THE DETERMINATION OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION USING GAS LIQUID CHROMATOGRAPHY

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by

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I hereby certify that this research is the result of my own investigation, which has not already been accepted in substance for any degree, and is not being concurrently submitted for any other degree.

signed :............................

I hereby certify that the above statement is correct.

signed :............................ TMLetcher

Prof. T.M. Letcher

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ABSTRACT

The aim of this investigation was to develop and test a theory that allowed for the calculation of the activity coefficients at infinite dilutions (γ_{13}^{∞}) from G.L.C. measurements using moderately volatile solvents. The solvents chosen for study were straight chained (C_5 to C_7) and cyclic (C_5, C_6 and benzene) liquid hydrocarbons using cis- and trans-decahydronaphthalene (decalin) as the stationary liquid phase (solvent). The systems were studied at two different temperatures, 283.15 K and 298.15 K. The solutes were n-pentane, n-hexane, n-heptane, cyclopentane, cyclohexane and benzene. This method for the determination of activity coefficients has the advantage of being able to work at infinite dilution, whereas in other techniques, extrapolation to infinite dilution of finite-concentration data is necessary. In addition solutes are separated from impurities when chromatographed so that only very small quantities of moderately pure material need be used. However the technique is also limited since the solute studied (injected reagent) needs to be volatile, while the solvent (liquid stationary phase) should be involatile. The solvents chosen in this experiment (cis- and trans-decalin) are moderately volatile which introduces many limitations since the theory developed for the determination of activity coefficients at infinite dilution is restricted to involatile solvents. However a novel method for working with moderately volatile solvents is developed by relating the loss of solvent to its partial pressure and modifying the existing theory. In the past the use of precolumns and/or saturators, coarse packing, small pressure gradients, and internal standards were used when working with volatile solvents. However employing this new method excludes the use of precolumns, saturators, or internal standards, and allows any type of packing and pressure gradient to be used.

The calculated activity coefficients are compared with literature values, where the workers employed G.L.C. techniques, and with predicted values. The activity coefficients calculated at both temperatures are used in the calculation of excess partial molar enthalpies. These results are compared with values obtained from finite concentration data by other workers.

TABLE OF CONTENTS

page

1. INTRODUCTION

The aim of this investigation is to develop and test a theory that allowed for the calculation of activity coefficients at infinite dilution (γ_{13}^{∞}), from gas liquid chromatography measurements using moderately volatile solvents (liquid stationary phase).

Activity coefficients at infinite dilution are macroscopic quantities related to interaction between molecules and are a measure of solution non-ideality. They are useful in analytical chemistry for the selection of suitable stationary phases for difficult separations and in chemical engineering for the design of separation processes.

Gas chromatography is an analytical method based on differences in free energy of the solute distributed between a static phase (usually of great surface area), and a moving gas phase. Simple physico-chemical considerations can be applied to the technique resulting in an equation from which the activity coefficient of the solute at infinite dilution (γ_{13}^{∞}), can be calculated. However the theory developed by Everett(1) and Cruickshank(2) can only be used to calculate γ_{13}^{∞} for systems that have volatile solutes and involatile solvents, and that do not show a Gibbs adsorption effect at the solvent surface.Their equation is (see chapter 2)

$$\ln\gamma_{13}^{\infty} = \ln\frac{n_3RT}{V_NP_1^*} - [\frac{(B_{11} - V_1^*)}{RT}]\ P_1^* + [\frac{(2B_{12} - V_1^{\infty})}{RT}]\ J_3^2P_O \qquad (1.1)$$

where V_N is the net retention volume, P_O the outlet pressure, $J_3^2P_O$ the mean column pressure, n_3 is the amount of liquid solvent on the column, T the column temperature, P_1^* the saturated vapour pressure of the solute at temperature T, B_{11} the second virial coefficient of the pure solute, V_1^* the molar volume of the solute as a liquid, V_1^∞ the partial molar volume of the solute at infinite dilution in the solvent, and B_{12} the mixed second virial coefficient of the solute and carrier gas. In this thesis the subscripts 1, 2 and 3 refer to the solute, carrier gas and solvent respectively.

Much work has been conducted using this technique to determine γ_{13}^∞ by Cruickshank(3), Letcher(4), Young(5), Everett(1), and other researchers.
The method has the obvious advantage of speed and also producing an accurate activity coefficient at infinite dilution using only moderately pure solutes. However the technique does suffer from several limitations. The most important being that the solvent must be sufficiently involatile to prevent it from evaporating off the column.

In this work the range of systems which can be studied have been extended to include solvents of moderate volatility. The theory has been modified to take this into account. Simple physico-chemical considerations result in a new equation(6) that relates the amount of solvent lost to its partial pressure ($P_3^/$). (see chapter 2)

$$\frac{V_N}{n_3 e^C} = \frac{RT}{\gamma_{13}^\infty P_1^*} - \frac{U_o t}{n_3} [\frac{P_3^/}{\gamma_{13}^\infty P_1^*}] \qquad (1.2)$$

where

$$C = - [\frac{B_{11} - V_1^*}{RT}] P_1^* + [\frac{2B_{12} - V_1^\infty}{RT}] P_o J_3^2 \qquad (1.3)$$

U_0 is the volumetric flow rate corrected for temperature and the presence of water vapour and t is the time of the injection of the solute on to the column.
The activity coefficient at infinite dilution was determined at two temperatures, 283.15 K and 298.15 K for solutes n-pentane, cyclopentane, n-hexane, cyclohexane, benzene and n-heptane using cis- and trans-decahydronapthalene as the solvents. The isomers cis- and trans-decahydronapthalene were chosen because of their moderate volatility. Also they provided a change from previous systems studied by replacing the normally straight chain stationary phase with a planar, bicyclic nonlinear hydrocarbon.

In order to calculate γ_{13}^{∞}, a gas liquid chromatograph was built along the lines of that described by the Bristol group(7-9). A detailed theory of gas liquid chromatography and the modifications to accommodate moderately volatile solvents is given in chapter 2. The apparatus used, the experimental procedure and the measurements obtained from them are described in chapters 3 and 4. Finally in chapter 5 the results obtained are discussed and compared with results obtained by other workers using similar methods. The activity coefficients at the two temperatures were then used to calculate the partial molar excess enthalpies of the solutes, and the results compared with data obtained from enthalpy measurements by other workers.

2.THEORY OF GAS LIQUID CHROMATOGRAPHY

2.1. Gas Chromatography Principles

The chromatographic process involves the distribution of a solute component between two phases, a mobile phase and a stationary phase. The two phases are mutually well dispersed with a large area of contact. In G.L.C. the liquid stationary phase (eg. hexadecane) is dispersed on an inert solid support, such as celite, which is packed into the column. The liquid is held on the surface and in the pores of the support, while the a stream of inert gas, the mobile phase, flows continuously through the spaces between the particles.(10)

In the elution process a small quantity of solute is introduced into the column at the inlet. The solute zone or peak is carried through the column by the mobile phase and its emergence at the other end is observed by a suitable detector, in this case a thermal conductivity detector. The velocity with which the peak travels through the column is less than that of the mobile phase and depends on the distribution coefficient of solute between the two phases.(10)

When the solute reaches the column, an equilibrium is set up between the liquid phase and the carrier gas phase so that a proportion of the sample always remains in the gas phase. This portion moves a little further along the column in the carrier gas stream, where it again equilibrates with the stationary phase. At the same time, material already dissolved in the stationary phase re-enters the gas phase so as to restore equilibrium with the clean carrier gas, which follows the zone of vapour.(11) This process in which carrier gas containing the vapour is stripped by the solvent in front of the zone, while vapour enters carrier gas at the rear of the zone, goes on continuously with the result that the zone of vapour moves along the column more or less compactly.

The speed at which the zone moves depends mainly on two factors, the rate of flow of the carrier gas and the partition coefficient of the solute between carrier gas and liquid phase. The faster the flow of carrier gas the faster the zone moves; and the more strongly the vapour is adsorbed on to the solvent, the more slowly the zone moves. When two or more components are present in the sample, each usually behaves independently of the other, so that for a given carrier gas flow rate, the speed of the zone of each component will depend on the extent to which it is adsorbed. Since different substances differ in their adsorption, they may therefore be separated by making use of their different speeds of progress through the column. When eluted the solutes will appear one after the other in the gas stream, the fastest first and the slowest last.

2.1.1. Assumptions

The theory for the determination of activity coefficients at infinite dilution rests on the following assumptions.(12)

(i) The column can be divided into a large number of theoretical plates.

(ii) The partition coefficient is constant throughout the range of concentration encountered, that is, Henry's Law is obeyed. This is only true for very low solute concentration.

(iii) The solute volume upon introduction into the column occupies only a small portion of the column length.

(iv) There is negligible resistance to mass transfer from gas to solvent i.e. the rate at which equilibrium is reached is very much greater than the rate of travel of solute down the column.

2.2. Summary of the G.L.C. Theory for γ_{13}^{∞}

In 1941 Martin and Purnell(13) related the equilibrium partition coefficient, K_R, to retardation properties using a plate theory, whereby they related the retention volume of the solute, V_R, to the gas hold up volume, V_G, and the solvent volume, V_3 (for zero pressure difference across the column).

$$V_R = V_G + K_R V_3 \qquad (2.1)$$

In 1952 James and Martin(14) took into account the compressibility of the mobile phase by using a correction factor which according to Everett's notation can be generalized as

$$J_n^m = \frac{n}{m}\frac{(P_i / P_o)^m - 1}{(P_i / P_o)^n - 1} \qquad (2.2)$$

where P_i is the inlet pressure and P_O the outlet pressure.

In 1956 Porter (15) related the net retention volume, V_N, to the activity coefficient of the solute at infinite dilution, γ_{13}^{∞}, by

$$V_N = \frac{n_3 RT}{\gamma_{13}^{\infty} P_1^*} \qquad (2.3)$$

where n_3 is the amount of solvent on the column and P_1^* the vapour pressure of the solute. The net retention volume is obtained from the outlet flow rate U_O using

$$\begin{aligned} V_N &= J_3^2 U_O (t_R - t_D) \\ &= J_3^2 U_O t_R - V_D \end{aligned} \qquad (2.4)$$

where t_R and t_D are the retention times for the solute and an unretained gas respectively, and V_D is the dead space volume. By taking into account imperfections of the solute vapour and the solute carrier gas, the net retention volume (V_N) can be calculated by extrapolating $ln\ V_N$ to $P_O = 0$ using [16]

$$\ln V_N = \ln V_N^0 + \beta P_O J_3^2 \qquad (2.5)$$

where

$$\beta = \frac{2B_{12} - V_1^\infty}{RT} \qquad (2.6)$$

in which B_{12} is the mixed second virial coefficient of the solute vapour in the carrier gas and V_1^∞ is the partial molar volume of the solute at infinite dilution in the solvent. The activity coefficient of the solute at infinite dilution in the solvent γ_{13}^∞ is related to V_N^0 by the equation(7)

$$\ln V_N^0 = \frac{n_3 RT}{\gamma_{13}^\infty P_1^*} - [\frac{B_{11} - V_1^*}{RT}] P_1^* \qquad (2.7)$$

where V_1^* is the molar volume of the pure solute, and B_{11} is the second virial coefficient of the pure solute vapour.

The Bristol group$^{(7-9)}$ took into account carrier gas imperfection and suggested a different extrapolation technique for ideal gases

$$\ln V_N = \ln V_N^O + \beta P_1^* J_3^4 \qquad (2.8)$$

2.3. Detailed Theory of G.L.C.

2.3.1. The Theoretical Plate Concept

In the theoretical plate model, the column is regarded as divided up into large number of theoretical plates small enough so that the concentration of sample in both mobile and stationary phases can be regarded as uniform.

Each plate consists of two volumes, ie. the volume of free gas (ΔV_G) and of liquid (ΔV_L); the sum of the volumes being the total plate volume Δx, thus

$$\Delta x = \Delta V_G + \Delta V_L \qquad (2.9)$$

The solute sample in the first theoretical plate is distributed between the stationary and mobile phases according to a partition coefficient, such that at equilibrium a fraction z of solute exists in the gas phase and a fraction y in the liquid phase.$^{(17)}$

If r volumes of carrier gas is passed through the column and we designate the number of any plate by N, the quantity of solute in the $(N + 1)^{\text{th}}$ plate can be shown to be: (APPENDIX 2)

$$Q_{N+1} = \frac{r!\ (y)^{r-N}\ (z)^{N}}{N!\ (r-N)!} \tag{2.10}$$

In order to have some measure of the rate of movement of a solute through a column, the maximum of the distribution curve is chosen as a reference point. Assuming that the $(N + 1)^{\text{th}}$ plate contains more solute than any other plate after r volumes of ΔV_G have passed, this would mean that this plate contains more solute than when (r-1) or (r+1) volumes have passed.$^{(18)}$

Thus we require

$$Q(r) > Q(r - 1) \tag{2.11}$$

and

$$Q(r) > Q(r + 1) \tag{2.12}$$

simultaneously

If $Q(r) > Q(r\text{-}1)$ then

$$\frac{r!\ y^{(r-N)}\ z^{N}}{N!\ (r-N)!} > \frac{(r-1)!\ y^{(r-N-1)} z^{N}}{N!\ (r-N-1)!} \tag{2.13}$$

ie

$$\frac{ry}{r - N} > y^{-1} \tag{2.14}$$

But

$$y = 1 - z \tag{2.15}$$

Hence (2.14) becomes

$$r\ (1 - z) > r - N \tag{2.16}$$

ie.

$$\Rightarrow \quad N > rz \tag{2.16}$$

Similarly

$$Q(r) > Q(r+1) \quad \Rightarrow \quad N < (r+1)z \tag{2.18}$$

Therefore to all intents and purposes for Q_{max}

$$N = rz \tag{2.19}$$

The fraction of solute in the gas phase in any plate is given by

$$z = \frac{C_G \Delta V_G}{C_G \Delta V_G + C_L \Delta V_L} \tag{2.20}$$

where C_G is the solute concentration in the gas and C_L is the solute concentration in the liquid. If the solute partition coefficient K_R is given by

$$K_R = \frac{C_L}{C_G} \tag{2.21}$$

$$\Rightarrow \quad z = \frac{\Delta V_G}{\Delta V_G + K_R \Delta V_L} \tag{2.22}$$

Equation 2.19 states that the maximum of an elution curve is found in the $(N+1)^{th}$

plate, where $N=rz$, hence if the $(N+1)^{th}$ plate is taken to be the detector system, N is therefore the total number of plates in the column and $r\Delta V_G$ is the peak retention volume of the solute.

$$\Rightarrow \quad V_R^/ = r\Delta V_G \qquad (2.23)$$

Hence

$$\Rightarrow \quad V_R^/ = N(\Delta V_G + K_R \Delta V_L) \qquad (2.24)$$

where $V_R^/$ is the apparent retention volume
If $N\Delta V_G = V_D^/$, the total free, or dead space in the column, and $N\Delta V_L$ the total volume of solute we get the retention volume equation

$$V_R = V_R^/ - V_D^/ \qquad (2.25)$$

where V_R is the true retention volume.

This is the basic equation of gas chromatography and is of considerable theoretical importance since it connects the thermodynamic quantity K_R with column parameters.

2.3.2. Relation of the Net Retention Volume and the Activity Coefficient to the Partition Coefficient

The distribution of a solute between stationary phase (*L*) and mobile phase, at constant temperature and pressure corresponds to equilibrium when the solute free energy is a minimum.$^{(19)}$ Its chemical potential in one phase is then equal to that in the other phase.

Thus

$$\Rightarrow \qquad \mu_L = \mu_G \qquad (2.26)$$

where

$$\mu_i = \mu_i^0 + RT \ln a_i \qquad (2.27)$$

a_i being the solute activity in the i^{th} phase and μ_i^0 is the solute chemical potential at some unit activity.

Approximating for the moment that activities can be replaced by concentration

$$\Rightarrow \qquad \mu_i^0 + RT \ln C_L = \mu_G^0 + RT \ln C_G \qquad (2.28)$$

$$\frac{C_L}{C_G} = \exp\left(\frac{\Delta \mu^0}{RT}\right) = K_R \qquad (2.29)$$

K_R being the solute partition coefficient

When the solute is dissolved in or adsorbed on the stationary phase, it is assumed to be immobile; movement occurs only when the solute vaporizes and is carried down the column by the mobile phase. (19)

The linear rate of travel is therefore equal to the average carrier velocity $\bar{u}$ multiplied by the fraction of time the solute spends in the mobile phase.

$$rate\ of\ travel = \bar{u}\left[\frac{C_G V_G}{C_G V_G + C_L V_L}\right] \qquad (2.30)$$

V_G being the mobile phase volume and V_L being the stationary phase volume.

$$rate\ of\ travel = \bar{u}\left[1 + \frac{C_L V_L}{C_G V_G}\right]^{-1} \qquad (2.31)$$

$$= \bar{u}\left[1 + K_R\frac{V_L}{V_G}\right]^{-1} \qquad (2.32)$$

since $C_L/C_G = K_R$

Alternatively

$$\text{rate of travel} = \frac{\text{column length } (L)}{\text{retention time } (t_R)} \qquad (2.33)$$

$$\Rightarrow \quad t_R = \frac{L}{\bar{u}}\left[1 + K_R\frac{V_L}{V_G}\right] \qquad (2.34)$$

The quantity $L/\bar{u}$ is just t_D, the (dead) time a nonsorbed ($K_R = 0$) solute requires to pass through the column.

$$\Rightarrow \quad t_R = t_D\left(1 + K_R\frac{V_L}{V_G}\right) \qquad (2.35)$$

To convert retention times to gas volumes the flow rate of the mobile phase generally measured at the column outlet, must be known. The measured flow rate (U_C) must therefore be corrected to the conditions prevailing in the column; that is

$$U_O = U_C \left(\frac{T}{T_{fm}}\right)\left(\frac{P_{fm} - P_w}{P_{fm}}\right) \tag{2.36}$$

where T is the column temperature, T_{fm} is the flowmeter temperature, P_{fm} is the flowmeter vapour pressure at T_{fm}, P_w is the water vapour pressure at T_{fm}. The dead (V'_D) and retention (V_R) volumes are now given by

$$V'_D = t_D U_O \tag{2.37}$$

$$V'_R = t_R U_O \tag{2.38}$$

$$\Rightarrow V'_R = V'_D \left(1 + K_R \frac{V_L}{V_G}\right) \tag{2.39}$$

by substituting eq.2.37 and 2.38 into eq.2.35

From eq.2.25

$$V_R = V'_R - V'_D = U_O(t_R - t_D) \tag{2.40}$$

In order for a mobile phase to flow through a column a pressure gradient must exist. This necessitates the introduction of a gas compression factor, as first recognized by James and Martin (14) in 1952.

