUFVE apparatus the Gibbs Free Energy of reaction is related to temperature according to the relation

$\Delta G = -14,97 + 350,0T$ . The extraction process overall is therefore thermodynamically unfavourable.

(iv) The ratio of the volume of the germanium-containing aqueous phase(a) to the volume of the ligand-containing organic phase(o). In Section 2.4.2.2.5, it was mentioned that for economic reasons it is desirable during extraction to contact as large a volume of aqueous phase with the minimum volume of organic phase. There is usually a range of a:o ratios over which optimal extraction can be obtained and the set of extraction data for Lix 26 shown in Figure (135) for the set of conditions summarised in Table (21), illustrates this effect. It is apparent from Figure (135) that low a:o ratios give the best observed extraction, i.e. 1:3 - 1:1, but these are not practical since ~ 80% extraction can be obtained in approximately 15 minutes with a 3:1 ratio. Over the same time period a 1:1 solution gives 90% extraction- such issues are always the subject of intense economic evaluation and beyond the scope of this work. Also evident in Figure (135) is the slow rate of extraction and attainment of equilibrium (~ 6 hours) observed for a phase ratio of 7:1. Economically this phase ratio is likely to be infeasible for development into an hydrometallurgical process.



Ratios shown are a:o, i.e. aqueous:organic

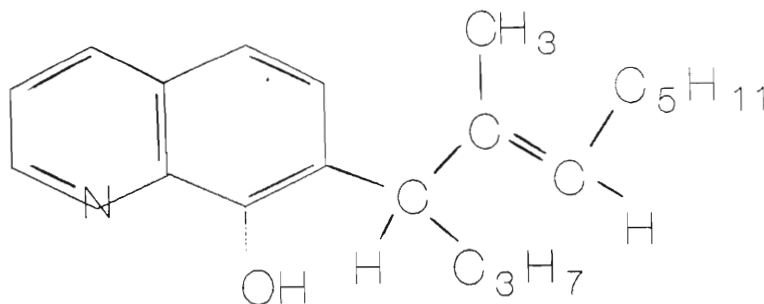
Figure (135). Percentage germanium extraction by a solution of 75 g/l Lix 26 in toluene as a function of the ratio of the aqueous phase(a) to the organic phase(o), see Section 2.4.2.2.5.

A final note which must be emphasized concerning the adjustment of parameters such as those above to favour extraction is the recognition that the solvent extraction process is an interlinked multivariate system and that the alteration of one parameter invariably changes other properties of the system. Of particular note are the close association between interfacial tension, viscosity and dielectric constant and the quantity of ligand, modifier, nature of the diluent and ligand, quantity and identity of constituent impurities and the pH and ionic strength of the aqueous medium. It is also important to acknowledge the effect of additives on the stripping process which, after all, is the process which ultimately yields germanium in some useful form.

CHAPTER 4SUMMARY OF CONCLUSIONS

(1) Three 7-alkylated-8-hydroxyquinoline extractants, two of which are untested in any metal extraction process (TN 02181 and TN 01787), and one (Lix 26) which has received little attention in the available literature, were supplied to this laboratory as possible formulations for the efficient removal of germanium from aqueous solution.

The structure of TN 01787 was confirmed via GC/ mass spectrometry to be an  $\alpha$ -unsaturated  $C_{12}$  -8-hydroxyquinoline (Figure (7b)) reagent. GC/MS data for TN 02181 confirm that this reagent is a mixture of isomers with a  $\beta$ -unsaturated 7-alkyl group, but one particular isomer, for which the structure is given below,



is suggested to be present in the proprietary reagent in greater quantity than other isomeric forms. On the basis of the mass spectrum fragmentation pattern, Lix 26 is proposed to

be an  $\alpha$ -unsaturated straight-chain, dodeceny-7-alkylated-8-hydroxyquinoline ligand (Section 2.2.2.3).

(2) All three of the reagents described in (1) above were supplied in an impure form, containing various 7-alkylated-8-hydroxyquinoline moieties, ketones, alcohols, furoquinolines and parent oxine in various quantity. The possible identities of three of these are proposed for the reagent TN 01787 (Table (11)). Semi-quantitative GC data suggest that Lix 26 contains 3-5% m/m oxine, somewhat more than the figure of ~ 0,2% for this impurity quoted by the suppliers for the reagents TN 02181 and TN 01787.

(3) A number of procedures were investigated for the purification of the three reagents. Preparative TLC and silica column chromatography offer reasonable resolution of the reagent components whilst acid-washing procedures and purification by recrystallization of the copper complex were experimentally unsuccessful. On the basis of germanium extraction data obtained with acid-wash pretreated Lix 26, it is suggested that this practice offers little simplification to the interpretation of kinetic data.

(4) Three techniques were investigated for the quantification of germanium in solution. A mannitol titration method yielded precise results but a relative error of  $8,43 \pm 0,2\%$  and was therefore rejected on the basis of this low accuracy. Similarly, the determination of germanium by direct atomic absorption was rejected on the basis of the inaccuracy of the method (errors of  $\pm 30\%$ ). This error is a result of the large dissociation energy of the Ge-O bond and results in the

inefficient production of germanium atoms. The final technique involved complexing the germanium ion with the chromophoric ligand phenylfluorone. In the presence of a polyol stabiliser and at low pH, this reagent complexes germanium with 2:1 ligand:metal stoichiometry and the product which is formed can be quantitated spectrophotometrically at 510 nm. Such germanium/ phenylfluorone solutions were found to be stable for up to 50 hours and gave a relative error of  $2,67 \pm 0,67\%$ , comparing favourably with a relative error of  $2,90 \pm 0,33\%$  obtained by electrothermal atomisation atomic absorption analysis of a few germanium samples.

(5) The germanium/phenylfluorone ligand complexation reaction is slow ( $\sim 90$  minutes for completion) and follows pseudo-first-order reaction kinetics. It is suggested that the rate-determining step in the reaction is the formation of the biligand chelate moiety  $\text{GePh}_2^{2+}$ , for which the observed rate constant is  $8,5 \times 10^{-4} \text{ s}^{-1}$ . Assuming pseudo-first-order kinetics apply facilitated the calculation of a rate constant for the rate-determining step,  $k_2$  of  $13,6 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ . This value of  $k_2$  and a value of  $20,0 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  for  $k_1$ , the rate constant for the formation of the monoligand moiety  $\text{GePh}^{3+}$ , were used as input to the kinetic simulation program CAKE. Computer predicted yields gave reasonable kinetic fit to the experimentally obtained data.