Consider a carrier gas flowing through a packed column of uniform cross section A at a pressure P, and velocity u. The volume throughout must be constant within the column so that by Boyles law, (20)

$$Pu = P_o u_o = \bar{P}\,\bar{u} \tag{2.41}$$

where $\bar{P}$ is the average pressure, P_O the outlet pressure, $\bar{u}$ the average velocity and u_O the outlet velocity. The velocity at any given point is given by

$$u = \frac{P_o u_o}{P} \tag{2.42}$$

The velocity can also be related to the pressure gradient ***dp*** within a length ***dx*** along the column, the column specific permeability coefficient ***K***, porosity ***e*** and gas viscosity, through Darcy's law(20)

$$u = -\frac{K\,dP}{\eta\,dx} \tag{2.43}$$

$$\Rightarrow \quad \frac{P_o u_o}{P} = -\frac{KdP}{e\eta dx} \tag{2.44}$$

$$\Rightarrow \quad dx = [-\frac{K}{e\eta u_o P_o}]\,PdP \tag{2.45}$$

Multiplying by P

$$Pdx = [\frac{K}{e\eta u_o P_o}]\,P^2dP \tag{2.46}$$

The average value of a continuous function $\overline{F(x)}$ is

$$\overline{F}(x) = \frac{\int F(x)dx}{\int dx} \qquad (2.47)$$

$$\Rightarrow \quad \overline{P} = \frac{\int (-\frac{K}{e\eta u_o P_o})P^2 dP}{\int (-\frac{K}{e\eta u_o P_o})P dP} \qquad (2.48)$$

$\overline{P}$ being the average pressure over the column. Integrating over the column pressure gradient, which is bounded by the inlet (P_i) and outlet (P_O) pressure

$$\Rightarrow \quad \overline{P} = \frac{2}{3}\left[\frac{(P_i^3 - P_O^3)}{(P_i^2 - P_O^2)}\right] \qquad (2.49)$$

$$\frac{\overline{P}}{P_O} = \frac{2}{3}\left[\frac{(\frac{P_i}{P_O})^3 - 1}{(\frac{P_i}{P_O})^2 - 1}\right] \qquad (2.50)$$

Since $\overline{P}/P_O = \overline{V}/VO$

$$\bar{V} = \frac{3}{2} V_O \left[\frac{\left(\frac{P_i}{P_O}\right)^2 - 1}{\left(\frac{P_i}{P_O}\right)^3 - 1}\right] = JV_O \qquad (2.51)$$

$$J = \frac{3}{2} \left[\frac{\left(\frac{P_i}{P_O}\right)^2 - 1}{\left(\frac{P_i}{P_O}\right)^3 - 1}\right] \qquad (2.52)$$

Gas volumes measured at the column outlet can therefore be corrected to the average column pressure by multiplying by the fraction $\bar{V}/VO$ which is given by the symbol J. Everett $^{(1)}$ suggested that the compressibility correction can be represented as

$$J_n^m = \frac{n}{m} \left[\frac{\left(\frac{P_i}{P_O}\right)^m - 1}{\left(\frac{P_i}{P_O}\right)^n - 1}\right] \qquad (2.53)$$

The fully corrected dead volume is given by $V_D = J_3^2\, V_D^/$

Therefore from eq.2.39

$$J_3^2 V_R^/ = V_D\left(1 + K_R\frac{V_L}{V_G}\right) \qquad (2.54)$$

The term $J_3^2 V_R^/$ is given the symbol V_R^O and is referred to as the corrected retention volume(1).

Since $V_D = V_G$

$$V_R^o = V_D + K_R V_L \tag{2.55}$$

The product $K_R V_L = V_N$, the net retention volume.
Therefore

$$\begin{aligned} V_N &= J_3^2 V_R^\prime = V_R^o - V_D = K_R V_L \\ &= U_O J_3^2 (t_R - t_G) \end{aligned} \tag{2.56}$$

The solute partial pressure over its infinitely dilute solution (Henry law region) in the liquid phase is

$$P_1 = \gamma_{13}^{\infty} x_1^L P_1^* \tag{2.57}$$

where γ_{13}^{∞} is the activity coefficient at infinite dilution and $P_3^\prime$ is the saturated vapour pressure of the solute.
Recognizing that $x_1^L = n_1^L / n_3$(19)
where x_1^L is the solute mole fraction in the liquid phase, n_1^L is the solute molar amount, and n_3 is the liquid phase molar amount.

$$\Rightarrow \quad P_1 = \gamma_{13}^{\infty} P_1^* \frac{n_1^L}{n_3} \tag{2.58}$$

Dividing by V_L

$$\frac{P_1}{V_L} = \frac{\gamma^{\infty}_{13} P^*_1 \dfrac{n^L_1}{n_3}}{V_L} \qquad (2.59)$$

$$\Rightarrow \quad \frac{n^L_1}{V_L} = \frac{n_3 P_1}{\gamma^{\infty}_{13} P^*_1 V_L} \qquad (2.60)$$

where P_1 is the solute partial vapour pressure and P^*_1 is the solute saturation vapour pressure.

For ideal gases

$$\frac{n^G_1}{V_G} = \frac{P_1}{RT} \qquad (2.62)$$

and

$$K_R = \frac{(n^L_1 V_G)}{(n^G_1 V_L)} \qquad (2.62)$$

From eq.(2.60)

$$\frac{n^L_1}{V_L} = \frac{n_3 P_1}{\gamma^{\infty}_{13} P^*_1 V_L} \qquad (2.63)$$

and from eq.(2.61)

$$\frac{n_1^G}{V_G} = \frac{P_1}{RT} \qquad (2.67)$$

Substituting into eq.(2.62)

$$K_R = [\frac{n_3\ P_1}{\gamma_{13}^{\infty}\ P_1^*}\ V_G] \ / \ [\frac{P_1 V_G}{RT}\ V_L] \qquad (2.65)$$

$$K_R = \frac{n_L\ P_1\ V_G}{\gamma_{13}^{\infty}\ P_1^*} \cdot \frac{RT}{P_1\ V_G\ V_L} \qquad (2.66)$$

$$\therefore \quad K_R = \frac{RT}{\gamma_{13}^{\infty}\ P_1^*\ \overline{V_L}} \qquad since \frac{V_L}{n_3} = \overline{V_L} \qquad (2.67)$$

where $\overline{V}_L$ is the molar volume of the liquid stationary phase

$$n_3 = \frac{\text{Mass of stationary phase } (W_L)}{\text{Molar mass of stationary phase } (M_L)} \qquad \mathbf{(2.68)}$$

$$K_R = \frac{W_L\ RT}{\gamma_{13}^{\infty}\ P_1^*\ M_L\ \overline{V_L}} \qquad (2.69)$$

$$\Rightarrow \quad K_R = \frac{n_3\, RT}{V_L\, \gamma_{13}^{\infty}\, P_1^*} \tag{2.70}$$

$$K_R\, V_L = \frac{n_3\, RT}{\gamma_{13}^{\infty}\, P_1^*} \tag{2.71}$$

But

$$K_R\, V_L = V_N \tag{2.72}$$

$$\Rightarrow \quad V_N = \frac{n_3\, RT}{\gamma_{13}^{\infty}\, P_1^*} \tag{2.73}$$

2.3.3. The Pressure Dependence of the Partition Coefficient(21)

The partition coefficient at infinite dilution, K_R, in a static system can be defined as

$$K_R = \lim_{x_i \to 0} \frac{n_1^L \, V_G}{V_L \, n_1^G} \qquad (2.74)$$

where n_1^L is the number of mols of 1 in volume V_L of liquid and n_1^G is the number of mols of 1 in volume V_G of gas. But $n^G = y_1 \, n^G$ and $n_1^L = x_1 n^L$ where n^G is the total number of mols of gas (solute + carrier gas) in volume, V_G, of carrier gas, n^L is the total number of mols of liquid (solute + solvent) in V_L, y_1 is the mole fraction of 1 in the gas, and x_1 is the mole fraction of 1 in liquid.

$$\Rightarrow \quad K_R = \lim_{x \to 0} \frac{x_1 \, n^L}{V_L} \cdot \frac{V_G}{y_1 \, n^G} \qquad (2.75)$$

$$K_R = \lim_{x \to 0} \frac{x_1 \, n^L}{V_L \, y_1} \, V_G^m \qquad (2.76)$$

where V_G^m is the molar volume in the gas phase.

In the limit of infinite dilution of the solute (1) in gas phase (2)(21)

$$V_G^m = \frac{RT}{P} + B_{22} + \frac{(C_{222} - B_{22}^2)}{RT} P \qquad (2.77)$$

where $\boldsymbol{P}$ is the carrier gas pressure, $\boldsymbol{B_{22}}$ is the second virial coefficient of carrier gas and C_{222} is the third virial coefficient of the carrier gas.

$$\Rightarrow \quad K_R = \lim_{x \to 0} \frac{x_1 n_3}{V_L y_1} \frac{RT}{P} [1 + \frac{B_{22}P}{RT} + \frac{(C_{222} - B_{22}^2}{(RT)^2} P^2 + ...] \qquad (2.78)$$

where $\boldsymbol{n3} = n^L$

Now since $y_I\, P = P_1$ (partial pressure),

$$K_R = \lim_{x \to 0} \frac{x_1 n_3 RT}{V_L P_1} [1 + \frac{B_{22}P}{RT} + \frac{(C_{222} + B_{22}^2)}{(RT)^2} P^2 + ...] \qquad (2.79)$$

$$\Rightarrow \quad \lim_{x \to 0} \frac{P_1}{x_1} = \frac{n_3 RT}{V_L K_R} [1 + B_{22} \frac{P}{RT} + \frac{C_{222} - B_{22}^2}{(RT)^2} P^2 + ...] \qquad (2.81)$$

multiplying by $1/P_1^*$

$$\Rightarrow \lim_{x \to 0} \frac{P_1}{x_1 P_1^*} = \frac{n_3 RT}{V_L K_R P_L^*} [1 + \frac{B_{22}P}{RT} + \frac{(C_{222} - B_{22}^2)}{(RT)^2} P^2 + ...] \quad (2.82)$$

But

$$\gamma_{13}^{\infty}(T,P) = \lim_{x_1 \to 0} \frac{P_1}{P_1^* x_1} \quad (2.83)$$

$$\therefore \quad \gamma_{13}^{\infty}(T,P) = \frac{n_3 RT}{V_L K_R P_1^*} [1 + \frac{B_{22}P}{RT}] + \frac{(C_{222} - B_{22}^2)}{(RT)^2} P^2 + ...] \quad (2.84)$$

It can be shown that γ_{13}^{∞} (T,P) is related to the activity coefficient at zero pressure and infinite dilution γ_{13}^{∞} $(T,0)$ by

$$\ln\gamma_{13}^{\infty}(T,0) = \ln\gamma_{13}^{\infty}(T,P) - \frac{B_{11} - V_1^{\infty}}{RT} P + [\frac{2C_{222} - 3B_{11}^2}{2RT}] P_1^{*2} + \frac{2B_{12} - B_{22} - V_1^*}{RT} P + \frac{(2C_{222} - 3C_{122} - 3B_{22}^2 + 4B_{12}B_{22})}{2(RT)} P^2 \quad (2.85)$$

Substituting into the equation for γ_{13}^{∞} (T,P)

$$\ln\gamma_{13}^{\infty}(T,0) = \ln \frac{n_3 RT}{V_L K_R P_1^*} - \frac{(2B_{12} - V_1^o)}{RT} P_1^* + \frac{(2B_{12} - V_1^{\infty})}{RT} + (3C_{122} - 4B_{12}B_{22}) \frac{P^2}{2RT} \quad (2.86)$$

where

$$\ln\left[1 + \frac{B_{22}P}{RT} + \frac{B_{22}^2P^2}{(RT)^2} + \frac{C_{222}P^2}{(RT)^2} + ...\right]$$

has been approximated by

$$\left[\frac{B_{22}P}{RT} - \frac{3}{2}\frac{B_{22}^2P^2}{(RT)^2} + \frac{C_{222}P^2}{(RT)^2} + ...\right]$$

Solving for K_R in eq. 2.86

$$\ln K_R = \ln \frac{n_3RT}{P_1^*V_L\gamma_{13}^{\infty}(T,0)} - \frac{(B_{11} - V_1^*)}{RT}P_1^* + \frac{(2B_{12} - V_1^{\infty})}{RT}P$$
$$+(3C_{122} - 4B_{12}B_{22})\frac{P^2}{2RT} \tag{2.87}$$

$$\Rightarrow \quad \ln K_R = \ln K_R(0) + \beta P + \zeta P^2 \tag{2.88}$$

where

$$\ln K_R(0) = \ln\left[\frac{n_3RT}{\gamma_{13}^{\infty}(T,0)\ P_1^*\ V_L}\right] - \left[\frac{B_{11} - V_1^*}{RT}\right] P_1^* \tag{2.89}$$

$$\beta = \frac{(2B_{12} - V_1^{\infty})}{RT} \qquad (2.90)$$

$$\zeta = \frac{(3C_{122} - 4B_{12}B_{22})}{2(RT)^2} \qquad (2.91)$$

The term P^2 is negligible at pressures below 15 atms. From equation 2.87

$$\ln[K_R(0)V_L] = \ln\left[\frac{n_3RT}{\gamma_{13}^{\infty}(T,0)P_1^*}\right] - \left[\frac{B_{11} - V_1^*}{RT}\right]P_1^* \qquad (2.92)$$

From eq.2.72

$$K_RV_L = V_N \quad \Rightarrow \quad K_R(0)V_L = V_N^o \qquad (2.93)$$

where V_N^o is the retention volume at zero mean column pressure

$$\Rightarrow \quad \ln V_N^o = \ln\left[\frac{n_3RT}{\gamma_{13}^{\infty}(T,0)P_1^*}\right] - \left[\frac{B_{11} - V_1^*}{RT}\right] P_1^* \qquad (2.94)$$

Equation 2.92 expresses the pressure dependence of the partition coefficient K_R.

2.3.4. The Elution Process

When the distribution coefficient is defined as(22)

$$K_R = \lim_{x \to 0} \frac{n_1^L V_G}{V_L n_1^G} \qquad (2.95)$$

the peak velocity *W* is given by

$$W = \frac{\bar{u} V_G}{V_G + K_R V_L} \qquad (2.96)$$

equation 2.96 can be written as

$$\frac{l}{W} = \frac{V_G + K_R V_L}{\bar{u} V_G} \qquad (2.97)$$

where ***l*** is the distance from the column inlet.

Also

$$\frac{l}{w} = \frac{dt}{dl} = \frac{V_G + K_R V_L}{\bar{u} V_G} \qquad (2.98)$$

where ***t*** is the retention time ie. the time taken for the peak to travel a distance ***l***. Now $\bar{u}$ is the volumetric flow rate of the carrier gas therefore $\bar{u} V_G$ can be replaced by ***U***

$$U dt = (K_R V_L + V_G) dl \qquad (2.99)$$

Since U varies along the column in proportion to the carrier gas molar flow, it is convenient to express this variation in terms of local pressure, using the approximate equation of state.

$$PV_2 = RT + B_{22}P \tag{2.100}$$

$$\Rightarrow \quad U = \frac{P_o(1 + bP)}{P(1 + bP_o)} U_o \tag{2.101}$$

where $b = B_{22}/RT$

U_O is the carrier gas flowrate at the column outlet and P_O is the pressure at the column outlet.

Equation 2.101 is derived as follows

$$\frac{PV_2}{RT} = 1 + \frac{B_{22}P}{RT} \tag{2.102}$$

Dividing eq. 2.100 by RT

since $b = B_{22}/RT$

$$V_2 = \frac{1 + \frac{B_{22}}{RT}P}{\frac{P}{RT}} \tag{2.103}$$

At the outlet of the column

$$\Rightarrow \quad V_2 = \frac{1 + bP}{\frac{P}{RT}} \qquad (2.104)$$

$$V_2^o = \frac{1 + bP_o}{\frac{P_o}{RT}} \qquad (2.105)$$

$$\Rightarrow \quad \frac{V_2}{V_2^o} = \frac{[\frac{1 + bP}{P}]\ RT}{[\frac{1 + bP_o}{P_o}]\ RT} \qquad (2.106)$$

$$\Rightarrow \quad \frac{V_2}{V_2^o} = \frac{P_o(1 + bP)}{P(1 + bP_O)} \qquad (2.107)$$

but V_2/V_2^O = ratio of molar volumes = U/U_O = ratio of volumetric flow rates

$$\Rightarrow \quad U = \frac{P_o(1 + bP)}{P(1 + bP_o)} U_o \qquad (2.108)$$

substituting for U in eq.2.97

$U_O\ dt$ is the volume of gas leaving the column outlet as the elution peak advances a

$$U_o dt = \frac{(K_R V_L + V_G)(1 + bP_o)}{P_o(1 + bP)} Pdl \qquad (2.109)$$

distance ***dl***. Because of the difficulty of defining V_G accurately it is more convenient to consider instead $U_o dt$, the volume of carrier gas measured at the column outlet which passes the elution peak during its progress from l to $l + dl$.

This is obtained by allowing $V_L = 0$ (value corresponding to no liquid phase). This is simply

$$dV_R = K_R V_L \frac{1 + bP_o}{P_o} \frac{P}{1 + bP} dl \qquad (2.110)$$

The retention volume V_R is the same given in equation 2.25 ie. the observed (apparent) retention volume minus the gas holdup at the column outlet. Since K_R is a function of pressure, the most direct way to integrate the equation is to change the variable from l to P by means of Darcy's law.

$$\frac{dP}{dl} = \frac{-ue\eta}{K} \qquad (2.111)$$

$$dl = dx \quad \Rightarrow \quad \frac{dP}{dx} = -\frac{u}{A} \qquad (2.112)$$

where A takes into account the column packing permeability. If the pressure < 50 atms the Chapman-Enskog(23) relation in approximation form can be used ie.

where

$$a = 0.175 \frac{B_{22}}{RT} \qquad (2.113)$$

Combining with Darcy's law

$$dl = -\frac{a}{u_o(1 + aP0)\eta} dP \qquad (2.114)$$

But carrier gas pressure varies according to

$$U = \frac{P_o(1 + bP)}{P(1 + P_o b)} U_o \qquad (2.115)$$

$$\Rightarrow \quad U_o = \frac{UP(1 + bP_o)}{P_o(1 + bP)} \qquad (2.116)$$

but

$$U_o = \frac{dP}{dl} \frac{A}{\eta} \qquad (2.117)$$

also

$$\eta = \eta_o(1 + aP) \qquad (2.118)$$

substituting eqs. 2.115 and 1.118 into eq. 2.117

$$\frac{UP(1 + bP_O)}{P_O(1 + bP)} = \frac{dP}{dL}\frac{A}{\eta_o(1 + aP)} \tag{2.119}$$

$$\Rightarrow \quad dl = \frac{AP(1 + bP_O)dP}{P_O(1 + bP)U\eta_o(1 + aP)} \tag{2.120}$$

Integrating

$$L = \frac{A(1 + bP)}{U(\eta_o)P}\int_{P_O}^{P_i}\frac{P}{(1 + bP_o)(1 + aP)}\,dP \tag{2.121}$$

Dividing eq. 2.120 by 2.121

$$\frac{dl}{L} = \frac{\dfrac{AP(1+bP_O)dP}{P_O(1+bP)\ U\eta_o(1+aP_O)}}{\dfrac{A(1+bP)}{U(\eta_o)P}\displaystyle\int_{P_O}^{P_i}\frac{P}{(1+bP_O)(1+aP_O dP)}} \tag{2.122}$$

$$dl = \frac{\dfrac{LPdP}{(1 + aP)(1 + bP)}}{\displaystyle\int_{P_o}^{P_i}\frac{PdP}{(1 + aP)(1 + bP)}} \tag{2.123}$$

$$\ln K_R = \ln K_R(0) + \beta P + \zeta P^2 \tag{2.124}$$

$$\Rightarrow \quad K_R = K_R(0) + e^{\beta P} + e^{\zeta P^2} \qquad (2.125)$$

eq.(2.110) states that

$$dV_R = K_R V_L \frac{1 + bP_O}{P_O} \frac{P}{1 + bP} dl$$

Substituting eqs.2.123 and 2.125 into eq.2.110

$$dV_R = \frac{K_R + e^{\beta P} + e^{\zeta P^2} . V_L(1 + bP_O)}{P_O} . \frac{P}{(1 + bP)} . \frac{\frac{LPdP}{(1+aP)(1+bP)}}{\int_{P_o}^{P_i} \frac{PdP}{(1+aP)(1+bP)}} \qquad (2.126)$$

Also by substituting eqs.2.125 and 2.120 into eq.2.110

$$\Rightarrow dV_R = [K_R(0) + e^{\beta P} + e^{\zeta P^2}][V_L \frac{1 + bP_O}{P_O} . \frac{P}{1 + bP}][\frac{AP(1 + bP_O)bP}{P_O(1 + bP)U\eta_O(1 + aP)}] \qquad (2.127)$$

By integration

$$V_R = K_R(0)V_L \, [\frac{1 + bP_O}{P_O}] \frac{\int_{P_o}^{P_i} \frac{P^2 e^{\beta P} e^{\zeta P^2}}{(1 + aP)(1 + bP)^2} dP}{\int_{P_o}^{P_i} \frac{P}{(1 + aP)(1 + bP)} dP} \qquad (2.128)$$

The above equation gives the required relationship between the retention volume V_R and the partition coefficient.

2.3.5. The Net Retention Volume of an Ideal Carrier Gas

In the case of an ideal carrier gas ***a*** and ***b*** in equation 2.128 and B_{22} (second viral coefficient of the carrier gas) are all zero.

$$\Rightarrow \quad V_R = \frac{K_R(0) V_L \int_{P_o}^{P_i} P^2\, e^{\beta P}\, e^{\zeta P^2}\, dP}{P_o \int_{P_o}^{P_i} P\, dP} \qquad (2.129)$$

By integration

$$\ln\left(\frac{V_R}{J_3^2}\right) = \ln V_N = \ln V_N(0) + \beta P_o J_3^4 + \zeta (P_o J_3^4)^2 \qquad (2.130)$$

where

$$V_N(0) = K_R(0)\ V_L \qquad (2.131)$$

since $(P_o J_3^4)^2$ is negligible at pressures below 15 atms eq.2.130 approximates to

$$\ln V_N = \ln V_N(0) + \beta P_o J_3^4 \qquad (2.132)$$

But

$$\ln V_N(0) = \ln\left[\frac{n_3 RT}{\gamma_{13}^{\infty}(T,0) P_1^*}\right] - \left[\frac{B_{11} - V_1^*}{RT}\right] P_1^* \qquad (2.133)$$

Therefore substituting for $\ln V_N(T,0)$ and β

$$\ln V_N = \ln[\frac{n_3RT}{\gamma_{13}^{\infty}(T,0)P_1^*}] - [\frac{B_{11} - V_1^*}{RT}]P_1^* + [\frac{2B_{12} - V_1^{\infty}}{RT}]P_O J_3^4 \quad (2.134)$$

This is identical to eq.(1.1) for pressures P_0 and P_i less than 1 atm since under these conditions $J_3^4 \approx J_3^2$ and $\gamma_{13(T,0)}^{\infty} = \gamma_{13}^{\infty}$

The above equation was developed by Everett^(1)^ and Cruickshank^(2)^ for the determination of activity coefficients at infinite dilution.

2.3.6. Treatment of a Volatile Solvent

The usual method for determining activity coefficients at infinite dilution developed by Everett(1) and Cruickshank(2) is restricted to volatile solutes (eg. n-pentane, n-hexane and n-heptane) and involatile solvents (eg. dotricontane,squalane, and dinonylpthlate).

2.3.6.1. Review of Work using Volatile Stationary Phases

Previously evaporation off the column by the stationary phase was avoided by pre-saturating the carrier gas with vapour of the volatile phase before it enters the column. The presaturator involved bubbling the carrier gas through the liquid or passing the carrier gas through a short precolumn which, like the main column, contained a stationary phase coated on a solid support. This technique was introduced by Kwantes and Rijnders.(23) However, even though the carrier gas was saturated with vapour it still removed stationary phase as it expanded along the column. Since a smaller pressure drop led to less evaporation of the stationary phase, a coarse packing was used which reduced the pressure drop considerably. While the use of a precolumn and coarse packing kept the bleed rate very low, the loss cannot be eliminated completely.

Kurkchi and Ioganssen(24) proposed weighing the column before and after use, assuming that the solvent loss was constant with time. Langer et al(25) monitored the loss of solvent by measuring the retention time of a solute at intervals, taking the first reading as soon as the column reached its operating temperature. A graph of retention time against elapsed time of operation was plotted. The graph was then extrapolated to zero time and the correct retention time obtained. Letcher(26) successfully used this method for the determination of the activity of various hydrocarbons with decahydronapthalene as the volatile stationary phase.

In the present work Everett's and Cruickshank's method has been extended to accommodate a solvent of low volatility. During its passage through the column the carrier gas becomes charged with solvent vapour. The total amount of solvent lost from the column, n_3^l, may be expressed in terms of the total volume of gas which has passed through the column, the partial pressure, P_3^l, of the solvent in the gas at the column outlet and the time t elapsed from the start of the carrier gas passing through the column. We assume that the observed retention times are negligible compared with the total flow time through the column. The gas flow rate, U_O, measured at the outlet is maintained constant during the whole experiment. The expression for n_3^l is given by

$$n_3^l = \frac{U_O t P_3^l}{RT} \qquad (2.135)$$

In this work we found the partial pressure of the solvent in the carrier gas to be very much less than 1 per cent of the total. It is probably further reduced in the flowmeter.

Therefore no correction was applied to the flowrate for the presence of the solvent. Equation (2.134) becomes

$$\ln V_N = \ln\left[\frac{n_3RT - P_3^{l}U_o t}{\gamma_{13}^{\infty}P_1^{*}}\right] + C \qquad (2.136)$$

where

$$C = -\left[\frac{B_{11} - V_1^{*}}{RT}\right]P_1^{*} + \left[\frac{2B_{12} - V_1^{\infty}}{RT}\right]P_o J_2^3 \qquad (2.137)$$

Hence

$$\frac{V_N}{e^{C}n_3} = \frac{RT}{\gamma_{13}^{\infty}P_1^{*}} + \left[\frac{U_o t}{n_3}\right]\frac{P_3^{l}}{\gamma_{13}^{\infty}P_1^{*}} = a + b\left[\frac{U_o t}{n_3}\right] \qquad (2.138)$$

By plotting V_N/n_3e^C against U_ot/n_3 a straight line is obtained, giving an intercept of $RT/\gamma_{13}^{\infty}P_1^{*}$ (*a*) and a slope of P_3^{l}/RT (*b*)

The values of γ_{13}^{∞} and P_3^{l} are obtained graphically from this linear relationship.

3. APPARATUS AND EXPERIMENTAL PROCEDURE

The gas-liquid chromatograph used for the determination of the activity coefficients at infinite dilutions was similar to that used by Cruickshank(2) and also by Letcher and Marsicano(27).

3.1 The Design of the Gas-Liquid Chromatograph

The basic plan of the gas chromatograph is shown in figure 3.1. This type of chromatograph is suitable for physico-chemical measurements. The scheme is similar to that of a commercial analytical chromatograph except for the addition of a manometer to register the column inlet pressure and an accurate flowmeter to measure the flowrate (0.01 s) and accurate temperature control of the column (± 0.01 K). Two thermal conductivity detector chromatographs were used differing only in the make and design of the detector. The advantage of using a thermal conductivity detector (T.C.D.) or a katharometer is that the flow-meter can be placed downstream of the column exit. The flow and pressure control unit was constructed mainly of 6.35 mm o.d. (1/4 inch) copper tubing and Swagelock couplings. The flow-meter and manometer were constructed of thick-walled glass tubing.

3.1.1. Flow Control

Good flow control was achieved by using a two-stage pressure regulator, attached to the cylinder head, in conjunction with a Negretti and Zambra precision pressure regulating valve which controlled the pressure to better than 0.1 torr.§ The column outlet in the experiment was open to the atmosphere. It was necessary to monitor the outlet pressure since variations in atmospheric pressure would have negligible effects on the flow-rate only if the column impedance was unusually high.(28) A buffer vessel was placed at the column outlet to minimise the effect of pressure changes due to slight disturbances in the laboratory atmosphere.

§ 1 torr = 1 mm Hg

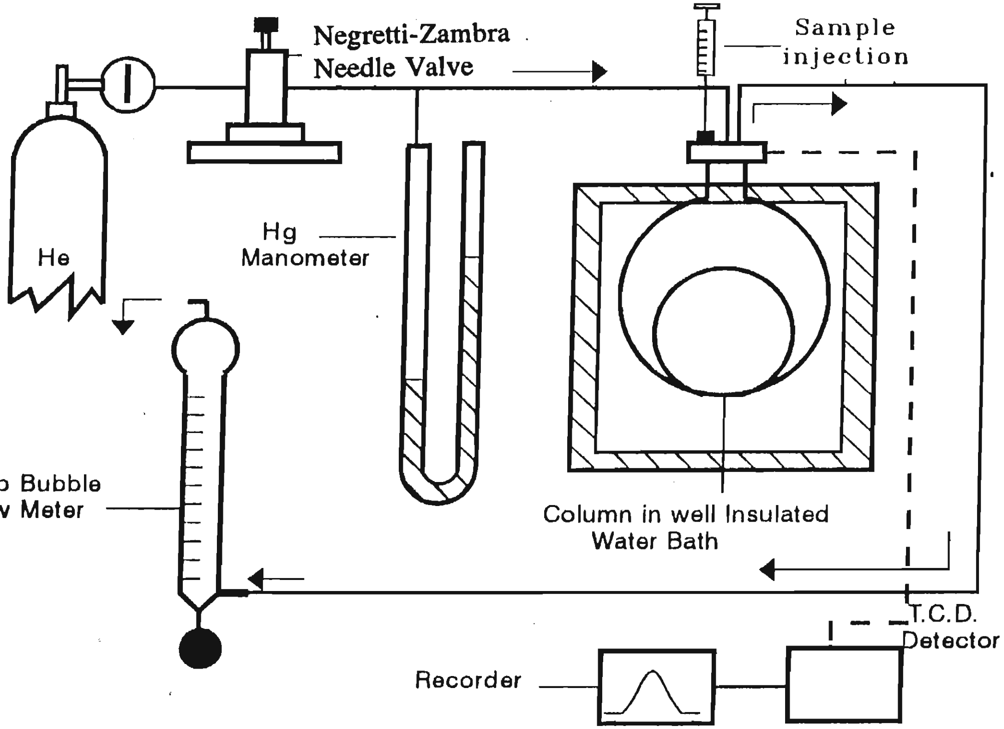


FIGURE 3.1. FLOW DIAGRAM OF G.L.C.

3.1.2. Pressure Measurement

The outlet pressure was considered to be atmospheric and was measured on a normal Fortin barometer. The column inlet pressure was measured by a mercury manometer using a kathetometer (± 0.01 mm Hg). A trap was attached to one end of the manometer to retain mercury in case of an accidental pressure surge.

3.1.3. Flow Rate Measurements

The measurement of the gas flow-rate is carried out with a soap bubble meter (figure 3.2), constructed from a graduated 100 ml burette, which was situated downstream of the column. Since helium was used as the carrier gas, it was necessary to ensure that air did not enter the burette during flow measurements since light gases, such as helium, diffuse more rapidly through soap films than air and this would cause the actual flow-rate to be different from the rate of film movement. To prevent back diffusion of air a rubber bung with a tiny hole was placed at the flowmeter outlet. The hole was not narrow enough to cause a significant pressure rise in the flow tubes.

3.1.4. Column Temperature Control

Good temperature control was essential since the vapour pressure (of the solute and the solvent) is temperature dependent. This was achieved by immersing the column in a well-stirred waterbath. The temperature at 298.15 K (using a single waterbath) was controlled by a Tronac temperature controller in conjunction with a simple on-off relay using a light bulb as a low thermal capacity heater (figure 3.3).

The temperature was measured using an accurate quartz thermometer. The bath temperature was always known to an accuracy of better than 0.01 K. For the control of the temperature at 283.15 K two water baths were used (figure 3.4). The temperature of the first bath was kept at approximately 280.15 K using a large cooling unit and an immersion heater. The bath was kept well stirred using two high speed mechanical stirrers. The temperature in the second bath (containing the column) was