(6) Germanium extraction data was obtained with three reaction assemblies, two of which created conditions of vigorous stirring or shaking of the two-phase mixture, and one (Lewis Cell) in which the interface was quiescent and of measurable area. Kinetic data for germanium extraction by Lix 26 obtained

in the Lewis Cell as a function of the impeller speed, showed that a constant rate of extraction was obtained by varying the impeller speed over the range 40-100 rpm and this suggests that the rate-determining step during extraction is reaction-controlled rather than a diffusion controlled process. For impeller speeds in excess of 100 rpm, the quiescent nature of the interface is destroyed and observed rates increase.

The observed rate of germanium extraction in the Lewis Cell was found to be proportional to the interfacial area and this suggests that the site of the rate-determining step is the interface since if the reaction were an homogeneous one, then the area of contact would not affect the rate. A three phase kinetic model for germanium extraction comprising the bulk aqueous and organic phases and the interface, is therefore appropriate for extraction by 7-alkylated-8-hydroxyquinoline reagents.

(7) In high speed shaking and mixing (AKUFVE) assemblies, the germanium extraction kinetics are characterised by two reaction regimes: a fast initial regime in which  $t_{\frac{1}{2}}$  (the time required for 50% of the equilibrium extraction value), is of the order of 2 minutes if the pH is low ( $\leq$  pH 0,25), and a slower 'equilibrium region'. In the latter kinetic region, the rate-determining step is proposed to be the stereochemically-controlled chelation of the third ligand in reaction with the biligand intermediate  $GeL_2^{2+}$  (L:ligand), whilst in the fast kinetic regime, it is proposed that it is the reaction of the same intermediate species with the protonated ligand moiety  $H_2L^+HSO_4^-$  which is rate-determining.

In both the high speed experimental assemblies the slow 'equilibrium' kinetics are first order in metal ion, but orders with respect to ligand are a function of the particular reagent used.

(8) For TN 01787 and Lix 26 at low pH (<1) the experimentally determined rate laws in the initial and subsequent slower reaction regimes are approximately second order in ligand concentration in the former region (2,10 for Lix 26 and 1,77 for TN 01787) and approximately third order in ligand concentration in the latter region (2,70 for Lix 26 and 3,08 for TN 01787). These orders can be rationalized via derived analytical functions of the rate processes and by invoking the steady state approximation for the species  $GeL^{3+}$  and  $GeL_2^{2+}$ .

Experimental data for TN 02181 shows that even at low ligand concentration (25 g/l) compared with Lix 26 and TN 01787 (> 75 g/l), the observed kinetics are first order in ligand concentration in both the fast and slower reaction regimes. Alchemy-minimized molecular models of the dominant active form of this reagent monomer and of the triligand chelate, shows that it is small compared with Lix 26 and TN 01787 (Tables (63) and (66)) and this suggests that (i) the interfacial concentration of ligand will be higher at any bulk concentration than either Lix 26 or TN 01787 and (ii) the triligand chelate of TN 02181 (during formation at the interface) does not exclude as large a surface area from unreacted species as do Lix 26 and TN 01787. It is therefore proposed that the approximations made in Section (3.1.3) for the slow 'equilibrium' regime, which predict first order behaviour with respect to ligand at high bulk organic ligand



concentration, become appropriate for TN 02181 when it is in lower concentration than Lix 26 or TN 01787. In addition, TN 02181 protonates to a greater extent than either of Lix 26 or TN 01787 at any aqueous pH and this is offered as an explanation (Section 3.4.6) for the apparent first order behaviour in the fast kinetic regime.

(9) The Lewis Cell and the shaking/mixing assemblies yield entirely different observed germanium extraction rates and suggest different extraction efficiencies for the three ligand reagents in low concentration. In the Lewis Cell, the following order of efficiencies is suggested:

TN 01787 < TN 02181 < Lix 26

whilst in the vigorously mixed assemblies, the efficiency is:

TN 01787 < Lix 26 < TN 02181.

For both techniques, TN 01787 is the least efficient reagent for germanium extraction, however the orders of TN 02181 and Lix 26 are reversed. Interfacial tension data at static equilibrium show that Lix 26 is the most interfacially active ligand at the toluene/ 1,5 M H<sub>2</sub>SO<sub>4</sub> interface (rapid decrease in  $\gamma$  with increasing concentration), followed by TN 02181 and then TN 01787 and this is the same as the order of efficiency given by the Lewis Cell above.

It is suggested in this work and implied by other workers in the field of solvent extraction that the interpretation of extraction kinetic data is a function of the experimental approach which is adopted. In this instance, it is the difference in the interfacial area which is important: for one technique (Lewis Cell) the area of phase contact is small and measurable (103,87 cm<sup>2</sup> for this work) and rates of solute

exchange are slow, whereas for the other technique (shaking), the interfacial area is maximized, extraction rates are by comparison fast, but the actual interfacial area can only be approximated ( $\sim 10600 \text{ cm}^2$ ). It is also suggested in this work, that average droplet sizes in vigorously shaken assemblies are within the fine dispersion to emulsion range- this factor alone suggests that data sets are unlikely to be comparable.

(10) Varying the pH of the germanium-containing aqueous phase has an effect on the rate of germanium extraction, the yields of germanium extracted at equilibrium and determines what organic soluble germanium-ligand species extracts. Three regions of pH dependence are proposed (i)  $\text{pH} < 0$  where  $\text{GeL}_3^+\text{HSO}_4^-$  (in sulphuric acid medium) is the extractable species, (ii)  $\text{pH} \geq 2-3$  where the species  $\text{Ge(OH)}_2\text{L}_2$  extracts and (iii) an intermediate region where both species extract ( $\text{pH} \sim 1-2$ ). In pH region (i), the extractable product is highly hydrophobic and this is suggested to account for the fast observed extraction and good equilibrium percentage extraction yields ( $> 97\%$ ), whilst in region (ii), the product possesses hydrophilic centres and the extraction kinetics and equilibrium yields are poor ( $< 25\%$ ). Orders with respect to  $[\text{H}^+]$  for  $\text{pH} < 1$  for the three ligand reagents vary from approximately inverse 1 to inverse 3 during the course of extraction and this suggests mixed-order kinetics with respect to this species. For  $\text{pH} > 1$ , all three ligand reagents show a tendency towards zeroth order dependence in  $[\text{H}^+]$ .

(11) Both the initial rate of germanium extraction and the rate constant for the slow reaction regime decrease for  $I \geq 2,2 \text{ M}$ . Linear analytical expressions from the experimental

data and use of the Primary Kinetic Salt Effect have been derived for Lix 26, and it is proposed that they would facilitate an estimation of  $k_{obs}$  or initial rates of germanium extraction at a particular medium ionic strength.