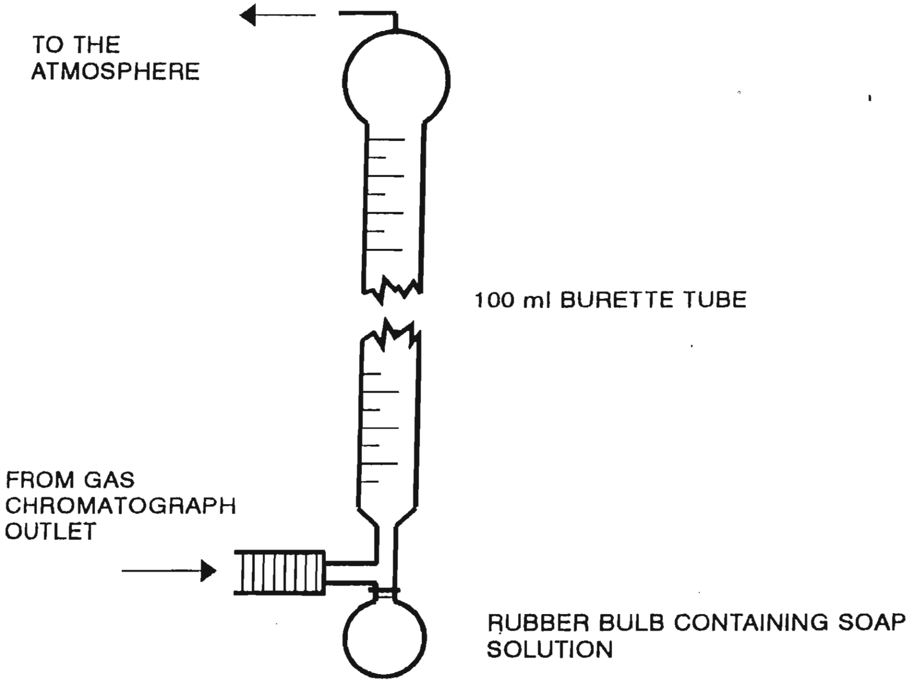


FIGURE 3.2. THE SOAP BUBBLE FLOW METER

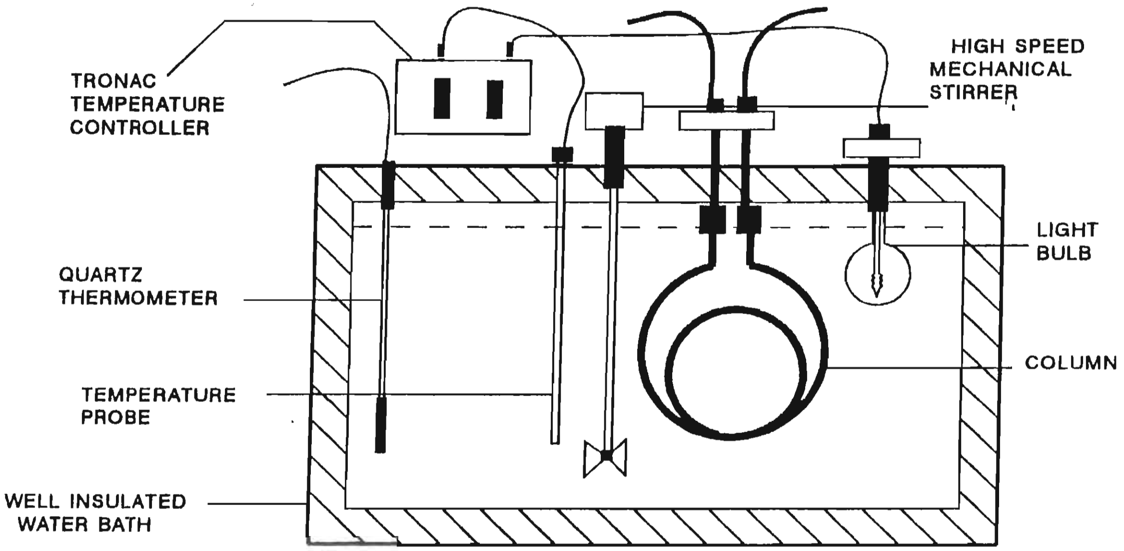


FIGURE 3.3. WATER BATH FOR TEMPERATURE CONTROL AT 298.15 K

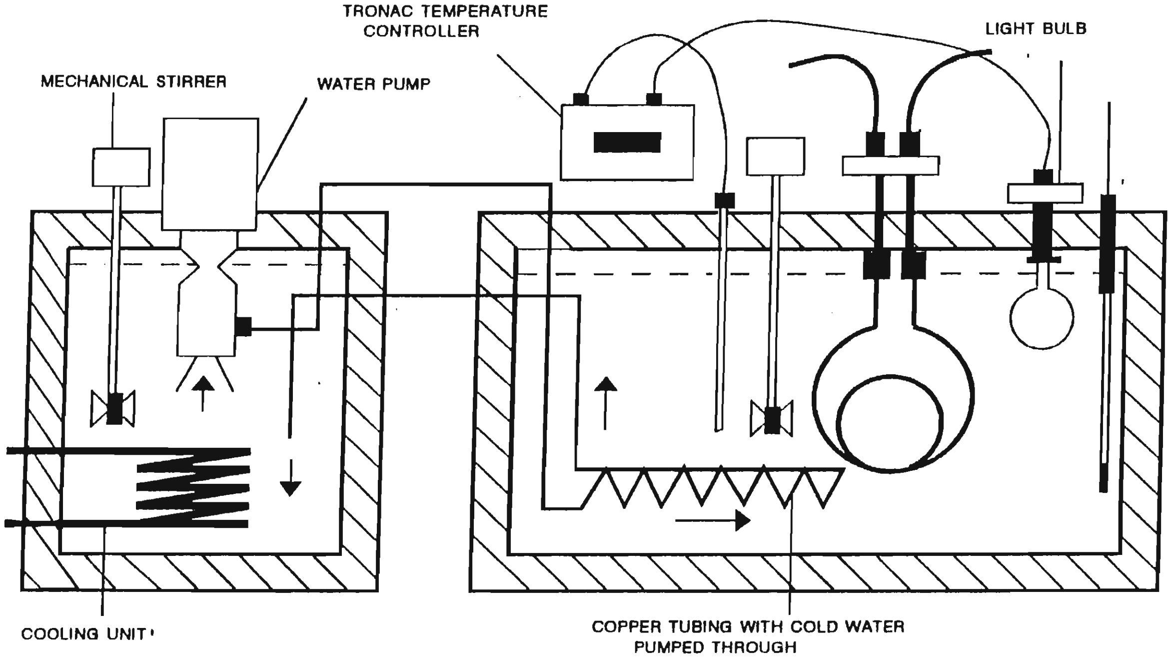


FIGURE 3.4. TWO WATER BATH SYSTEM FOR TEMPERATURE CONTOL AT 283.15 K

lowered to 283.15 K by pumping water from the first bath through a 6 m coil of copper tubing placed on the floor of the second bath. As with temperature control at 298.15 K the temperature in the second bath was controlled by a Tronac temperature controller and a light bulb and the temperature was monitored using a quartz thermometer.

3.1.5 Sample Injection and the Injection System

The solutes used were usually of the purest grade available although this was not necessary. Samples were injected using a microsyringe and sample sizes varied from 0.1 μl to 1.0 μl. It is shown later that this yields infinite dilute conditions in the column. The injection system for both the Gow-Mac and Shandon detectors was the same and was specially designed to minimise back diffusion, dead volume, multiple septum perforation and damage to the syringe. It consisted of an inner tube located concentrically inside an outer tube (figure 3.5). Carrier gas entering at the one end of the annulus between the tubes is deflected into the inner tube by the septum at the other end. The entry of the gas at the one end of the narrow annulus in conjunction with the high velocity purge of the gas through it, ensured that there was no upswept dead volume, back diffusion of the sample, or its retention on the underside of the septum. The diaphragm injection system was mounted in a tapered bore. It was retained under compression by a funnel shaped needle guide, which was screwed down on its upper surface. This needle guide ensures that the needle penetration was always at the same spot in the septum.

3.1.6. G.L.C. Columns

The packed columns used were all stainless steel which are inert to the solutes and does not cause adsorption or react with the solutes in any way.The columns were all 6.35 mm o.d. (1/4 inch) and 1 to 1.5m in length.

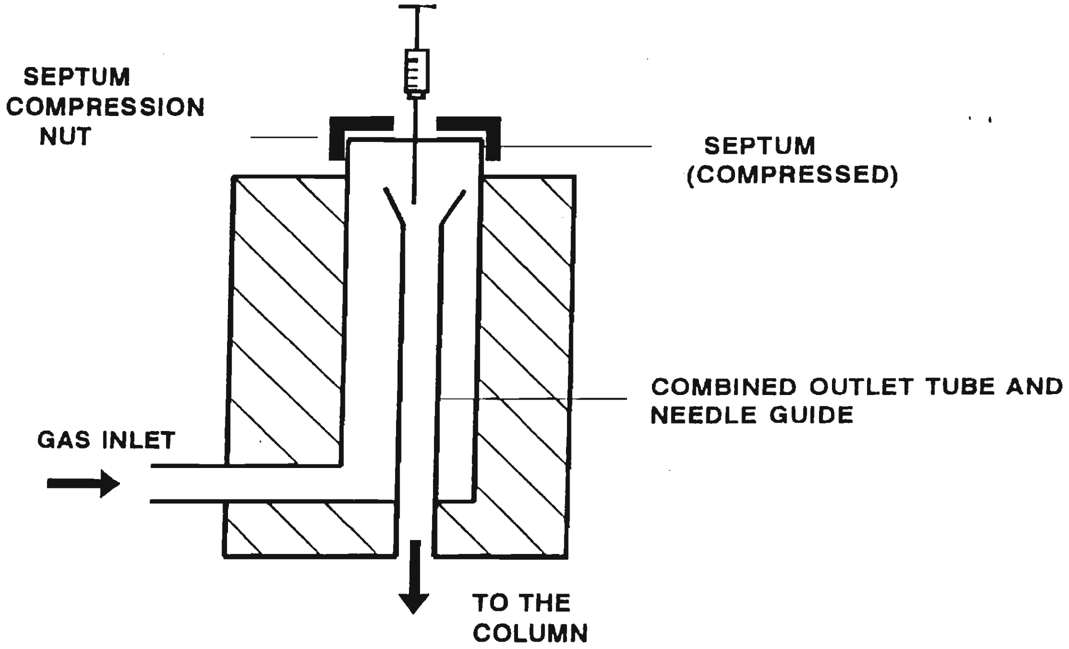


FIGURE 3.5. THE INJECTION SYSTEM

3.1.7. Detectors

Two types of thermal conductivity detectors were used, a Shandon U.K.3 gas chromatograph and a Gow-Mac gas chromatograph.

The Shandon U.K.3 Detector.- A circuit diagram of the detector system is shown in figure 3.6. The detector consists of two matched, electrically heated, helically coiled, tungsten filaments. These are mounted in the brass detector body by means of mechanical seal tube-nuts. In this way the two filaments are inserted directly into the gas stream, one (reference) in the pure carrier gas before it enters the column, and the other (measuring) in the column effluent. The geometrical configuration of each filament was identical. The filament forms two arms of an electrical Wheatstone bridge circuit. This bridge is unbalanced by a change in the temperature (and hence the resistance) of the filament in the effluent, which is caused by a change in the composition of the gas stream as a component is eluted. The signals are recorded on a Phillips recorder.

The Gow-Mac Detector.- A circuit diagram of the four filament Gow-Mac detector cell is shown in figure 3.7. In this detector four tungsten filaments lie in the gas path. It is a semi-diffusion cell of a flow-through design with a response time less than 1.0 seconds. The stream of pure gas is split so that half of the pure gas enters the reference chamber and passes over the two reference filaments and the other half of the gas enters the column. The gas emerging from the column flows over the measuring filaments. The filaments used are of the same design as those used in the Shandon detector.

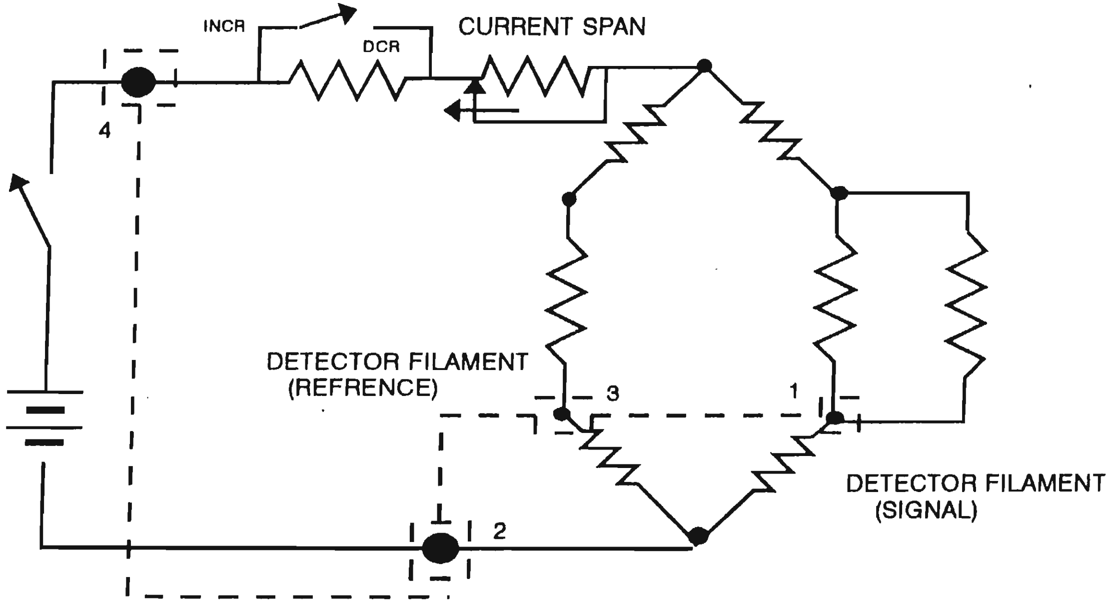


FIGURE 3.6. CIRCUIT DIAGRAM OF
SHANNDON UK3 T.C.D. DETECTOR

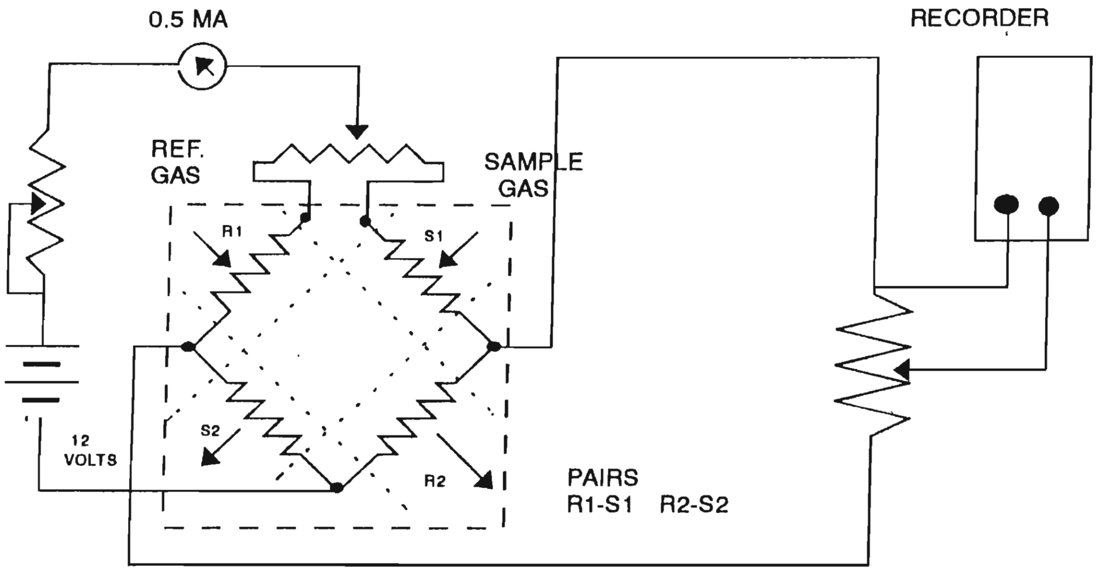


FIGURE 3.7. CIRCUIT DIAGRAM OF GOW-MAC T.C.D. DETECTOR

3.2. Experimental Procedure

3.2.1. Preparation of the Stationary Phase

The stationary phase was prepared following the procedure used by Marsicano.(27) The columns were cleaned with hot soap solution, rinsed with distilled water, and dried with nitrogen. Celite was used as the solid support for the stationary phase. The column loading (mass solute/total mass coated solid support) ranged between 3 to 15 mass per cent. The packing was prepared by adding a known mass of solvent to a known mass of celite. The combined mass was noted. A solvent in which the stationary phase is soluble (diethyl ether) was added (approx. 50 ml) and the contents were swirled gently in order to dissolve the stationary phase and distribute it throughout the celite. The ether was slowly removed by the application of a vacuum using a Buchi rotary evaporator without heating. The flask was rotated slowly to minimise disintegration of the fragile celite. The last trace of ether was removed by allowing the flask to stand in a fume hood. The coated celite was weighed and reweighed on completion to check that all the ether had been removed and that no stationary phase had been lost. The column was then straightened. It was packed using a plastic funnel and rubber tubing of known mass. The funnel was attached to the column by the tubing and the coated celite was poured into the funnel. The other end of the column was plugged with glass wool. A rubber stopper was attached to this end which was lightly tapped on the floor during packing. The column was also lightly tapped with a rubber-covered metal rod. On completion the funnel and tubing were weighed and the amount of stationary phase added was determined by difference. The column was plugged with glass wool at the open end and coiled. The small amount of compression produced on coiling does not significantly change the properties of the packing, nor its adsorptive properties.

3.2.2. Measurement Procedure

Measurements of flow-rate (which was kept constant), retention times of solute and unretained gas (nitrogen), and temperature were made for each column. The flowrate was set, depending on the length of the column and the amount of solvent on the column, so that the column would have a life of about 3-4 hours. The system was allowed to equilibrate for about 10-15 min before the first injection was made. When several solutes are studied on a single column, the solutes are injected simultaneously as a mixture. Solutes chosen for such measurements must have significantly different retention times to allow each component to be fully resolved at the detector. Incorporation of air to determine the gas holdup was accomplished by first taking up the desired volume of solute into the syringe and withdrawing the plunger further to admit a suitable volume of air before making an injection.

Retention times were calculated from distance measurements on the chart from the point of injection to the point at which the tangents to the peak intersect (figure 3.8). These are then converted to retention times using the chart speed which was accurately measured using a stopwatch.

The carrier gas flow-rate was measured regularly throughout each run using an accurate stopwatch. Prior to measuring the flow-rate a stream of bubbles were sent through the flowmeter to allow the interior walls of the burette to be thoroughly wetted by the soap solution to avoid errors arising from uneven movement of the bubble film due to surface tension effects and the possibility that the burette was not fully saturated with water vapour.

3.3. Calculation of Results

From the experimental readings, values of V_N were calculated using the programme GAMMA (see Appendix 1) which uses the following equation.

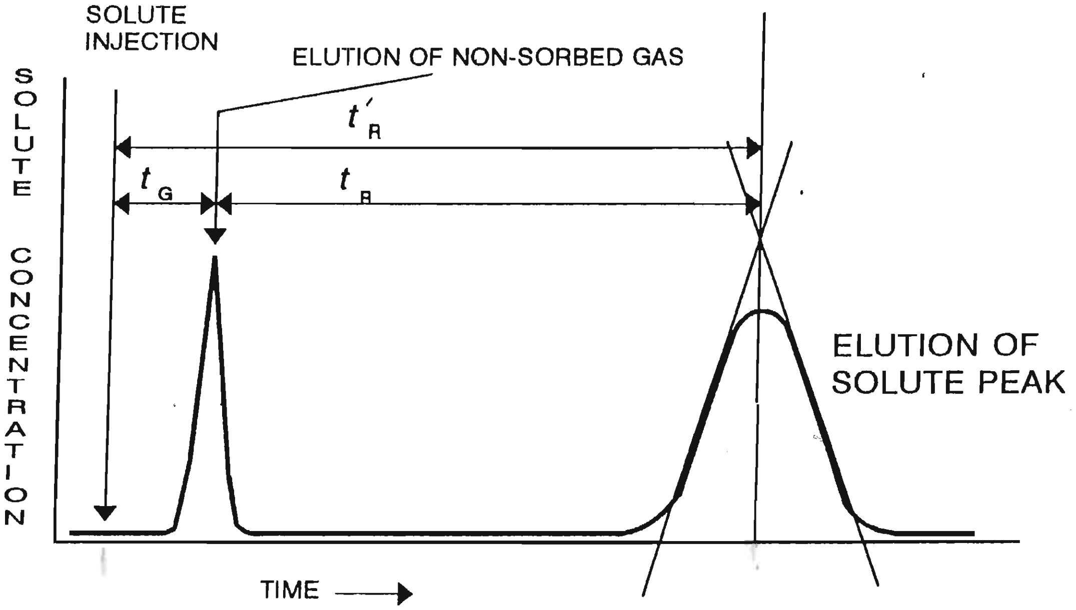


FIGURE 3.8. A Typical Chromatogram Showing the Determination of the Retention Time of a Solute Using the Tangents to The Peak Method

$$\ln\gamma_{13}^{\infty} = \ln\frac{n_3RT}{V_NP_1^*} - [\frac{(B_{11} - V_1^*)}{RT}]P_1^* + [\frac{(2B_{12} - V_1^{\infty})}{RT}]J_2^3P_O \qquad (3.1)$$

The values of V_N/n_3e^C and U_ot/n_3 are fitted to the best straight line (eq.3.2) using a regression analysis.

$$\frac{V_N}{n_3e^C} = \frac{RT}{\gamma_{13}^{\infty}P_1^*} - \frac{U_ot}{n_3}[\frac{P_3^l}{\gamma_{13}^{\infty}P_1^*}] \qquad (3.2)$$

From the intercept of that line the value of the quantity $(RT/\gamma_{13}^{\infty}P_1^*)$ was obtained and the activity coefficient at infinite dilution (γ_{13}^{∞}) was calculated. From the ratio of the slope to the intercept the quantity (RT/P_3^l) was obtained and consequently, P_3^l, the partial pressure of the solvent at the temperature of the experiment was calculated.

3.4. Disadvantages of Conventional methods of Determining γ_{13}^{∞}

Conventional methods of studying solution phenomena, which depend on the measurement of vapour pressure, suffer from the disadvantage that the percentage experimental error of measurement at low concentration is usually much greater than at higher concentration.(29) Great errors are incurred if properties at infinite dilution are calculated from finite concentration data.(30) Another disadvantage of conventional vapour pressure measurements on systems of the type volatile solute + involatile solvent is that the measurements are usually very time consuming and require both solvent and solute in a state of high purity.

3.5. Advantages and Disadvantages of Physico-chemical Methods by G.L.C.

3.5.1 Advantages

Speed.- A gas chromatographic experiment is relatively rapid taking no more than a few minutes. Such speed is possible since the stationary phase is highly dispersive and has a large area of interface with the gas. Path lengths for mass transport are small and so phase equilibrium is rapidly attained. Another time saving feature is that several solutes can often be studied in one run. The components can be injected as a mixture provided that their retention times differ.(31)

Quantity of material.- In the normal elution mode the amount of solute injected onto the column is such a small quantity that they are effectively at infinite dilution in the solvent.(31) In addition the amount of stationary phase required is usually small.(31)

Purity of Material.- A chromatographic column can separate and purify the components of a mixed sample at the same time as it measures their properties. Hence small quantities of moderately pure material can be used without preliminary purification.(32)

Temperature Variation.- Since a chromatographic column is normally made into a compact shape, such as a coil, and housed in a small thermostated enclosure, it is a simple matter to operate it at any temperature within the capacity of the equipment. Thus a wide temperature range is available.

Solubility of Solutes.- Non-chromatographic methods are often unsuitable for highly unstable solutes. Reaction of the solute with the reaction vessel or trace impurities can lead to pressure changes and false experimental values. Chromatographic methods of measurement are often preferred for reactive solutes since quantities are small and the contact time is short.

3.5.2. Disadvantages

Gas chromatography, although well established as a means of studying interactions in solutions however has certain limitations that may necessitate the choice of another technique. The technique is simplest to operate if the solute is at infinite dilution, the solvent is involatile, and the solute does not show a Gibbs adsorption effect at the liquid surface.(33)

Interferences.-It is characteristic of chromatography that the column may contain more components or phases than those being studied. For example the gas liquid chromatographic system contains a total of five or more phases: three bulk phases and two interfacial phases. The measurements may reflect equilibrium interactions in more than one phase. A study of one interaction may be subject to interferences from other interactions present in the system. An example being the adsorption on the solid support particularly prevalent with polar solutes. Such adsorption, if not the subject of study, interferes with measurements concerning the stationary phase held on the support.(34)

Solvent Volatility.- Another problem, associated with solute volatility, is the temperature limit of the stationary phase. Liquid phases are limited normally to operation at temperatures at which their vapour pressure is less than about 0.01 torr, ie 1.2 Pa,(33) if one is to ensure that the amount of stationary phase in the column remains virtually constant over a reasonable period.

If there exists a finite pressure drop across the column, a volatile or moderately volatile solvent will be gradually stripped off. This is partially offset by employing coarse packing, internal standards, saturators and/or precolumns .(34) The main objective of this work was to overcome the problem associated with the loss of solvent from the column without employing the use of saturators, precolumns or an internal standard. In this work a theory has been developed (chapter 2) that not only enables the determination of activity coefficients using a moderately volatile solvent, but also relates the amount of solvent lost to its vapour pressure.

4.Results

Data was collected for 19 columns (12 trans-decalin and 7 cis-decalin columns) at two different temperatures, 298.15 K and 283.15 K. The solutes used were n-pentane, cyclopentane, n-hexane, cyclohexane, benzene and n-heptane and solvents cis- and trans-decalin. Helium was used as the carrier gas and the retention time t_G was determined using nitrogen. Two thermal conductivity detectors were used (a Gow-Mac T.C.D. and a Shandon U.K.3 T.C.D.). For each experiment the retention time was kept constant.

The effect of the type of packing used (silanized or unsilanized) is also investigated by running eight columns (three cis- and five trans-decalin columns) with silanized chromasorb as the packing. The amount of solute injected (to determine the solute volume required for infinite dilution conditions) is also investigated by varing the injection size between 1.0 μl and 0.1 μl.

The column loading ranged from three to fifteen mass per cent.

The mixed virial coefficients, B_{12}, were calculated from McGlashan and Potter's equation(35) and Hudson and McCoubrey's combining rules (36) following Letcher et al(37).

$$B_{12}/V_{C,12} = 0.43 - 0.886(T_{C,12}/T) - 0.694(T_{C,12}/T)^2 - 0.0375(n_{12} - 1)(T_{C,12}/T)^{4.5} \qquad (4.1)$$

where

$$T_{C,12} = 128(T_{C,11}T_{C,22})^{1/2}(I_{C,11}I_{C,22})^{1/2}V_{C,11}V_{C,22}/I_{C,12} \tag{4.2}$$

$$V_{C,12} = (V_{C,11}^{1/3} + V_{C,22}^{1/3})^3/8 \tag{4.3}$$

$$I_{C,12} = (I_{11} + I_{22})(V_{C,11}^{1/3} + V_{C,22}^{1/3})^6 \tag{4.4}$$

and

$$n_{12} = (n_1 + n_2)/2 \tag{4.5}$$

The critical data and ionization energies used in the calculation of B_{12} are given in table 26 using $n_1 = 5$ (n-pentane and cyclopentane), $n_1 = 6$ (n-hexane, cyclohexane and benzene), $n_1 = 7$ (n-heptane) and $n_2 = 1$ (helium). The values for B_{12} was found to be 2.429×10^{-6} m^3 mol^{-1} (n-pentane), 18.0477×10^{-6} m^3 mol^{-1} (cyclopentane), 29×10^{-6} m^3 mol^{-1} (n-hexane), 21.579×10^{-6} m^3 mol^{-1} (cyclohexane), 17.6579×10^{-6} m^3 mol^{-1} (benzene) and 31.532×10^{-6} m^3 mol^{-1} (heptane).

TABLE 4.1. Definition of symbols

Symbol	Definition
n_3	Moles of decalin (trans or cis) on the column
P_i	Inlet pressure
P_O	Outlet pressure (atmospheric)
J_3^2	Correction factor for the compressibility of the mobile phase
U_O	Flow rate corrected for temperature and water-vapour pressure
t_G	Retention time of an unretained gas (nitrogen)
t_R	Retention time of the solute studied
t	Time of injection of the solute

TABLE 4.2. Column Specifications

Column number	Solvent decalin isomer	$U_O x10^{-6}$ $m^3\ s^{-1}$	n_3 mmols	percentage loading mass per cent
1	trans[§]	0.8872	3.393	15
2	trans[§]	0. 9541	2.124	10
3	trans[§]	0.8370	2.329	8
4	trans[§]	0.9542	3.684	10
5	cis[§]	0.9828	1.790	10
6	cis[§]	0.5715	1.786	3
7	trans	1.7177	4.086	5
8	trans	1.9916	6.350	10
9	cis	1.8935	6.082	10
10	trans	1.0702	2.615	5
11	trans	2.3727	2.233	3
12	cis	1.2387	2.310	5
13	cis	2.6964	2.217	3
14	trans[§]	1.2542	5.991	10
15	cis[§]	2.9239	2.512	5
16	trans[£]	1.8196	1.091	5
17	trans[£]	2.1629	2.527	10
18	cis[£]	1.9212	5.812	10
19	cis[£]	2.8041	3.911	5

[§] : silanized Chromasorb

[£] : Columns run at 283.15 K

Experiment 1. n-Hexane in trans-decalin (15%) on Column 1 (Gow-Mac T.C.D. Detector) at 298.15 K.

n_3/mol	3.3935×10^{-3}	J_3^2	0.914
P_i/Pa	119652.72	$U_O/m^3\ s^{-1}$	8.872×10^{-7}
P_O/Pa	100633.50	t_G/s	20.31

TABLE 4.3. Results obtained from column 1 (trans-decalin 15%) with n-hexane as solute.

Time / s	t_R / s	$V_N \times 10^{-4}$ / m^3	V_N/n_3e^C / $m^3\ mol^{-1}$	U_Ot/n_3 / $m^3\ mol^{-1}$
1200	428.82	3.312	0.0975	0.313
2400	419.22	3.234	0.0953	0.627
4800	413.88	3.191	0.0904	1.255
5700	413.28	3.182	0.0937	1.490
6600	401.22	3.088	0.0910	1.725
7200	401.10	3.087	0.0909	1.882
9000	399.66	3.076	0.0906	2.353
9600	396.06	3.046	0.0897	2.509

Experiment 2. n-Hexane in trans-decalin (10%) on column 2 (Gow-Mac T.C.D. detector) at 298.15 K.

n_3/mol	2.124×10^{-3}	J_3^2	0.901
P_i/Pa	120035.45	$U_O/m^3\ s^{-1}$	9.541×10^{-7}
P_O/Pa	99967.10	t_G/s	19.68 s

TABLE 4.4. Results obtained from column 2 (trans-decalin 10%) with n-hexane as the solute.

Time / s	t_R / s	$V_N \times 10^{-4}$ / m^3	V_N/n_3e^C / $m^3\ mol^{-1}$	U_Ot/n_3 / $m^3\ mol^{-1}$
3900	228.57	1.936	0.0901	1.752
4200	228.49	1.935	0.0900	1.889
4800	224.44	1.894	0.0881	2.156
5100	223.51	1.884	0.0876	2.291
5700	219.03	1.838	0.0855	2.560
6300	218.53	1.833	0.0852	2.850

Experiment 3. n-Hexane in trans-decalin (8%) on column 3 (Gow-Mac T.C.D. detector) at 298.15 K.

n_3/mol	$2.329\text{x}10^{-3}$	J_3^2	0.913
P_i/Pa	121099.81	$U_O/m^3\ s^{-1}$	$8.37\text{x}10^{-7}$
P_O/Pa	102233.01	t_G/s	23.7

TABLE 4.5. Results obtained from column 3 (trans-decalin 10%) with hexane as the solute

$\frac{\text{Time}}{\text{s}}$	$\frac{t_R}{\text{s}}$	$\frac{V_N \times 10^{-4}}{m^3}$	$\frac{V_N/n_3e^C}{m^3\ mol^{-1}}$	$\frac{U_Ot/n_3}{m^3\ mol^{-1}}$
1200	312.88	2.211	0.0937	0.431
2100	311.49	2.200	0.0934	0.754
3000	310.37	2.192	0.0930	1.078
4200	309.17	2.182	0.0926	1.509
6000	297.31	2.091	0.0887	2.156

Experiment 4. n-Hexane in trans-decalin (10%) on column 4 (Gow-Mac T.C.D. detector) at 298.15 K.

n_3/mol	3.682×10^{-3}	J_3^2	0.888
P_i/Pa	141016.73	$U_O/m^3\ s^{-1}$	9.542×10^{-7}
P_O/Pa	101758.29	t_G/s	22.08

TABLE 4.6. Results obtained from column 4 (trans-decalin 10%) with n-hexane as the solute.

Time / s	t_R / s	$V_N \times 10^{-4}$ / m^3	V_N/n_3e^C / $m^3\ mol^{-1}$	U_Ot/n_3 / $m^3\ mol^{-1}$
2100	335.94	2.659	0.0939	0.921
3300	334.98	2.651	0.0936	1.125
3900	330.30	2.611	0.0923	1.330
4500	328.14	2.593	0.0916	1.535
5160	326.16	2.576	0.0910	1.760
6300	315.78	2.488	0.0879	2.149

Experiment 5. n-Hexane in cis-decalin (10%) on column 5 (Gow-Mac T.C.D. detector) at 298.15 K.

n_3/mol	1.790×10^{-3}	J_3^2	0.923
P_i/Pa	116166.31	U_O/m^3 s^{-1}	9.828×10^{-7}
P_O/Pa	99967.11	t_G/s	30.99

TABLE 4.7. Results obtained from column 5 (cis-decalin 10%) with n-hexane as the solute.

Time / s	t_R / s	$V_N \times 10^{-4}$ / m^3	V_N/n_3e^C / m^3 mol^{-1}	U_Ot/n_3 / m^3 mol^{-1}
1800	204.72	1.708	0.0942	0.882
3300	200.94	1.967	0.0924	1.811
4200	196.56	1.633	0.0901	2.305
5400	194.58	1.615	0.0891	2.946
9300	173.34	1.422	0.0785	5.105

Experiment 6. n-Hexane in cis-decalin (3%) on column 6 (Gow-Mac T.C.D. detector) at 298.15 K.

n_3/mol	1.786x10^{-3}	J_3^2	0.913
P_i/Pa	121099.48	U_O/m^3 s^{-1}	5.715x10^{-7}
P_O/Pa	100731.71	t_G/s	90.12

TABLE 4.8. Results obtained from column 6 (cis-decalin 3%) with n-hexane as the solute.

Time / s	t_R / s	V_N x 10^{-4} / m^3	V_N/n_3e^C / m^3 mol^{-1}	U_Ot/n_3 / m^3 mol^{-1}
630	406.79	1.646	0.0922	2.016
1330	391.87	1.569	0.0879	4.257
1459	390.95	1.564	0.0876	4.671
1519	388.19	1.550	0.0868	4.862
1787	383.95	1.528	0.0856	5.718
2000	372.95	1.470	0.0824	6.403
2150	358.28	1.394	0.0781	6.881

Experiment 7. 5% trans-decalin column 7 (Shandon UK3 T.C.D. detector) at 298.15 K

n_3/mol	4.0865×10^{-3}	J_3^2	0.789
P_i/Pa	148758.02	$U_O/m^3\ s^{-1}$	1.7177×10^{-6}
P_O/Pa	100831.71	t_G/s	13.89

TABLE 4.9. Results obtained from column 7 (a 5% trans-decalin column) with solutes cyclohexane and benzene run seperately.

Time	t_R	$V_N\ x10^{-4}$	V_N/n_3e^C	U_Ot/n_3
s	s	m^3	$m^3\ mol^{-1}$	$m^{-3}mol^{-1}$
solute: Cyclohexane				
1205	541.23	7.232	0.176	0.506
2904	520.30	6.942	0.169	1.221
4396	494.69	6.594	0.161	1.847
4954	485.15	6.463	0.157	2.083
5512	461.64	6.141	0.149	2.318
6043	462.45	5.152	0.150	2.541
7167	443.61	5.893	0.1430	3.013
7780	433.21	5.751	0.1399	3.270
solute: Benzene				
690	429.88	5.568	0.135	0.290
960	399.11	5.428	0.1285	1.2213
4395	378.89	5.006	0.1218	1.847
4956	371.15	4.900	0.1192	2.083

TABLE 4.9
cont.

Time s	t_R s	$V_N \times 10^{-4}$ m^3	V_N/n_3e^C $m^3\ mol^{-1}$	U_0t/n_3 $m^3\ mol^{-1}$
5515	356.04	4.692	0.1142	2.318
6571	347.98	4.582	0.1115	2.762
7144	340.41	4.478	0.1089	3.003
7749	332.41	4.368	0.1063	3.257

Experiment 8. 10% trans-decalin on column 8 (Shandon UK3 T.C.D. detector) at 298.15 K.

n_3/mol	6.3501×10^{-3}	J_3^2	0.769
P_i/Pa	158051.25	$U_O/m^3\ s^{-1}$	1.9916×10^{-6}
P_O/Pa	101351.66	t_G/s	14.38

TABLE 4.10. Results obtained from column 8 (a 10% trans-decalin column) with solutes n-pentane, cyclopentane, benzene, and n-hexane run as a mixture.

Time / s	t_R / s	$V_N \times 10^{-4}$ / m^3	V_N/n_3e^C / $m^3\ mol^{-1}$	U_Ot/n_3 / $m^3\ mol^{-1}$
3857	121.94	1.647	0.02525	1.209
4950	118.30	1.592	0.02439	1.553
5657	114.29	1.530	0.02346	1.7798
6394	112.20	1.498	0.02296	2.005
7016	113.71	1.521	0.02332	2.193
8418	108.87	1.447	0.02218	2.640
9192	103.00	1.357	0.02080	2.883

Solute : Cyclopentane

315	259.81	3.759	0.0577	0.122
3857	247.94	3.577	0.0549	1.209
4950	238.30	3.429	0.0526	1.553
5675	234.89	3.377	0.0519	1.780
7216	225.69	3.239	0.0498	2.194
7819	223.05	3.196	0.0491	2.452
8418	218.07	3.119	0.0479	2.640
9871	209.43	2.987	0.0459	3.096

TABLE 4.10 cont.