(12) The germanium extraction kinetics by Lix 26 dissolved in four different organic diluents viz. paraffin, toluene, hexane and BDH 'Distillate' have been compared. Paraffin and hexane are suggested to be unsuitable in this role because they result in precipitation of reagent (and perhaps the products of the reaction between ligand, germanium and  $H^+$ ) on the walls of the contact vessel, even though an observed extraction rate comparable with the other two diluents was obtained. Toluene was observed to give the best extraction performance overall for the Lix 26 system.

(13) The effect upon the rate and equilibrium percentage germanium extraction by the inclusion of four aliphatic alcohol modifiers: n-propanol, n-butanol, n-pentanol and n-octanol, and one aromatic alcohol, benzyl alcohol, in the ligand/toluene system have been investigated. For the three ligand reagents, observed rate constants were of the order of 6-51 times greater than those in the absence of any modifier reagent. For TN 01787 and Lix 26, the order of efficiency of the modifiers for the system studied is:

$$\begin{aligned} & n\text{-propanol} < n\text{-octanol} < n\text{-pentanol} < n\text{-butanol} \\ & < \text{benzyl alcohol} \end{aligned}$$

whereas for TN 02181 the observed order is:

$$\begin{aligned} & n\text{-propanol} < n\text{-octanol} < n\text{-pentanol} \equiv n\text{-butanol} \\ & \equiv \text{benzyl alcohol} \end{aligned}$$

It is proposed that these reagents hydrogen-bond to the active

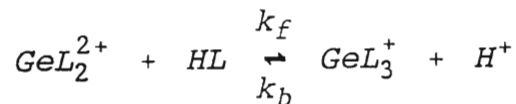
ligand molecules in the organic phase and that the ligand-modifier aggregate has greater interfacial activity than the ligand alone. The difference in the efficiency of these modifier reagents is proposed to be related to the number of them which can pack around the ligand, the size of the ligand itself and the modes of orientation of the two species. *Inter alia*, the modifiers also prevent emulsion and three phase formation. It is also proposed that the dielectric constant is a good indicator of the extent to which these reagents improve the germanium extraction characteristics by 7-alkylated-8-hydroxyquinoline reagents.

(14) Compared with kinetic extraction data obtained in a vigorous shaker, the AKUFVE yields smaller values of  $k_{obs}$  and slightly retarded observed percentage extraction. This is a function of the volume of the phases which are not in intimate contact (~ 30% of the total volume) during a cycle through the instrument.

(15) Observed germanium extraction rates by Lix 26 decrease with increasing temperature. A negative value of  $E_a$  was calculated via an Arrhenius treatment ( $E_a = -12,49 \text{ kJ mol}^{-1}$ ) and at 25°C, values of the enthalpy of activation  $\Delta H^\ddagger = -14,97 \text{ kJ mol}^{-1}$ , the entropy of activation  $\Delta S^\ddagger = -350,0 \text{ J K}^{-1} \text{ mol}^{-1}$  and the Gibbs free energy of activation  $\Delta G^\ddagger = 89,4 \text{ kJ mol}^{-1}$  were calculated. It is suggested that the lower rates of extraction at high temperature indicated by these parameters is a function of the increased mobility of the surface-active molecule which results in a decrease in the available ligand in the reaction zone due to

less tight packing. This inference is supported by the Langmuir concept of molecular adsorption at an interface which predicts that the time of stay of a molecule (a gas molecule onto a solid and in this case a liquid phase species onto an interface) at the phase boundary is proportional to the inverse of the temperature.

Thermodynamic parameters applicable to the reverse reaction in the rate-determining step for the process:



have also been calculated.

(16) In contrast with the rates of extraction observed under optimal operating conditions (100% extraction in approximately 15 minutes with ligand concentrations of 50-75 g/l, aqueous phase at very low pH, 10% v/v modifier), the rates of stripping of germanium from the loaded ligand are slow (100% in 24 hours; < 10% in 15 minutes for a 0,5 M NaOH strip liquor), equilibrium yields decrease with increasing  $[\text{OH}^-]$  and the kinetics are characterised by a slow induction period in which little or no stripping is observed, followed by a faster first-order kinetic regime. It is proposed that the  $\text{GeL}_3^+$  chelate is not interfacially active and that the slow kinetics observed are a function of the rate at which hydroxide becomes available in the organic phase where it reacts with the triligand chelate. This rate-determining process is assisted by the presence of a modifier with which the triligand chelate is proposed to form an aggregate which is (i) more reactive towards  $\text{OH}^-$  in the organic bulk and (ii) more surface active

and therefore amenable to an interfacial reaction.

(17) Infrared data for Lix 26, TN 02181 and TN 01787 indicate that in non-dissociating solvents the active ligand is intramolecularly hydrogen-bonded. This therefore excludes the possibility of polymeric species such as  $(HL)_2$  forming in the organic phase and this result is a simplification to the kinetic model.

(18) The Gibbs Adsorption Isotherm has been used to calculate the interfacial excess,  $\Gamma$ , for all three reagents at low pH and for Lix 26 at various aqueous phase pH's. At low pH ( $\sim -0,21$ ), Lix 26 was observed to be the most surface active reagent, whilst TN 02181 and TN 01787 have approximately equivalent surface activities.

For Lix 26 at pH  $\sim 0$  and at pH  $> 10$ , the calculated values of interfacial excess are high compared with those for the region  $0,24 < \text{pH} < 10$ . This is attributed to the forms of the ligand reagent which occupy the interface: at pH  $\sim 0$  the interface is populated by  $H_2L^+HSO_4^-$  whilst at pH  $> 10$  the ligand deprotonates and is present in its anionic form  $Na^+L^-$ . The apparent interfacial area of the ligand molecule, calculated from interfacial tension data, is at a minimum when it is in its charged forms as a result of the rearrangement of the molecule which occurs as it adopts its most stable configuration (which is a resultant of repulsive and attractive energies), and at a maximum in its neutral form.

(19) Interfacial tension data obtained for Lix 26 at various aqueous phase pH's was used to calculate an approximate value for  $pK_a^{int}$ , the apparent interfacial acid dissociation constant. An approximate value of 10,14 was obtained.

(20) A form of the Langmuir Isotherm utilising interfacial pressure data and the bulk organic concentration of ligand and appropriate to the adsorption of extractant molecules from a bulk organic phase onto an organic/aqueous interface gave linear plots for Lix 26 at a number of aqueous phase pH's. The constants  $p$  and  $q$  in the Langmuir-type expression can be calculated from the linear plots of  $c/\pi$  versus  $c$  and have physical meanings analogous to the constants  $b$  and  $V_m$  in the conventional definition of the isotherm, viz.  $q$  is an indication of the number of extractant molecules adsorbed into the interfacial monolayer and  $p$  is an indication of the attractive forces experienced by the molecules at the interface. Values of  $p$  calculated in this work are highest when the Lix 26 molecule is in its protonated ( $pH \sim -0,21$ ) and partially deprotonated ( $pH \sim 10$ ) forms and lowest when neutral. This trend is in agreement with the values of the interfacial excess calculated from interfacial tension data and utilising the Gibbs Adsorption Isotherm.

(21) The viscosity of the organic medium increases with ligand loading. It is suggested that layers of ligand and the products of the metal-ligand reaction at the interface, may separate bulk organic monomer from the reaction zone and this is partly responsible for the observed fractional order dependence of the rate of germanium extraction on  $[HL]$  at high bulk organic ligand concentration.

(22) All three 7-alkylated-8-hydroxyquinoline reagents are selective for germanium over zinc provided the pH of the extraction process is less than 4. For an aqueous solution containing a 10-fold stoichiometric excess of zinc over germanium in contact with a toluene solution of Lix 26, no extraction of zinc was obtained and no interference to the characteristics of germanium extraction were observed.

(23) The computer modelling program Alchemy has been used to calculate the minimum energy conformations of each of the ligand monomers, some of the important constituent impurities and of the germanium-triligand chelates. A visual representation of the rate-determining step of the germanium extraction process is presented and the energy terms of the  $\text{GeL}_2^{2+}$  intermediate and  $\text{GeL}_3^+$  were compared. The latter moiety is characterised by greater angle bending and bond stretching energy contributions as a result of accommodation of the third ligand. Some differences in the total energy are apparent for the triligand chelate structures of facially and meridionally oriented ligand in the  $\text{GeL}_3^+$  structure. For Lix 26 there is a reasonably large difference in the apparent interfacial area between the two modes of coordination ( $504,7 \text{ \AA}^2$  for facial and  $647,9 \text{ \AA}^2$  for meridionally-coordinated ligand).

(24) The chelation reaction mechanism of the 7-alkylated-8-hydroxyquinoline ligand with Ge(IV) is suggested to be analogous to the series of events which have been postulated for the interaction between hydroxyoximes and metal ions viz. coordination of the phenolic oxygen to the Ge(IV) species, followed by an intramolecular inversion and then coordination



of the  $sp^3$  lone pair of the tertiary nitrogen with an  $sp^3d^2$  metal orbital.

(25) A kinetic model is presented for the three-phase extraction of germanium by 7-alkylated-8-hydroxyquinoline reagents and includes all partition equilibria, the reactions between metal-ion and ligand which occur at all possible aqueous phase pH's and any dissociation equilibria. The importance of each of these reactions and equilibria to the overall observed kinetics is discussed in order to identify those processes which have the greatest relevance.

CHAPTER 5SUGGESTIONS FOR FUTURE WORK

(1) In this work the kinetics of germanium extraction by 7-alkylated-8-hydroxyquinoline derivatives has been shown to be controlled by a stereochemical reaction which occurs at the interface. The extraction kinetics have been followed experimentally by monitoring the decrease in the bulk aqueous phase germanium concentration as a function of time. This has its limitations. For instance, the hypotheses which have been presented for the initial fast rate of germanium extraction are postulated on the basis of the calculation of the initial rates, for which the data set in the linear portion of the  $[\text{Ge}]_{\text{aq}}$  versus time curve includes only the first 2-5 minutes of the reaction and the tangential construction used to estimate initial rates often traversed only one or two of the experimental points. In order to fully test the hypotheses which are proposed in this work for the rate-determining process occurring in this initial regime, it is necessary to obtain a greater data set, i.e. 10-15 data points are required in this reaction regime and this suggests that a continuous monitoring technique is required. The shaking/mixing assemblies used in this work are not adaptable to this mode of data collection (or in the case of the AKUFVE, give unsatisfactory kinetic data), however suggestions are made below which may give the desired experimental control:

(A) The Microporous Teflon Phase Separator (MPTS) has been mentioned in this thesis as a possible technique for the acquisition of a larger data set. The apparatus comprises a Morton flask fitted with a high speed stirrer and teflon phase separator (a cylinder wrapped with a teflon cloth), which is capable of selectively filtering water-immiscible solvents from an aqueous/organic admixture. The apparatus is described by its inventors<sup>(76,78)</sup> as a significant improvement on other high speed mixing assemblies and is reported to give less equivocal data in extraction kinetic studies than other high speed mixing assemblies. The use of a teflon phase separator facilitates the continuous monitoring of the rate of extraction and, if connected to a spectrophotometer, essentially instantaneous data analysis. The usefulness of such an apparatus for the further development of this work will depend upon whether a monitoring wavelength can be selected which distinguishes between complexed and uncomplexed ligand and absorption by the various impurities in the ligand reagents.

(B) The rates of germanium extraction reported in this work (rate constants in the range  $10^{-3} - 10^{-6} \text{ s}^{-1}$ ), suggest that a relaxation technique may be employed in the reaction rate analysis.

Since the reaction which occurs is **heterogeneous**, it is difficult to imagine an adaptation of the classical methods for studying reactions by relaxation methods e.g. a stopped-flow system or T-jump arrangement, because the

phases would require to be vigorously mixed in order for the reaction kinetics to be elucidatory to the situation prevailing in commercial equipment but would require separation prior to such an experimental analysis. Kinetic data would not therefore be instantaneously relevant. The quality of data acquired by stopped-flow studies of mixed phases and for emulsion type solutions is also questionable.

It is therefore suggested that the MPTS offers the best investigative route to larger data set acquisition during the first few minutes of extraction. Additionally, such an apparatus facilitates calculation of the interfacial area in vigorously stirred systems which is a useful parameter in the interpretation of extraction data obtained in vessels with different geometries and with different rates of agitation:- the suggestion here is that there is probably a droplet size which gives the maximum reaction surface area and optimal rate of coalescence after agitation has ceased, but is not prone to the formation of stable emulsions. Such microemulsion formation has already been suggested (Section 3.2.1.7) as one reason for the incomparability of Lewis Cell and shaking data.