Time s	t_R s	V_N x10^{-4} m^3	V_N/n_3e^C m^3 mol^{-1}	U_Ot/n_3 m^3 mol^{-1}
3857	696.14	1.044	0.164	1.209
4950	670.30	1.004	0.157	1.552
4675	659.69	9.883	0.154	1.780
6375	644.49	9.650	0.151	2.005
7016	632.11	9.461	0.148	2.194
7819	619.05	9.261	0.145	2.452
8418	609.27	9.111	0.143	2.640
9192	597.40	8.929	0.139	2.883
9871	581.43	8.684	0.136	3.096
	Solute	: Benzene		
3857	526.34	7.902	0.1228	1.209
4950	502.90	7.841	0.1172	1.553
4675	491.09	7.482	0.1143	1.779
6394	484.89	7.301	0.1128	2.005
7016	473.11	7.206	0.1100	2.194
7819	465.75	6.913	0.1081	2.452
8418	459.87	6.823	0.107	2.640
9192	448.01	6.641	0.10394	2.883
9871	437.43	6.479	0.1015	3.096

Table 4.10 cont.

Solute : Hexane

3857	397.34	5.865	0.09153	1.209
4950	382.31	5.635	0.08794	1.553
5675	374.69	5.518	0.08612	1.780
6394	366.09	5.387	0.08406	2.005
7016	360.09	5.303	0.08275	2.193
7819	354.15	5.204	0.08121	2.452
8418	350.37	5.146	0.08031	2.64
9192	340.00	4.987	0.0778	2.883
9871	333.63	4.889	0.0763	3.096

Experiment 9. 3 % cis-decalin on column 9 (Shandon U.K.3 T.C.D. detector) at 298.15 K.

n_3/mol	6.882x10^{-3}	J_3^2	0.7605
P_i/Pa	158997.07	U_O/m^3 s^{-1}	1.8935x10^{-6}
P_O/Pa	100271.75	t_G/s	15.68

TABLE 4.11. Results obtained from column 9 (a 3% cis-decalin column) with solutes n-pentane, cyclopentane, n-hexane, cyclohexaneand benzene run as a mixture.

Time s	t_R s	V_N x10^{-4} m^3	V_N/n_3e^C m^3 mol^{-1}	U_Ot/n_3 m^3 mol^{-1}
soulte: Pentane				
250	120.51	1.509	0.0241	0.0778
1482	123.97	1.559	0.0255	0.461
2335	122.43	1.537	0.0246	0.727
3164	122.43	1.537	0.026	0.985
3958	120.30	1.506	0.0241	1.2322
4798	117.34	1.468	0.0235	1.485
5554	117.14	1.464	0.0234	1.729
6315	113.41	1.407	0.0225	1.966
7061	113.62	1.414	0.0263	2.198
7800	111.05	1.377	0.0220	2.428
8524	109.45	1.354	0.0217	2.654
10564	108.81	1.345	0.0215	3.288
11319	105.81	1.320	0.0208	3.524
11536	90.61	1.083	0.0173	3.59
13535	103.42	1.267	0.0203	4.214

TABLE 4.11 cont.

Time s	t_R s	V_N x10^{-4} m^3	V_N/n_3e^C m^3 mol^{-1}	U_Ot/n_3 m^3 mol^{-1}
solute: Cyclopentane				
412	253.87	3.434	0.05509	0.128
1482	258.97	3.503	0.0562	0.461
2335	256.04	3.465	0.0556	0.727
3164	252.63	3.412	0.0547	0.985
3958	250.50	3.386	0.0543	1.232
4798	248.74	3.360	0.0539	1.485
5554	241.94	3.262	0.0523	1.729
6315	240.21	3.233	0.0519	1.966
7061	237.22	3.190	0.0512	2.198
7800	235.25	3.1664	0.0508	2.428
8524	229.15	3.078	0.0494	2.654
10564	222.81	2.987	0.0479	3.289
11319	219.78	2.943	0.0472	3.524
11536	200.4	2.664	0.0427	3.59
13535	210.8	2.815	0.0451	4.214
14566	206.75	2.756	0.0442	4.535
15549	201.40	2.679	0.04298	4.841
16195	200.31	2.663	0.0427	5.042
16805	196.75	2.607	0.0418	5.232
17620	195.66	2.596	0.04165	5.474

TABLE 4.11 cont.

Time s	t_R s	V_N x10^{-4} m^3	V_N/n_3e^C m^3 mol^{-1}	U_Ot/n_3 m^3 mol^{-1}
Cyclohexane				
2335	749.24	1.056	0.173	0.727
3164	738.63	1.027	0.170	0.985
3958	728.63	1.017	0.168	1.232
4798	722.14	1.041	0.1663	1.485
5554	709.34	9.876	0.1615	1.729
6315	700.34	9.735	0.1592	1.966
7061	691.42	9.663	0.158	2.198
7800	689.45	9.447	0.154	2.428
8524	671.35	9.165	0.1499	2.654
10564	651.81	9.078	0.148	3.289
11319	645.78	8.728	0.143	3.524
11536	621.	8.578	0.1403	3.59
13535	612.5	8.523	0.1394	4.214
14566	607.25	8.260	0.1351	4.535
15549	589	8.255	0.1349	4.841
16195	586.11	8.215	0.1343	5.042
16805	577.45	8.094	0.1324	5.232
17260	563.46	7.89	0.129	5.474

Table 4.11.cont solute: Hexane

1482	404.17	5.598	0.0912	0.461
2335	400.04	5.539	0.09024	0.727
3164	396.03	5.487	0.08939	0.985
3958	388.5	5.373	0.0875	1.2322
4798	386.44	5.343	0.0870	1.485
5554	397.94	5.25	0.0858	1.729
6315	373.81	5.16	0.0855	1.966
7061	371.62	5.13	0.08408	2.198
7800	366.05	5.05	0.0836	2.428
8524	359.35	4.953	0.0823	2.654
1064	348.18	4.792	0.0807	3.289
11319	345.18	4.749	0.07807	3.524
11536	327	4.487	0.07738	3.59
13535	327.2	4.490	0.0731	4.214
14566	324.35	4.449	0.07315	4.535
15549	318.8	4.365	0.07248	4.841
16195	316.7	4.335	0.07111	5.042
16805	310.45	4.252	0.0706	5.232
17620	302.46	4.135	0.06924	5.474

Solute : Cyclohexane

708	556.83	7.793	0.127	0.207
1482	586.57	8.221	0.130	0.461
2335	580.64	8.135	0.133	0.727
3164	573.63	8.034	0.131	0.985
3958	563.70	7.892	0.129	1.232

Table 4.11
cont.

4798	559.54	7.832	0.128	1.485
5554	549.14	7.687	0.1256	1.729
6315	541.21	7.555	0.1235	1.966
7061	706.02	7.493	0.1225	2.198
7800	531.05	7.273	0.1213	2.428
8524	520.75	7.069	0.1189	2.654
10564	506.61	6.991	0.1156	3.289
11319	501.81	7.421	0.1143	3.524
11536	478.8	6.669	0.1090	3.59
13535	475	6.614	0.1081	4.214
14566	470.15	6.544	0.107	4.535
15549	457	6.355	0.103	4.841
16195	455.91	6.339	0.1036	5.042
16805	447.25	6.091	0.1016	5.232
17620	438.66	6.215	0.0996	5.474

Experiment 10. 5% trans-decalin on column 10 (Shandon U.K.3 T.C.D. detector) at 298.15 K.

n_3/mol	$2.6151\text{x}10^{-4}$	J_3^2	0.840
P_i/Pa	139846.37	$U_O/m^3\ s^{-1}$	$1.0702\text{x}10^{-6}$
P_O/Pa	102718.22	t_G/s	25.67

TABLE 12. Results obtained from column 10 (a 5% trans-decalin column) with solutes n-pentane, cyclopentane, n-hexane, and cyclohexane run as a mixture.

Time s	t_R s	$V_N\ \text{x}10^{-4}$ m^3	V_N/n_3e^C $m^3\ mol^{-1}$	U_Ot/n_3 $m^3\ mol^{-1}$
3312	97.55	6.462	0.0240	1.355
4062	97.04		0.0238	1.662
4723	95.31	6.260	0.0233	1.933
5332	94.40	6.179	0.0230	2.182
6000	92.24	5.984	0.0222	2.474
6636	89.84	5.769	0.0214	2.716
7193	89.06	5.698	0.0212	2.944
9364	84.03	5.246	0.0195	3.929
9853	83.56	5.204	0.0194	4.032
13401	75.29	4.461	0.0166	5.484
13884	71.71	4.139	0.0154	5.682

Solute : Cyclopentane

3312	184.85	1.431	0.0534	1.355
4062	181.94	1.405	0.0525	1.662
4723	177.81	1.368	0.0510	1.933
5332	174.8	1.311	0.0500	2.185
6000	170.24	1.299	0.0485	2.474

TABLE 4.12
cont.

Time s	t_R s	V_N x10^{-4} m^3	V_N/n_3e^C m^3 mol^{-1}	U_Ot/n_3 m^3 mol^{-1}
6636	166.64	1.267	0.0473	2.716
7193	164.36	1.247	0.0465	2.944
9364	153.63	1.150	0.0429	3.929
9853	152.56	1.141	0.0425	4.032
13401	131.69	9.531	0.0355	5.484
13884	126.46	9.061	0.0338	5.682
14245	124.15	8.853	0.0330	5.829
14994	124.22	8.859	0.0331	6.136
16300	113.8	7.653	0.0286	6.671

Solute: Hexane

3312	291.95	2.394	0.0907	1.355
4062	287.24	2.351	0.0891	1.662
4762	278.31	2.271	0.0860	1.933
5333	276.8	2.258	0.0855	2.183
6000	267.59	2.175	0.0824	2.474
6636	263.84	2.141	0.0811	2.716
13884	199.66	1.564	0.0593	5.682
14245	194.35	1.516	0.0574	5.829

Solute : Cyclohexane

3312	496.52	4.327	0.1609	1.355
4062	489.89	4.173	0.1587	1.662
4724	488.76	4.163	0.1583	1.933
5332	470.6	4.000	0.1521	2.182
6000	457.19	3.879	0.1475	2.474
6636	449.84	3.818	0.1451	2.716

TABLE 4.13
cont.

Time s	t_R s	V_N x10^{-4} m^3 mol^{-1}	V_N/n_3e^C m^3 mol^{-1}	U_Ot/n_3 m^3 mol^{-1}
7193	442.46	3.747	0.1425	2.944
9364	415.23	3.502	0.1332	3.929
9853	409.66	2.452	0.1313	4.032
13401	350.09	2.916	0.1109	5.484
13884	343.66	2.859	0.1087	5.682
14245	329.65	2.732	0.1039	5.829
14994	322.83	2.671	0.1016	6.139
16300	299.77	2.464	0.0937	6.671

Experiment 11. 3% trans-decalin on column 11 (Shandon U.K.3 T.C.D. detector) at 298.15 K.

n_3/mol 2.2325x10^{-3}

P_i/Pa 148056.23

P_O/Pa 101658.3

J_3^2 0.805

U_O/m^3 s^{-1} 2.3727x10^{-6}

t_G/s 10.33

TABLE 4.13. Results obtained from column 10(a 3% trans-decalin column) with solutes n-hexane, n-pentane, cyclopentane, and benzene.

$\frac{\text{Time}}{\text{s}}$	$\frac{t_R}{\text{s}}$	$\frac{V_N X10^{-4}}{m^3}$	$\frac{V_N/n_3e^C}{m^3\ mol^{-1}}$	$\frac{U_Ot/n_3}{m^3\ mol^{-1}}$
280	124.76	2.185	0.0970	0.2977
750	118.9	2.073	0.0926	0.797
1356	111.95	1.941	0.0862	1.442
1960	106.94	1.845	0.0819	2.084
2576	100.59	1.724	0.0765	2.739
3134	95.26	1.622	0.072	3.332
4451	82.9	1.386	0.0615	4.733
4935	78.48	1.302	0.0578	5.247
5540	74.38	1.223	0.0543	5.704

Solute : Hexane (single)

1180	113.2	1.965	0.0872	1.255
1785	107.23	1.851	0.0823	1.878
2380	101.85	1.748	0.0776	2.54
2873	95.5	1.627	0.0722	3.1611
3547	91.35	1.547	0.0687	3.771
4086	86.54	1.454	0.0645	4.345
4787	79.72	1.325	0.0578	5.089

TABLE 4.13 cont.

Time s	t_R s	V_N x10^{-4} m^3	V_N/n_3e^C m^3 mol^{-1}	U_Ot/n_3 m^3 mol^{-1}
solute: Cyclopentane				
750	76.90	1.271	0.0558	0.797
1356	72.8	1.193	0.0522	1.442
1960	69.29	1.126	0.049	2.084
2576	67.59	1.093	0.047	2.739
3134	62.71	1.000	0.0437	3.332
4451	55.00	8.310	0.0363	4.733
4935	52.08	7.973	0.0348	5.247
5340	49.17	7.418	0.0324	5.704

Solute : Benzene

280	161.81	2.893	0.128	0.2977
750	154.37	2.751	0.1226	0.797
1356	144.52	2.562	0.114	1.442
1960	138.89	2.455	0.1094	2.084
2576	130.74	2.299	0.1025	2.739
3134	123.84	2.168	0.0966	3.332
3732	120.24	2.099	0.0935	3.966
4451	109.63	1.896	0.0845	4.733
4935	102.18	1.754	0.0782	5.247
5540	97.78	1.670	0.0744	5.704

TABLE 4.13 cont.

Time s	t_R s	V_N x10^{-4} m^3	V_N/n_3e^C m^3 mol^{-1}	U_Ot/n_3 m^3 mol^{-1}
solute: Heptane				
750	375.85	6.981	0.3123	0.797
1356	351.48	6.515	0.2915	1.442
1960	336.35	6.245	0.279	2.084
2576	316.9	5.855	0.2619	2.739
3134	299.41	5.521	0.2470	3.332
3732	283.37	5.215	0.2333	3.966
4451	256.95	4.519	0.2022	4.733
4935	240.14	4.389	0.1963	5.247
5540	226.86	4.135	0.1850	5.704

Experiment 12. 5% cis-decalin on column 12 (Shandon U.K.3 T.C.D. detector) at 298.15 K.

n_3/mol	$2.31017\mathrm{x}10^{-3}$	J_3^2	0.837
P_i/Pa	152761.72	$U_O/m^3\ s^{-1}$	$1.2387\mathrm{x}10^{-6}$
P_O/Pa	101431.75	t_G/s	18.73

TABLE 4.14. Results obtained from column 12 (a 5% cis-decalin column) with solutes n-pentane, cyclopentane, n-hexane, cyclohexane, benzene, and heptane run as a mixture.

Time / s	t_R / s	$V_N\ \mathrm{x}10^{-4}$ / m^3	V_N/n_3e^C / $m^3\ mol^{-1}$	U_Ot/n_3 / $m^3\ mol^{-1}$
	solute:	Pentane		
260	72.72	6.118	0.0257	0.1508
903	71.22	5.924	0.0249	0.524
1657	69.85	5.794	0.0244	0.9611
2382	68.10	5.598	0.0236	1.382
3082	67.19	5.495	0.0232	1.788
8841	57.38	4.391	0.0185	5.128
9412	56.94	4.341	0.0183	5.456
9959	56.22	4.260	0.01794	5.775
10504	52.69	3.863	0.0163	6.093
11062	53.16	3.917	0.0165	6.416
13327	50.17	3.657	0.0154	7.730
13787	49.15	3.464	0.0146	7.997

TABLE 4.14 cont.

Time s	t_R s	$V_N X10^{-4}$ m^3	V_N/n_3e^C $m^3\ mol^{-1}$	U_0t/n_3 $m^3\ mol^{-1}$
	solute:	Cyclopentane		
260	140.22	1.3715	0.0579	0.1508
903	137.54	1.340	0.0566	0.5238
1657	133.36	1.264	0.0565	0.9611
2382	130.27	1.259	0.0532	1.382
3082	126.89	1.2215	0.0516	1.7877
4414	106.55	0.9925	0.0419	2.56
8841	105.46	0.9802	0.0413	5.128
9412	103.15	0.9543	0.0403	5.459
9959	102.12	0.9427	0.0398	5.775
10504	99.16	0.9094	0.0384	6.093
11062	96.97	0.8847	0.0373	6.416
13327	90.61	0.8081	0.0341	7.730
13787	87.85	0.7821	0.0330	7.997
	Solute	: Hexane		
260	206.82	2.121	0.0910	0.1508
903	202.02	2.067	0.0886	0.5238
2382	191.1	1.944	0.0837	1.382
3082	188.39	1.914	0.0821	1.788
4414	163.39	1.636	0.0702	2.56
8841	153.76	1.524	0.0654	5.282
9412	151.44	1.499	0.0643	5.459
9959	148.01	1.459	0.0640	5.775
10504	144.56	1.420	0.0609	6.093

TABLE 4.14
cont.

11062	141.07	1.381	0.0592	6.416
13327	130.66	1.264	0.0542	7.730
13787	162.7	1.219	0.0523	7.997

Solute : Benzene

260	287.67	3.031	0.130	0.1508
903	280.62	2.952	0.127	0.5238
2382	265.8	2.785	0.1198	1.3817
3082	259.26	2.711	0.1167	1.7877
4414	233.25	2.417	0.1040	2.56
8841	210.45	2.162	0.0931	5.1282
9412	206.64	2.119	0.0912	5.459
9959	203.07	2.079	0.0895	5.778
10504	197.67	2.018	0.0869	6.093
11062	193.57	1.972	0.0849	6.416
13327	178.96	1.808	0.0778	7.730
13787	173.65	1.748	0.0752	7.997

solute: :Cyclohexane

903	365.82	3.991	0.168	0.5238
2382	348.59	3.717	0.1599	1.3817
3082	334.12	3.554	0.1529	1.7877
4414	308.3	3.263	0.1404	2.56
8841	274.06	2.878	0.1239	2.82
9412	268.44	2.815	0.1212	5.459
9959	262.47	2.747	0.1182	5.775
10504	257.67	2.694	0.1159	6.093
11062	252.07	2.631	0.1132	6.416
13327	227.86	2.358	0.1015	7.730

TABLE 4.14 cont.