(2) In Section 3.10, it was shown that the kinetics of hydroxide stripping of germanium from loaded Lix 26 were slow. The presence of a modifier, however was shown to assist the stripping process and it has been suggested that this is a result of the formation of an aggregate species which renders the metal/ligand moiety more reactive to  $\text{OH}^-$  both at the

interface and in the organic bulk. An interesting extension (and one which would draw attention from the suppliers of the reagents since the slow stripping is currently a notable commercial problem) to this work could include the following:

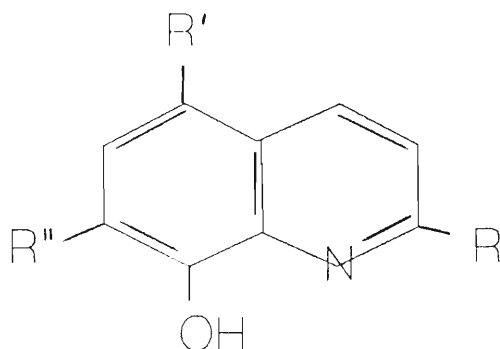
- (i) Testing of the other alcoholic modifiers utilised in this work and possibly other commercial reagents such as dodecanol etc. in order to identify any trend in efficiency which may exist,
- (ii) Optimization of the volume percent quantity of modifier to achieve maximum rates of stripping,
- (iii) A comparison of stripping rates from germanium-loaded Lix 26 with those from TN 02181, TN 01787 and Kelex 100. Such a study would elucidate any structural/stereochemical influence on the rate of stripping,
- (iv) An investigation of the effect of increasing  $[\text{OH}^-]$  on the rate of stripping from organic phases containing modifiers. This would make a useful comparison with data obtained in this work in which the rate of stripping and equilibrium yields of germanium decreased with increasing  $[\text{OH}^-]$ .

(3) The mineral wealth in the Southern African region extends from the base metals such as Co, Ni, Cu, Zn, and Fe, to the platinum group metals to the rare-earths. There is therefore almost unlimited scope for application of the ligand reagents reported in this work in solvent extraction processes which could have some commercial relevance to the local mining industry. Kelex 100 has been used effectively in solvent extraction processes for many of the base metals, particularly Cu and Fe for a number of years and these metals are therefore

suggested as a suitable solvent extraction study for Lix 26, TN 02181 and TN 01787. It is possible that any of these reagents may be more effective than those utilised in existing processes.

(4) In section 3.14, a mechanism was proposed for the germanium chelation reaction involving a 7-alkylated-8-hydroxyquinoline moiety and a germanium hydroxy species and it was suggested that the acidity of the phenolic proton could be tested by adding electron-withdrawing or electron donating groups onto the 8-hydroxyquinoline structure. It is suggested that by rendering the phenolic group more or less acidic, the reactivity of the molecule towards germanium may change and thus it may be possible to (i) recommend structural enhancements to the manufacturer's of the reagents and (ii) expand the current knowledge of the kinetics and the reaction mechanism by which these chelating ligands complex metal ions.

Consider, for example the values of the equilibrium formation constants for the three cases of substituted 8-hydroxyquinoline moieties with germanium given below<sup>(90)</sup>:



$$\log K_{eq} (\text{Ge}(\text{OH})_2\text{L}_2)$$

|       |   |   |                 |   |    |   |                   |  |      |
|-------|---|---|-----------------|---|----|---|-------------------|--|------|
| (i)   | R | = | CH <sub>3</sub> | ; | R' | = | H                 |  | 3,4  |
| (ii)  | R | = | H               | ; | R' | = | SO <sub>3</sub> H |  | 6,55 |
| (iii) | R | = | CH <sub>3</sub> | ; | R' | = | SO <sub>3</sub> H |  | 2,2  |

-CH<sub>3</sub> is a weakly activating (electron donating) and -SO<sub>3</sub>H is an intermediate strength deactivating (electron withdrawing) group. Although these values are of equilibrium data and therefore irrelevant to the rate at which reaction processes occur, they do illustrate that structural modifications can have profound effects upon the yields of metal obtained and the suggestion is that the inductive effects of the substituted moieties may also affect the rate of metal chelation by altering the electron occupancy of the nitrogen donor and the acidity of the phenolic proton.

This discussion suggests two possibilities for extension to this work:

(a) The addition of electron withdrawing groups at R' or R", therefore rendering the phenolic proton more acidic, may give improved reaction rates and this would prove (or disprove) that the acidity of the phenolic proton plays a significant role in the rate of reaction and

(b) The difference in the reactivity of the ligand species of interest to this work could be partly associated with the difference in the inductive effect of a saturated, an  $\alpha$ -unsaturated and a  $\beta$ -unsaturated 7-alkyl group. This could be tested via kinetic data obtained with a series of 7-alkylated-8-hydroxyquinoline extractants with the same alkyl side chain but differing

with respect to the position of unsaturation. The major problem associated with this suggestion would be in obtaining pure reagents in order that any observed change may be directly ascribed to the difference in electronic induction by the alkyl group.



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## APPENDIX A

(1) Mass/Charge ratios and relative abundances of the ion fragments of 8-hydroxyquinoline, see Figure (14).

(2) Mass/Charge ratios and relative abundances for some of the constituents of Lix 26. Elution times from Figure (15) are as follows: (A) 8,67 min; (B) 5,03 min; (C) 4,7 min; (D) 3,6 min.

(3) Mass/Charge ratios and relative abundances for the ion fragments of the constituents of TN 01787, see Figure (16). Elution times for the data shown are (A) 8,14 min- peak 2; (B) 8,40 min- peak 3; (C) approx 8,67 min-peaks 4 and 5 of the GC spectrum and (D) 9,38 min- peak 6.

(4) Mass/Charge ratios and relative abundances for the ion fragments of the constituents of TN 02181 which elute at 8,81 and 9,10 minutes on the gas chromatograph (Figure (18)).

| m/z   |       | m/z   |        | m/z    |        | m/z    |        |
|-------|-------|-------|--------|--------|--------|--------|--------|
| 41.05 | 13688 | 62.00 | 148416 | 87.00  | 42200  | 111.00 | 1500   |
| 42.05 | 4574  | 63.00 | 297152 | 88.10  | 38548  | 112.10 | 1082   |
| 43.10 | 8316  | 64.00 | 107504 | 89.10  | 406208 | 113.00 | 273    |
| 44.60 | 4303  | 65.00 | 33576  | 90.10  | 310848 | 114.10 | 14361  |
| 45.50 | 5732  | 66.00 | 13843  | 91.10  | 44128  | 115.10 | 15240  |
| 48.00 | 1809  | 67.00 | 7854   | 92.10  | 4018   | 116.10 | 128944 |
| 49.00 | 18360 | 68.00 | 1081   | 93.00  | 568    | 117.10 | 759616 |
| 50.00 | 85728 | 72.70 | 12162  | 96.10  | 225    | 118.10 | 85672  |
| 51.00 | 89520 | 74.00 | 44072  | 97.10  | 1718   | 119.10 | 3605   |
| 52.00 | 51520 | 75.00 | 39248  | 98.10  | 7306   | 123.10 | 744    |
| 53.00 | 29600 | 76.00 | 38520  | 99.10  | 7461   | 126.15 | 1214   |
| 54.00 | 12266 | 77.00 | 24296  | 100.10 | 4824   | 127.15 | 1149   |
| 55.00 | 3862  | 78.00 | 29440  | 101.10 | 3214   | 128.15 | 339    |
| 56.10 | 986   | 79.00 | 6764   | 102.10 | 3348   | 144.25 | 14855  |
| 56.50 | 1186  | 80.00 | 942    | 103.10 | 1072   | 145.25 | 767424 |
| 57.50 | 15086 | 84.00 | 3530   | 104.10 | 1093   | 146.25 | 99176  |
| 58.50 | 79360 | 85.00 | 14508  | 105.10 | 343    | 147.25 | 5768   |
| 60.00 | 5714  | 86.00 | 30976  | 110.00 | 726    | 148.25 | 427    |
| 61.00 | 61632 |       |        |        |        |        |        |