Time s	t_R s	$V_N X10^{-4}$ m^3	V_N/n_3e^C $m^3\ mol^{-1}$	U_0t/n_3 $m^3\ mol^{-1}$
solute: Heptane				
903	648.71	7.095	0.3066	0.5238
2382	609.59	6.655	0.2876	1.3817
3082	596.77	6.510	0.2876	1.7877
4414	483.39	5.234	0.2262	2.56
8841	472.8	5.115	0.2211	5.282
9412	463.4	5.009	0.2164	5.459
9959	453.14	4.893	0.2114	5.775
11062	442.54	4.774	0.206	6.416
13327	407.54	4.380	0.1893	7.7303
13787	392.38	4.209	0.1819	7.997

Experiment 13. 10 % trans-decalin on column 13 (Shandon U.K.3 T.C.D. detector) at 298.15 K.

n_3/mol	$1.2542\text{x}10^{-6}$	J_3^2	0.778
P_i/Pa	155360.56	$U_O/m^3\ s^{-1}$	$1.2542\text{x}10^{-6}$
P_O/Pa	101364.99	t_G/s	16.55

TABLE 4.15. Results obtained from column 13 (a 10% trans-decalin column) with varing injection volumes of solutes n-pentane and n-hexane.

Time / s	t_R / s	V_N x10^{-4} / m^3	V_N/n_3e^C / $m^3\ mol^{-1}$	U_Ot/n_3 / $m^3\ mol^{-1}$
	solute:	Hexane (0.1μl)		
3351	589.31	5.5892	0.0948	0.7016
5414	559.71	5.294	0.08755	1.1335
8770	527.01	4.9813	0.0824	1.836
10742	513.86	4.853	0.08025	2.249
15018	4.6723	4.3979	0.0727	3.144
20174	424.49	3.9808	0.0658	4.224
	solute:	Hexane (0.5μl)		
4019	581.62	5.5142	0.09118	0.8415
6090	560.39	5.3069	0.08776	1.275
9419	530.83	5.018	0.08298	1.972
11421	508.98	4.8053	0.0795	2.391
15572	463.08	4.3608	0.0721	3.26
16819	448.82	4.218	0.0697	3.521

TABLE 4.15 cont.

Time s	t_R s	V_N x10^{-4} m^3	V_N/n_3e^C m^3 mol^{-1}	U_0t/n_3 m^3 mol^{-1}
solute: Hexane(1.0μl)				
993	623.76	5.9234	0.09796	0.208
2626	604.33	5.7358	0.0948	0.5499
4696	581.69	5.515	0.0912	0.983
8116	548.83	5.1942	0.0859	1.699
10050	529.73	5.0078	0.0828	2.104
16193	466.63	4.3979	0.0726	3.39
17545	443.46	4.166	0.0697	3.673
solute: Pentane(1.0μl)				
993	188.46	1.677	0.02736	0.208
2626	181.33	1.608	0.02613	0.5499
6812	168.93	1.487	0.02416	1.426
1760	168.67	1.484	0.02412	1.499
8115	167.83	1.476	0.02399	1.699
10050	161.33	1.413	0.02296	2.104
12052	155.01	2.391	0.02195	2.523
15572	145.73	3.144	0.0218	3.26
20177	130.28	1.113	0.1809	4.224
solute: Pentane(0.5μl)				
4019	177.22	1.568	0.02547	0.8415
6090	173.9	1.535	0.02494	1.275
9419	165.33	1.453	0.0236	1.972
10743	159.25	1.393	0.02264	2.249
17545	138.96	1.194	0.0194	3.673

Experiment 14. 5% trans column on column 14 (silanized chromasorb) Shandon U.K.3 T.C.D. detector at 298.15 K.

n_3/mol	2.2171x10^{-3}	J_3^2	0.821
P_i/Pa	156813.35	U_O/m^3 s^{-1}	2.6964x10^{-6}
P_O/Pa	103214.42	t_G/s	18.27

TABLE 4.16. Results obtained from column 14 (a 5% trans-decalin column) containing silanized chromasorb as its packing and solutes n-heptane and cyclohexane run separately.

Time s	t_R s	V_N x10^{-4} m^3	V_N/n_3e^C m^3 mol^{-1}	U_Ot/n_3 m^3 mol^{-1}
	solute:	n-heptane		
998	317.35	6.621	0.300	1.21
1981	285.53	5.916	0.2681	2.41
2754	269.47	5.561	0.252	3.35
3141	264.52	5.451	0.247	3.82
4275	235.59	4.811	0.218	5.21
4851	225.66	4.591	0.208	5.91
	solute:	cyclohexane		
668	191.81	3.835	0.173	0.81
1241	180.27	3.592	0.162	1.51
2219	170.44	3.369	0.152	2.72
3141	159.17	3.119	0.141	3.82
4448	148.43	2.882	0.130	5.41
5213	143.44	2.771	0.125	6.34

Experiment 15. 3% cis-decalin on column 15 (silanized chromasorb) Shandon U.K.3 T.C.D. detector at 298.15 K.

n_3/mol	2.5121×10^{-3}	J_3^2	0.860
P_i/Pa	150082.11	U_O/m^3 s^{-1}	2.9239×10^{-6}
P_O/Pa	100823.52	t_G/s	15.01

TABLE 4.17. Results obtained from column 15 (a 3% cis-decalin column) containing silanized chromasorb as its packing and solutes n-heptane and cyclohexane run separately.

Time / s	t_R / s	$V_N \times 10^{-4}$ / m^3 mol^{-1}	V_N/n_3e^C / m^3 mol^{-1}	U_Ot/n_3 / m^3 mol^{-1}
solute: n-heptane				
765	319.71	7.662	0.305	0.89
1090	311.44	7.461	0.297	1.32
1501	294.72	7.034	0.280	1.62
2156	276.12	6.581	0.262	2.51
2672	264.68	6.280	0.253	3.11
4287	234.94	5.526	0.222	4.99
solute: cyclohexane				
1288	175.83	4.044	0.161	1.59
1984	165.85	3.793	0.151	2.31
2758	150.86	3.416	0.136	3.21
3883	137.85	3.089	0.123	4.52
4639	128.87	2.836	0.114	5.46

Experiment 16. A 5% trans-decalin column run at 283.15 K (Shandon U.K.3 T.C.D. detector)

n_3/mol	$1.0910\text{x}10^{-3}$	J_3^2	0.838
P_i/Pa	137543.76	$U_O/m^3\ s^{-1}$	$1.8196\text{x}10^{-6}$
P_O/Pa	100678.38	t_G/s	15.68

TABLE 4.18. Results obtained from column 16 (a 5% trans-decalin column run at 283.15 K) wiyh solutes n-pentane, cyclopentane, n-hexane, cyclohexane, benzene and heptane run as a mixture.

Time / s	t_R / s	$V_N\text{x}10^{-5}$ / m^3	V_N/n_3e^C / $m^3\ mol^{-1}$	U_Ot/n_3 / $m^3\ mol^{-1}$
		solute: n-pentane		
513	48.92	5.838	0.0457	0.67
906	49.02	4.629	0.0486	1.192
2151	46.04	4.594	0.04176	2.829
2746	45.81	3.742	0.0414	3.612
5773	40.22	3.6244	0.03376	7.594
6237	39.45	3.607	0.03267	8.2048
7192	39.47	3.627	0.03311	8.852
7662	37.01	3.525	0.0327	9.469
8105	37.03	3.296	0.0293	10.07
8863	35.52	3.0252	0.0297	10.66
9755	34.42	2.919	0.0257	11.26
10157	34.82	2.8575	0.0263	12.83

Time s	t_R s	$V_N x10^{-4}$ m^3	V_N/n_3e^C $m^3\ mol^{-1}$	U_Ot/n_3 $m^3\ mol^{-1}$
		solute: cyclopentane		
513	90.92	1.1473	0.1035	0.674
906	90.42	1.139	0.101	1.192
1518	88.61	1.112	0.0977	1.997
2151	86.24	1.0759	0.09489	2.829
5773	72.17	0.8614	0.0782	3.612
6237	70.05	0.8290	0.0753	7.594
6729	69.15	0.8290	0.0775	8.204
7192	67.99	0.8532	0.0724	8.852
7662	65.81	0.7976	0.0694	9.461
8105	63.11	0.7644	0.06569	10.07
8563	61.62	0.7231	0.0636	10.66
9755	59.92	0.7005	0.06129	11.26
10157	59.57	0.6746	0.06078	12.833
		solute : hexane		
513	144.92	1.9706	0.1798	0.67
906	142.62	1.9509	0.1781	1.192
1518	137.21	1.853	0.1691	1.997
2151	136.04	1.8352	0.1675	2.829
2746	132.21	1.7769	0.1622	3.612
5773	112.37	1.474	0.1345	7.594
6237	107.55	1.400	0.1275	8.2048
6729	105.75	1.373	0.1253	8.852
7192	105.49	1.3694	0.1249	9.46
7662	102.11	1.3179	0.1203	10.07

TABLE 4.18 cont.

Time s	t_R s	$V_N x10^{-4}$ m^3	V_N/n_3e^C m^3 mol^{-1}	U_0t/n_3 m^3 mol^{-1}
8563	96.12	1.2266	0.1119	10.66
9755	91.72	1.159	0.1063	12.83
10157	89.42	1.124	0.1026	13.36

solute: benzene

906	245.22	2.539	0.232	1.192
1518	235.61	2.393	0.219	1.997
2151	229.94	2.366	0.2165	2.829
2746	225.21	2.3075	0.2111	3.612
5773	190.07	1.959	0.179	7.594
6237	180.45	1.858	0.170	8.205
6729	177.75	1.831	0.165	8.852
7192	175.99	1.738	0.1591	10.07
7662	168.71	1.643	0.150	11.26
8563	159.33	1.543	0.141	12.83

solute : cyclohexane

513	180.32	3.5001	0.3179	1.192
906	182.22	3.3535	0.3046	1.997
1518	172.61	3.2671	0.2968	2.829
2151	170.61	3.1949	0.2903	3.612
2746	167.01	2.659	0.2416	7.594
5773	144.17	2.512	0.2282	8.282
6237	137.55	2.473	0.2245	8.852
6729	133.79	2.444	0.220	10.07

TABLE 4.18
cont.

7192	135.79	2.333	0.2119	10.66
8563	129.42	2.190	0.1989	11.26
9755	123.42	2.056	0.1027	12.83
10157	116.92	2.030	0.1014	13.36

solute: n-heptane

906	506.82	3.159	0.228	0.67
2151	468.88	2.921	0.211	1.192
2746	458.73	2.855	0.206	1.997
5773	379.66	2.346	0.169	2.829
6237	367.76	2.268	0.1638	3.612
6729	356.71	2.197	0.158	7.594
7192	356.51	2.196	0.157	8.852
7662	339.75	2.088	0.150	10.07
8563	319.45	1.957	0.1413	11.26
9755	301.56	1.844	0.1331	12.83

Experiment 17. A 10% trans-decalin column at 283.15 K (Shandon U.K.3 T.C.D. detector)

n_3/mol	2.162×10^{-3}	J_3^2	0.866
P_i/Pa	148160.49	$U_O/m^3\ s^{-1}$	2.527×10^{-7}
P_O/Pa	103271.22	t_G/s	13.08

TABLE 4.19. Results obtained from column 17 with solutes n-pentane, cyclopentane, n-hexane, cyclohexane, benzene and heptane run as a mixture.

$\dfrac{\text{Time}}{\text{s}}$	$\dfrac{t_R}{\text{s}}$	$\dfrac{V_N \times 10^{-5}}{\text{m}^3}$	$\dfrac{V_N/n_3e^C}{\text{m}^3\ \text{mol}^{-1}}$	$\dfrac{U_Ot/n_3}{\text{m}^3\ \text{mol}^{-1}}$
solute: n-pentane				
727	53.90	9.671	0.0447	0.851
1390	53.36	9.543	0.0441	1.758
3335	50.39	8.839	0.0409	4.22
7835	45.26	7.6247	0.0351	9.914
8753	39.09	6.162	0.0285	11.07
11417	35.82	5.387	0.0249	14.41
12581	35.31	5.267	0.0243	15.92
solute: cyclopentane				
727	105.28	2.184	0.101	0.85
1390	101.81	2.1022	0.0977	1.758
3335	99.61	2.050	0.0948	4.22
7835	80.41	1.592	0.0737	9.914
8753	77.97	1.537	0.0711	11.07
11417	69.35	1.333	0.0616	14.4
12581	67.73	1.294	0.0599	15.92

TABLE 4.19 cont.

Time s	t_R s	$V_N x10^{-4}$ m^3	V_N/n_3e^C $m^3\ mol^{-1}$	U_0t/n_3 $m^3\ mol^{-1}$
solute: n-hexane				
1390	173.05	3.790	0.175	1.758
3335	169.31	3.7015	0.1712	4.22
7835	162.35	3.536	0.1635	9.914
8753	126.85	2.693	0.1245	11.07
11417	112.85	2.363	0.1092	14.41
12581	105.56	2.1911	0.1013	15.92
solute: benzene				
727	218.33	4.863	0.222	0.85
1390	212.64	4.728	0.218	1.758
3335	205.07	4.548	0.2103	4.22
7835	165.30	3.606	0.1667	9.914
8753	132.72	2.835	0.1311	11.07
11417	123.77	2.623	0.1213	14.4
solute: cyclohexane				
727	308.01	6.987	0.323	0.85
1390	297.02	6.727	0.311	1.758
3335	275.62	6.220	0.288	4.22
7835	218.08	4.857	0.225	9.914
8753	215.58	4.799	0.222	11.07
11417	185.56	4.086	0.189	14.41
12581	181.28	3.985	0.184	15.92

TABLE 4.19 cont.

Time s	t_R s	$V_N x 10^{-3}$ m^3	V_N/n_3e^C $m^3\ mol^{-1}$	U_0t/n_3 $m^3\ mol^{-1}$
727	648.62	1.5057	0.696	0.311
1390	597.63	1.3849	0.6406	0.621
3335	564.65	1.3069	0.6045	1.49
7835	443.78	1.020	0.047	3.50
8753	427.27	1.0123	0.0468	3.91
11417	391.69	0.8970	0.04148	5.13

Experiment 18. A 5% cis-decalin column run at 283.15 K (Shandon U.K 3 T.C.D. Detector)

n_3/mol	5.8121x10^{-6}	J_3^2	0.771
P_i/Pa	145380.26	$U_O/m^3\ s^{-1}$	1.9212x10^{-6}
P_O/Pa	100245.87	t_G/s	16.07

TABLE 4.20. Results obtained from column 18 at 283.15 K for solutes n-pentane, cyclopentane and n-hexane run as a mixture.

t	t_R / s	V_Nx10^{-4} / m^3	V_N/n_3e^C / $m^3\ mol^{-1}$	U_Ot/n_3 / $m^3\ mol^{-1}$
	solute:	Pentane		
1455	183.91	2.487	0.0428	0.481
5203	180.87	2.441	0.0422	1.72
7623	177.69	2.394	0.0412	2.52
11525	159.73	2.366	0.0407	3.81
13068	158.09	2.342	0.0402	4.32
	solute :Cyclopentane			
1455	248.30	3.440	0.0592	0.35
3479	238.11	3.289	0.0566	1.15
7623	220.89	3.033	0.0522	2.52
11525	208.7	2.854	0.0491	3.81
13068	201.27	2.743	0.0472	4.32

TABLE 4.20 cont.

t / s	t_R / s	$V_N x10^{-4}$ / m^3	V_N/n_3e^c / m^3 mol^{-1}	U_0t/n_3 / m^3 mol^{-1}
solute: Hexane				
1455	698.81	1.0113	0.174	0.35
5203	629.22	9.183	0.158	1.72
7623	616.41	8.893	0.153	2.52
11525	553.59	7.962	0.137	3.81
13068	534.01	7.672	0.132	4.32

Experiment 19 . Column 19 (8%) cis decalin run at 283.15 K (Shandon U.K.3 T.C.D. Detector)

n_3/mol	$3.9112\text{x}10^{-3}$	J_3^2	0.747
P_i/Pa	165290.02	$U_O/m^3\ s^{-1}$	$2.8041\text{x}10^{-6}$
P_O/Pa	101631.64	t_G/s	1301

TABLE 4.21. Results odtained from column 19 at 283.15 K with solute benzene, cyclohexane and n-heptane run as a mixture.

t / s	t_R / s	$V_N\text{x}10^{-4}$ / m^3	V_N/n_3e^c / $m^3\ mol^{-1}$	U_Ot/n_3 / $m^3\ mol^{-1}$
solute Benzene				
712	556.05	1.075	0.275	0.51
2066	536.44	1.036	0.265	1.48
3491	529.63	1.005	0.257	2.52
3910	508.77	9.8141	0.251	2.84
5878	490.99	9.4622	0.242	4.21
7135	473.22	9.1103	0.233	5.11

solute : Cyclohexane

712	670.72	1.302	0.333	0.51
2066	634.35	1.231	0.316	1.48
3910	609.59	1.181	0.302	2.52
3491	599.49	1.161	0.276	2.84
5878	558.26	1.071	0.262	4.21
7135	528.26	1.024	0.297	5.11

TABLE 4.21 cont.

t / s	t_R / s	$V_N \times 10^{-4}$ / m^3	V_N/n_3e^c / $m^3\ mol^{-1}$	U_0t/n_3 / $m^3\ mol^{-1}$
solute	Heptane			
712	1213.75	2.377	0.607	0.51
2066	1154.41	2.259	0.578	1.48
3491	1097.06	2.146	0.549	2.52
3910	1067.79	2.092	0.535	2.84
5878	962.97	1.880	0.481	4.21
7135	911.67	1.779	0.455	5.11

TABLE 4.22. Summary of results obtained giving the values of the parameters ***a*** and ***b*** from equation 2.140, γ_{13}^{∞} (the activity coefficient at infinite dilution), and P_3' the solute partial pressure.