(1) Mass/Charge ratios and relative abundances of the ion fragments of 8-hydroxyquinoline, see Figure (14).

## 2A

| m/z   |      | m/z    |      | m/z    |      | m/z    |      |
|-------|------|--------|------|--------|------|--------|------|
| 41.00 | 6070 | 93.05  | 211  | 155.20 | 265  | 210.05 | 1048 |
| 42.00 | 410  | 95.15  | 684  | 158.20 | 7129 | 211.05 | 293  |
| 43.00 | 4904 | 97.15  | 411  | 159.30 | 2339 | 212.15 | 2006 |
| 44.05 | 332  | 98.55  | 229  | 160.30 | 279  | 213.05 | 367  |
| 51.05 | 400  | 103.15 | 582  | 165.40 | 126  | 222.05 | 213  |
| 52.25 | 291  | 104.25 | 138  | 166.10 | 172  | 224.15 | 403  |
| 53.05 | 1142 | 113.15 | 169  | 167.20 | 471  | 225.15 | 165  |
| 55.05 | 3582 | 115.15 | 301  | 168.30 | 416  | 226.05 | 2427 |
| 56.05 | 477  | 116.15 | 409  | 170.20 | 1058 | 227.15 | 379  |
| 57.05 | 2422 | 117.15 | 1032 | 172.30 | 4225 | 238.15 | 368  |
| 63.05 | 432  | 123.25 | 252  | 173.30 | 1145 | 240.05 | 1513 |
| 65.05 | 571  | 127.20 | 230  | 180.30 | 342  | 252.15 | 223  |
| 67.05 | 1156 | 128.20 | 483  | 182.30 | 968  | 254.25 | 1658 |
| 69.05 | 1721 | 129.10 | 277  | 183.30 | 562  | 255.15 | 383  |
| 70.05 | 311  | 130.20 | 981  | 184.30 | 1775 | 266.15 | 349  |
| 71.15 | 591  | 137.30 | 171  | 185.30 | 220  | 268.15 | 1247 |
| 77.05 | 1307 | 139.30 | 195  | 186.30 | 786  | 269.15 | 437  |
| 78.05 | 281  | 141.20 | 381  | 194.40 | 336  | 282.15 | 819  |
| 79.05 | 644  | 142.30 | 396  | 195.20 | 232  | 283.15 | 216  |
| 81.15 | 896  | 143.20 | 359  | 196.30 | 1429 | 295.30 | 182  |
| 82.15 | 327  | 144.30 | 238  | 197.30 | 665  | 296.30 | 604  |
| 83.15 | 1017 | 145.20 | 3484 | 198.30 | 2839 | 297.30 | 1136 |
| 84.15 | 141  | 146.20 | 1038 | 199.30 | 399  | 310.20 | 235  |
| 89.05 | 725  | 152.30 | 211  | 200.30 | 254  | 311.30 | 2189 |
| 90.15 | 283  | 153.20 | 189  | 208.05 | 247  | 312.30 | 452  |
| 91.15 | 600  | 154.30 | 630  | 209.05 | 223  |        |      |

## 2B

| m/z   |      | m/z   |       | m/z   |       | m/z    |       |
|-------|------|-------|-------|-------|-------|--------|-------|
| 41.00 | 2355 | 59.95 | 469   | 78.05 | 1409  | 98.15  | 279   |
| 42.00 | 543  | 60.95 | 2408  | 79.05 | 588   | 99.05  | 266   |
| 43.15 | 2453 | 62.05 | 7488  | 81.05 | 635   | 101.15 | 162   |
| 43.95 | 386  | 63.05 | 14030 | 82.05 | 439   | 104.15 | 196   |
| 44.85 | 449  | 64.05 | 4546  | 83.05 | 518   | 109.15 | 315   |
| 45.55 | 615  | 65.05 | 1975  | 84.05 | 448   | 110.25 | 182   |
| 49.05 | 789  | 65.95 | 732   | 85.05 | 799   | 111.15 | 186   |
| 50.05 | 5893 | 67.05 | 1158  | 86.05 | 1047  | 114.05 | 399   |
| 51.05 | 4566 | 68.15 | 203   | 87.05 | 1676  | 115.05 | 552   |
| 52.05 | 2919 | 69.05 | 958   | 88.05 | 1372  | 116.05 | 4427  |
| 53.05 | 2370 | 70.15 | 608   | 89.05 | 14594 | 117.15 | 26968 |
| 54.05 | 703  | 71.15 | 686   | 90.05 | 10883 | 118.15 | 3007  |
| 55.05 | 1418 | 72.55 | 1310  | 91.05 | 1784  | 119.15 | 152   |
| 55.95 | 646  | 74.05 | 1496  | 92.15 | 217   | 144.20 | 556   |
| 57.15 | 1387 | 75.05 | 2072  | 95.15 | 538   | 145.20 | 33432 |
| 57.55 | 1265 | 76.05 | 1838  | 96.15 | 319   | 146.20 | 3958  |
| 58.55 | 6389 | 77.05 | 1362  | 97.15 | 379   | 147.30 | 314   |

## 2C

| m/z   |      | m/z   |      | m/z   |     | m/z    |      |
|-------|------|-------|------|-------|-----|--------|------|
| 41.00 | 2341 | 58.15 | 141  | 82.05 | 434 | 97.15  | 1693 |
| 43.15 | 2517 | 65.05 | 217  | 83.05 | 981 | 98.15  | 256  |
| 44.15 | 192  | 67.05 | 1135 | 84.15 | 366 | 103.05 | 373  |
| 45.25 | 173  | 69.15 | 1373 | 85.15 | 470 | 105.05 | 192  |
| 50.95 | 218  | 70.05 | 883  | 91.05 | 533 | 110.15 | 186  |
| 53.05 | 836  | 71.15 | 1009 | 93.15 | 244 | 117.15 | 244  |
| 55.05 | 1973 | 77.05 | 407  | 95.15 | 724 | 123.15 | 300  |
| 55.95 | 665  | 79.05 | 413  | 96.15 | 330 | 132.20 | 420  |
| 57.05 | 1665 | 81.05 | 649  |       |     |        |      |

## 2D

| m/z   |     | m/z   |     | m/z    |      | m/z    |      |
|-------|-----|-------|-----|--------|------|--------|------|
| 41.00 | 339 | 59.05 | 345 | 116.95 | 1474 | 168.00 | 385  |
| 43.00 | 345 | 60.95 | 215 | 118.95 | 1577 | 170.10 | 122  |
| 43.85 | 213 | 81.95 | 456 | 121.05 | 476  | 199.10 | 1501 |
| 46.25 | 130 | 83.95 | 250 | 129.00 | 370  | 201.10 | 2628 |
| 47.05 | 546 | 94.05 | 371 | 164.00 | 699  | 203.10 | 1560 |
| 47.55 | 123 | 95.15 | 173 | 166.00 | 947  | 205.00 | 563  |
| 57.05 | 193 | 96.05 | 404 |        |      |        |      |

(2) Mass/Charge ratios and relative abundances for some of the constituents of Lix 26. Elution times from Figure (15) are as follows: (A) 8,67 min; (B) 5,03 min; (C) 4,7 min; (D) 3,6 min.

| m/z   |      | m/z   |      | m/z    |      | m/z    |     |
|-------|------|-------|------|--------|------|--------|-----|
| 41.05 | 1898 | 69.10 | 1569 | 94.10  | 151  | 121.20 | 216 |
| 42.25 | 144  | 71.10 | 363  | 95.20  | 1012 | 123.20 | 282 |
| 42.95 | 2454 | 79.10 | 405  | 97.10  | 808  | 137.25 | 306 |
| 44.10 | 167  | 81.00 | 637  | 98.10  | 1910 | 151.35 | 350 |
| 53.00 | 282  | 82.00 | 507  | 99.20  | 220  | 152.35 | 776 |
| 54.10 | 177  | 83.10 | 1341 | 107.10 | 320  | 155.35 | 168 |
| 55.10 | 2141 | 85.20 | 196  | 109.10 | 400  | 195.45 | 646 |
| 56.10 | 249  | 91.10 | 184  | 111.10 |      |        |     |
| 57.10 | 1873 | 93.10 | 1157 | 112.20 |      |        |     |
| 67.10 | 512  |       |      |        |      |        |     |

### 3A

|       |      |       |      |        |      |        |      |
|-------|------|-------|------|--------|------|--------|------|
| 41.05 | 2736 | 67.10 | 685  | 84.10  | 181  | 111.10 | 2478 |
| 41.95 | 321  | 69.10 | 1886 | 85.20  | 261  | 121.20 | 173  |
| 43.10 | 2817 | 70.00 | 364  | 91.20  | 175  | 137.35 | 248  |
| 43.90 | 256  | 71.10 | 575  | 95.10  | 958  | 152.35 | 778  |
| 44.10 | 286  | 77.10 | 229  | 96.20  | 215  | 153.35 | 226  |
| 55.10 | 2538 | 79.20 | 280  | 97.20  | 1012 | 195.35 | 1585 |
| 56.10 | 499  | 81.10 | 754  | 98.10  |      |        |      |
| 57.00 | 2572 | 82.00 | 744  | 99.10  |      |        |      |
| 65.10 | 193  | 83.10 | 2433 | 110.10 |      |        |      |

### 3B

|        |      |        |      |        |       |        |      |
|--------|------|--------|------|--------|-------|--------|------|
| 41.05  | 1352 | 129.15 | 213  | 167.25 | 513   | 186.25 | 397  |
| 43.10  | 1016 | 130.25 | 251  | 168.25 | 307   | 191.25 | 103  |
| 55.00  | 543  | 140.25 | 113  | 169.25 | 144   | 195.35 | 223  |
| 57.00  | 1130 | 141.15 | 262  | 170.25 | 626   | 196.35 | 1011 |
| 69.10  | 301  | 142.25 | 416  | 171.25 | 247   | 197.25 | 494  |
| 71.20  | 175  | 145.25 | 129  | 172.25 | 953   | 198.35 | 3426 |
| 77.10  | 320  | 152.25 | 228  | 173.35 | 384   | 199.25 | 551  |
| 91.60  | 248  | 153.25 | 262  | 178.35 | 141   | 210.20 | 300  |
| 98.10  | 193  | 154.25 | 1138 | 180.25 | 567   | 240.20 | 1446 |
| 102.50 | 119  | 155.25 | 462  | 182.25 | 907   | 241.00 | 196  |
| 103.10 | 127  | 158.25 | 1200 | 183.35 | 1216  | 268.10 | 1105 |
| 115.10 | 373  | 159.25 | 272  | 184.25 | 17000 | 297.35 | 2557 |
| 127.25 | 196  | 166.15 | 289  | 185.25 | 2374  | 298.35 | 576  |
| 128.15 | 237  |        |      |        |       |        |      |

### 3C

| m/z    |      | m/z    |      | m/z    |       | m/z    |      |
|--------|------|--------|------|--------|-------|--------|------|
| 41.05  | 3090 | 117.00 | 364  | 168.25 | 1124  | 208.00 | 504  |
| 42.05  | 336  | 126.15 | 306  | 170.25 | 692   | 209.10 | 246  |
| 43.10  | 1713 | 127.15 | 439  | 172.25 | 521   | 210.10 | 328  |
| 51.10  | 382  | 128.15 | 324  | 177.25 | 239   | 220.10 | 285  |
| 53.10  | 292  | 139.25 | 803  | 178.25 | 475   | 222.10 | 649  |
| 55.00  | 862  | 140.15 | 647  | 179.25 | 320   | 223.20 | 236  |
| 56.10  | 182  | 141.25 | 591  | 180.35 | 477   | 224.20 | 244  |
| 57.10  | 1896 | 142.25 | 547  | 182.25 | 1513  | 236.20 | 252  |
| 63.00  | 409  | 143.35 | 156  | 183.25 | 1519  | 238.10 | 969  |
| 73.90  | 132  | 151.25 | 594  | 184.25 | 2125  | 240.10 | 234  |
| 77.00  | 333  | 152.25 | 474  | 191.35 | 167   | 252.10 | 309  |
| 83.80  | 128  | 153.25 | 478  | 194.25 | 1168  | 266.20 | 902  |
| 89.10  | 411  | 154.25 | 1014 | 195.35 | 1829  | 267.20 | 305  |
| 101.10 | 204  | 155.25 | 133  | 196.25 | 44464 | 294.35 | 163  |
| 102.00 | 223  | 158.15 | 454  | 197.35 | 15956 | 295.25 | 8296 |
| 114.10 | 327  | 166.15 | 1123 | 198.35 | 2614  | 296.25 | 1919 |
| 115.00 | 685  | 167.25 | 4462 | 199.35 | 220   | 297.25 | 446  |
| 116.20 | 433  |        |      |        |       |        |      |

3D

(3) Mass/Charge ratios and relative abundances for the ion fragments of the constituents of TN 01787, see Figure (16). Elution times for the data shown are (A) 8,14 min- peak 2; (B) 8,40 min- peak 3; (C) approx 8,67 min-peaks 4 and 5 of the GC spectrum and (D) 9,38 min- peak 6.

| m/z   |       | m/z    |      | m/z    |      | m/z    |      |
|-------|-------|--------|------|--------|------|--------|------|
| 41.05 | 22584 | 79.00  | 1221 | 127.15 | 545  | 170.25 | 1230 |
| 42.05 | 2422  | 81.10  | 793  | 128.15 | 946  | 171.25 | 324  |
| 43.10 | 18312 | 82.10  | 149  | 129.15 | 486  | 172.25 | 1852 |
| 44.10 | 522   | 83.10  | 344  | 130.15 | 1539 | 173.25 | 446  |
| 51.00 | 1584  | 84.00  | 179  | 139.15 | 411  | 180.25 | 472  |
| 52.10 | 653   | 84.30  | 190  | 140.25 | 278  | 182.25 | 1361 |
| 53.10 | 2770  | 88.00  | 161  | 141.15 | 480  | 183.25 | 660  |
| 54.10 | 771   | 89.00  | 981  | 142.15 | 614  | 184.35 | 1004 |
| 55.00 | 6074  | 90.20  | 436  | 143.25 | 411  | 186.35 | 324  |
| 56.00 | 1118  | 91.10  | 562  | 144.25 | 355  | 194.35 | 305  |
| 57.10 | 3302  | 91.60  | 329  | 145.25 | 1217 | 195.25 | 196  |
| 63.00 | 766   | 92.10  | 238  | 146.25 | 607  | 196.35 | 1201 |
| 65.00 | 1015  | 93.10  | 245  | 151.25 | 117  | 197.25 | 629  |
| 66.10 | 329   | 95.10  | 318  | 152.25 | 284  | 198.35 | 1366 |
| 67.00 | 1398  | 101.00 | 396  | 153.25 | 233  | 208.10 | 186  |
| 68.00 | 273   | 102.10 | 692  | 154.25 | 1081 | 210.10 | 668  |
| 69.10 | 1415  | 103.10 | 718  | 155.25 | 417  | 212.10 | 1065 |
| 70.20 | 450   | 104.20 | 343  | 156.15 | 222  | 225.10 | 507  |
| 71.00 | 794   | 113.20 | 123  | 158.25 | 4702 | 240.20 | 398  |
| 74.00 | 116   | 114.10 | 239  | 159.25 | 1470 | 254.20 | 465  |
| 75.10 | 286   | 115.10 | 734  | 166.25 | 426  | 255.10 | 186  |
| 76.10 | 495   | 116.10 | 599  | 167.25 | 964  | 268.20 | 168  |
| 77.00 | 2890  | 117.00 | 1323 | 168.25 | 398  | 282.20 | 237  |
| 78.10 | 661   | 126.15 | 246  | 169.25 | 155  | 297.35 | 293  |

| m/z   |       | m/z    |      | m/z    |      | m/z    |      |
|-------|-------|--------|------|--------|------|--------|------|
| 41.05 | 24112 | 78.00  | 707  | 129.15 | 516  | 173.35 | 472  |
| 42.05 | 1809  | 79.10  | 1320 | 130.25 | 1307 | 180.25 | 408  |
| 43.10 | 17728 | 80.20  | 226  | 131.25 | 202  | 182.25 | 976  |
| 44.20 | 735   | 81.10  | 798  | 139.15 | 372  | 183.25 | 709  |
| 51.00 | 1016  | 82.10  | 290  | 140.25 | 288  | 184.25 | 1212 |
| 52.00 | 715   | 83.10  | 447  | 141.15 | 510  | 186.25 | 373  |
| 53.10 | 3155  | 88.00  | 179  | 142.25 | 639  | 191.35 | 125  |
| 54.00 | 632   | 89.00  | 1080 | 143.25 | 423  | 195.35 | 243  |
| 55.00 | 6515  | 90.10  | 536  | 144.25 | 301  | 196.25 | 1041 |
| 56.00 | 1095  | 91.10  | 748  | 145.25 | 1815 | 197.25 | 574  |
| 57.00 | 4759  | 92.20  | 261  | 146.25 | 479  | 198.35 | 1057 |
| 58.20 | 347   | 93.10  | 274  | 152.15 | 440  | 199.35 | 201  |
| 63.00 | 733   | 95.10  | 406  | 154.25 | 1109 | 208.10 | 262  |
| 64.00 | 376   | 101.10 | 379  | 155.25 | 306  | 210.00 | 657  |
| 65.00 | 996   | 102.10 | 673  | 156.25 | 272  | 211.10 | 155  |
| 66.00 | 384   | 103.10 | 940  | 158.25 | 4748 | 212.10 | 906  |
| 67.10 | 2193  | 105.20 | 125  | 159.25 | 1487 | 226.10 | 712  |
| 68.10 | 304   | 113.10 | 130  | 166.25 | 491  | 227.10 | 313  |
| 69.00 | 1530  | 114.10 | 278  | 167.25 | 703  | 240.30 | 390  |
| 70.00 | 402   | 115.10 | 587  | 168.25 | 354  | 254.20 | 381  |
| 71.10 | 1005  | 116.10 | 462  | 169.25 | 214  | 268.30 | 293  |
| 75.00 | 337   | 117.00 | 1387 | 170.25 | 1088 | 297.35 | 283  |
| 76.10 | 517   | 127.25 | 337  | 171.25 | 320  | 311.45 | 198  |
| 77.10 | 2672  | 128.15 | 769  | 172.25 | 1782 |        |      |

4B

(4) Mass/Charge ratios and relative abundances for the ion fragments of the constituents of TN 02181 which elute at 8,81 and 9,10 minutes on the gas chromatograph (Figure (18)).