Column number	***a*** m^3 mol^{-1}	***b*** m^3 mol^{-1}	γ_{13}^{∞}	P_3' Pa
n-Pentane				
8	0.0282±0.0003	0.0024±0.0003	1.29±0.06	213.6±20.0
9	0.0265±0.0004	0.0014±3.8x10^{-5}	1.41±0.08	135.2±6.7
11	0.0271±0.0003	0.0019±5.9x10^{-5}	1.34±0.05	179.2±4.1
12	0.0567±0.0003	0.0013±5.8x10^{-5}	1.42±0.06	126.9±1.7
13	0.0288±0.0002	0.0022±4.2X10^{-5}	1.32±0.04	194.6±4.9
Cyclopentane				
8	0.0589±0.0005	0.0041±0.00018	0.99±0.01	197.6±7.4
9	0.0578±0.0025	0.0030±3.6x10^{-5}	1.01±0.07	129.1±10.2
10	0.0599±0.0006	0.0045±9.1x10^{-5}	0.99±0.02	187.4±2.0
11	0.0593±0.0005	0.0047±9.6x10^{-5}	0.98±0.01	173.5±3.3
12	0.0577±0.0005	0.0031±5.8x10^{-5}	1.01±0.02	134.4±1.2
n-hexane				
1	0.0980±0.0031	0.00337±0.0004	1.29±0.03	85.21± 8.9
2	0.0977±0.0042	0.00399±0.0010	1.30±0.02	101.21±12.6
3	0.0967±0.0021	0.0028±0.00065	1.31±0.02	71.74±3.4
4	0.1002±0.0033	0.0048±0.00081	1.27±0.01	120.51±7.9
5	0.0977±0.0024	0.00262±0.00032	1.28±0.03	67.2±8.2
8	0.1003±0.0005	0.0078±0.0004	1.27±0.06	192.53±6.1
9	0.0981±0.0009	0.0049±9.4x10^{-5}	1.32±0.01	131.21±2.1
10	0.1009±0.0006	0.0073±0.0001	1.26±0.08	180.19±10.6
11	0.0977±0.0005	0.0076±0.0002	1.27±0.01	192.53±4.2

TABLE 4.22
cont.

12	0.0935±0.0004	0.0047±5.5X10^{-5}	1.28±0.05	122.22±4.8
13	0.0984±0.0009	0.0795±0.00018	1.28±0.012	200.27±4.2
Cyclohexane				
7	0.1854±0.0002	0.013±0.0002	1.06±0.05	236.09±11.29
8	0.1791±0.0004	0.0139±0.0003	1.03±0.02	184.02±3.42
11	0.1804±0.0017	0.128±0.00026	1.04±0.02	201.34±12.31
12	0.1804±0.0017	0.0106±0.0002	1.11±0.06	130.09±5.66
15	0.1781±0.006	0.0136±0.0002	1.06±0.02	190.21±2.18
14	0.1763±0.0052	0.0094±0.0004	1.08±0.02	131.87±5.07
Benzene				
8	0.134±0.0009	0.0106±0.0005	1.44±0.07	181.07±2.3
9	0.140±0.0014	0.0068±0.0002	1.39±0.09	125.48±7.7
10	0.027±0.00027	0.0019±5.9X10^{-5}	1.42±0.06	173.17±3.8
11	0.128±0.0012	0.0094±0.0003	1.46±0.09	198.83±12.2
12	0.138±0.0012	0.0069±0.0002	1.42±0.09	120.48±6.8
n-heptane				
12	0.306±0.004	0.0156±0.0041	1.35±0.02	121.80±2.6
14	0.145±0.005	0.0086±0.0019	1.31±0.02	127.42±2.2
15	0.336±0.004	0.0257±0.0007	1.21±0.04	190.23±3.5
11	0.332±0.003	0.0795±0.0002	1.22±0.04	194.29±5.3

TABLE 4.23. Data used in the caculation of V_N, where P_1^* is the vapour pressure of the pure solute, V_1^* is the molar volume of the solute, B_{12} is the mixed virial coefficient and B_{11} is the second virial coefficient of the solute at 298.15 K.

Solute	P_1^* (38) Pa	V_1^* (38) $m^3\ mol^{-1}$	B_{12} $m^3\ mol^{-1}$	$-B_{11}$ $m^3\ mol^{-1}$
n-pentane	68325.66	$117.38x10^{-6}$	$2.429x10^{-6}$	$992.81x10^{-6}$
cyclopentane	42324.21	$93.71x10^{-6}$	$18.048x10^{-6}$	$1066.23x10^{-6}$
n-hexane	19778.28	$131.59x10^{-6}$	$29.0x10^{-6}$	$1519.31x10^{-6}$
cyclohexane	13009.88	$108.74x10^{-6}$	$21.576x10^{-6}$	$1577.10x10^{-6}$
benzene	12689.62	$89.40x10^{-6}$	$17.658x10^{-6}$	$1570.35x10^{-6}$
n-heptane	6095.26	$147.46x10^{-6}$	$31.532x10^{-6}$	$2197.63x10^{-6}$

TABLE 4.24. Data used in the caculation of V_N, where P_1^* is the vapour pressure of the pure solute, V_1^* is the molar volume of the solute, B_{12} is the mixed virial coefficient and B_{11} is the second virial of the solute at 283.15 K.

Solute	P_1^* (38) Pa	$B_{12}x10^{-6}$ $m^3\ mol^{-1}$	$-B_{11}x10^{-6}$ $m^3\ mol^{-1}$
n-pentane	37827.56	2.3828	1118.99
cyclopentane	22597.87	17.4516	1728.29
n-hexane	10091.17	28.9528	1730.89
cyclohexane	6320.68	20.9011	1806.41
benzene	6070.16	17.0044	1583.78
n-heptane	2743.77	33.1766	2523.74

TABLE 4.25. Summary of results obtained for n-hexane (0.1μ, 0.5μ and 1.0μ) and n-pentane (0.5μl and 1.0μl) in trans-decalin at 298.15 K .

solute	solute volume / μl	γ_{13}^{∞}	P_3^l / Pa
n-hexane	0.1	1.28	204.1
n-hexane	0.5	1.28	199.5
n-hexane	1.0	1.27	197.9
n-pentane	0.1	1.32	201.0
n-pentane	1.0	1.31	197.8

TABLE 4.26. The critical constants and ionization energies, I, used in the calculation of mixed second virial coefficient, B_{12} at 298.15 and 283.15 K.

Compound	V_C(38) / m^3 mol^{-1}	T_C(38) / K	I(38) / kJ.mol^{-1}
Pentane	304.0	469.7	0.994
Cyclopentane	260.2	511.6	1.014
Hexane	370.0	507.3	0.982
Cyclohexane	308.3	553.4	0.943
Benzene	259.4	562.1	0.924
Heptane	432.6	540.1	0.953
Helium	5.2	57.8	5.248

TABLE 4.27. Results obtained from figures 1 to 6 for solutes in cis-decalin at 298.15K where ***a*** is the intercept and ***b*** the slope.

Figure	Solute	a / $m^3\ mol^{-1}$	b / $m^3\ mol^{-1}$
1	Pentane	0.0257 ± 0.0003	$0.00139 \pm 2.88 \times 10^{-5}$
2	C_5H_{10}*	0.0579 ± 0.0004	$0.00312 \pm 3.5 \times 10^{-5}$
3	Hexane	0.0944 ± 0.0019	0.00451 ± 0.00015
4	C_6H_{12}*	0.1783 ± 0.0032	0.00980 ± 0.00029
5	Benzene	1.3772 ± 0.0019	0.00663 ± 0.00015
6	Heptane	0.3066 ± 0.0041	0.01560 ± 0.00408

TABLE 4.28. Calculated values for γ_{13}^{∞} (activity coefficient at infinite dilution) and P_3^l (partial pressure of solvent at 298.15 K) for solutes in cis-decalin using equation 2.139.

Figure	Solute	γ_{13}^{∞}	P_3^l / Pa
1	Pentane	1.41 ± 0.07	134.0 ± 6.3
2	C_5H_{10}*	1.01 ± 0.07	133.4 ± 18.4
3	Hexane	1.31 ± 0.03	118.4 ± 3.0
4	C_6H_{12}§	1.07 ± 0.10	136.3 ± 13.1
5	Benzene	1.42 ± 0.01	119.3 ± 2.5
6	Heptane	1.35 ± 0.02	121.8 ± 2.6

* : Cyclopentane § : Cyclohexane

TABLE 4.29. Results obtained from figures 7 to 13 for solutes in trans-decalin at 298.15 K where ***a*** is the intercept and ***b*** the slope.

Figure	Solute	$\frac{a}{\text{m}^3\ \text{mol}^{-1}}$	$\frac{b}{\text{m}^3\ \text{mol}^{-1}}$
7	Pentane	0.02739 ± 0.00029	0.0021 ± $3.37\text{x}10^{-5}$
8	C_5H_{10}*	0.05962 ± 0.00079	0.0045 ± $8.19\text{x}10^{-5}$
9	Hexane	0.09823 ± 0.00019	0.0074 ± 0.0002
10	C_6H_{12}§	0.17994 ± 0.00255	0.0128 ± 0.0003
11	Benzene	0.13467 ± 0.00319	0.0105 ± 0.0005
12	Heptane	0.33235 ± 0.00343	0.0261 ± 0.0007
13	Pentane	0.02752 ± 0.00024	0.0022 ± $4.23\text{x}10^{-5}$
	Hexane	0.09840 ± 0.00092	0.0795 ± 0.0002

* : Cyclopentane § : Cyclohexane

TABLE 4.30. Calculated values for γ_{13}^{∞} (activity coefficient at infinite dilution) and P_3' (partial pressure of solvent at 298.15 K) for solutes in trans decalin using equation 2.139.

Figure	Solute	γ_{13}^{∞}	$\frac{P_3'}{\text{Pa}}$
7	Pentane	1.32 ± 0.05	189.1 ± 2.7
8	C_5H_{10}*	0.98 ± 0.02	189.1 ± 2.3
9	Hexane	1.28 ± 0.02	186.7 ± 2.3
10	C_6H_{12}§	1.06 ± 0.08	175.6 ± 13.2
11	Benzene	1.45 ± 0.02	193.1 ± 9.3
12	Heptane	1.22 ± 0.04	194.3 ± 5.1
13	Pentane	1.32 ± 0.04	194.6 ± 4.8
	Hexane	1.28 ± 0.01	200.3 ± 4.2

: * : Cyclopentane § : Cyclohexane

TABLE 4.31 Results obtained from figures 14 to 18 for solutes in trans-decalin at 283.15K where *a* is the intercept and *b* the slope.

Figure	Solute	a / $m^3\ mol^{-1}$	$-b$ / $m^3\ mol^{-1}$
16	Pentane	0.0046 ± 0.0003	0.00151 ± 0.00031
17	$C_5H_{10}^*$	0.1004 ± 0.0002	0.00324 ± 2.98×10^{-5}
18	Hexane	0.0782 ± 0.0007	0.00592 ± 0.00023
19	$C_6H_{12}^*$	0.0328 ± 0.0038	0.00103 ± 0.00032
20	Benzene	0.0236 ± 0.0015	0.00781 ± 0.00023
21	Heptane	0.2355 ± 0.0041	0.01097 ± 0.00268

TABLE 4.32. Calculated values for γ_{13}^{∞} (activity coefficient at infinite dilution) and $P_3^{/}$ (partial pressure of solvent at 283.15 K) for solutes in trans-decalin using equation 1.139.

Figure	Solute	γ_{13}^{∞}	$P_3^{/}$ / Pa
16	Pentane	1.33 ± 0.01	75.9 ± 15.2
17	$C_5H_{10}^*$	0.97 ± 0.07	73.9 ± 5.2
18	Hexane	1.27 ± 0.03	75.1 ± 8.8
19	$C_6H_{12}^§$	1.14 ± 0.10	78.1 ± 6.5
20	Benzene	1.63 ± 0.01	73.5 ± 2.2
21	Heptane	1.22 ± 0.02	79.8 ± 6.8

* : Cyclopentane § : Cyclohexane

TABLE 4.33 Calculated values for γ_{13}^{∞} (activity coefficient at infinite dilution) and $p_3^{\prime}$ (partial pressure of solvent at 283.15 K) for solutes in cis decalin using equation 2.139.

Figure	Solute	$P_3^{\prime}$	γ_{13}^{∞}
14	Pentane	32.6±6.7	1.44 ± 0.031
14	C_5H_{10}*	116.4±116.4	1.014 ± 0.036
14	Hexane	131.7±19.1	1.292 ± 0.017
15	C_6H_{12}§	121.9±9.0	1.096 ± 0.025
15	Benzene	75.8±15.2	1.387 ± 0.031
15	Heptane	126.6±7.2	1.363 ± 0.0476

* : Cyclopentane

§ : Cyclohexane

4.1 Error Analysis

4.1.1. Determination of the Error in *a* and *b*.

The equation for the determination of γ_{13}^{∞} is

$$\frac{V_N}{n_3 e^{C}} = \frac{RT}{\gamma_{13}^{\infty} P_1^{*}} - \frac{U_o t}{n_3}\left[\frac{P_3^{l}}{\gamma_{13}^{\infty} P_1^{*}}\right] \qquad (4.6)$$

where

$$C = \left[\frac{B_{11} + V_1^{*}}{RT}\right] P_1^{*} + \left[\frac{2B_{12} - V_1^{\infty}}{RT}\right] P_o J_2^3 \qquad (4.7)$$

The functional relationship between y and x can be approximated by a straight line

$$y = a - bx \qquad (4.8)$$

where

$$y = \frac{V_N}{e^{C} n_3} \qquad (4.9)$$

and

$$x = \frac{U_0 t}{n_3} \qquad (4.10)$$

To find the uncertainty in the estimation of coefficients ***a*** and ***b*** the following equations are used

$$\sigma_a = \frac{\sigma}{\Delta^2}(\Sigma x_i)^2 \; [N\Sigma x_i^2 - (\Sigma x_i)^2] = \frac{\sigma^2}{\Delta} \Sigma x_i^2 \qquad (4.11)$$

$$\sigma_b = \frac{N\sigma^2}{\Delta^2} \; [N\Sigma x_i^2 - (\Sigma x_i)^2] = N \frac{\sigma^2}{\Delta} \qquad (4.12)$$

where

$$\Delta = N \; \Sigma x_i^2 - (\Sigma x_i)^2 \qquad (4.13)$$

and σ, the apparent standard deviation is given by

$$\sigma^2 = \frac{1}{N-2} \Sigma(y_i - a - bx_i)^2 \qquad (4.14)$$

4.1.2. Determination of the error in γ_{13}^{∞}

From equation 4.6 γ_{13}^{∞} is obtained from the intercept of the graph V_N/n_3e^C against U_0t/n_3.

Therefore

$$a = \frac{RT}{\gamma_{13}^{\infty} P_1^*} \qquad (4.15)$$

The standard deviation of any function $x = f(u,v,\ldots)$ is given by

$$\sigma_x^2 = \sigma_u^2 \left(\frac{\partial x}{\partial u}\right)^2 + \sigma_v^2 \left(\frac{\partial x}{\partial v}\right)^2 + \ldots \qquad (4.16)$$

Therefore

$$\sigma_a^2 = \sigma_{\gamma_{13}^{\infty}}^2 \left(\frac{\partial a}{\partial \gamma_{13}^{\infty}}\right)^2 \qquad (4.17)$$

But $$\frac{\partial a}{\partial \gamma_{13}^{\infty}} = \frac{RT}{\gamma_{13}^{\infty\,2} P_1^*} \qquad (4.18)$$

Substituting eq. 4.18 into 4.17

$$\sigma_{\gamma_{13}^{\infty}} = \frac{\sigma_a \, \gamma_{13}^{\infty\,2} \, P_1^*}{RT} \qquad (4.19)$$

4.1.3. Determination of the error in $P_3^{/}$

From equation 4.6 $P_3^{/}$ is obtained from the slope

$$b = \frac{P_3^{/}}{\gamma_{13}^{\infty} P_1^*} \qquad (4.20)$$

In this case the dependant variable is a function of more than one variable

$$\Rightarrow \quad b = [f \, (P_3^{/} \, ; \, \gamma_{13}^{\infty})] \qquad (4.21)$$

$$\therefore \quad \sigma_b^2 = \left(\frac{\partial b}{\partial P_3^{/}}\right)^2 \sigma_{P_3^{/}}^2 + \left(\frac{\partial b}{\partial \gamma_{13}^{\infty}}\right) \sigma_{\gamma_{13}^{\infty}}^2 \qquad (4.22)$$

$$\Rightarrow \qquad \sigma_b^2 = \left(\frac{\sigma_{P_3^l}}{\gamma_{13}^{\infty} P_1^*}\right)^2 + \left(\frac{P_3^l}{\gamma_{13}^{\infty\,2} P_1^*}\right)^2 \sigma_{\gamma_{13}^{\infty}}^2 \qquad (4.23)$$

4.1.4. Determination of the Error in the Partial Molar Enthalpy

The partial molar enthalpy of mixing at infinite dilution is given by

$$\frac{H_1^{E\infty}}{RT^2} = \left[\frac{\partial \ln\gamma_{13}^{\infty}}{\partial T}\right]_p \qquad (4.24)$$

Solving for $H_1^{E\infty}$

$$\frac{R}{\frac{1}{T_1} - \frac{1}{T_2}} \left[\ln\gamma_{13(T_1)}^{\infty} - \ln\gamma_{13(T_2)}^{\infty}\right] = H_1^{E\infty} \qquad (4.25)$$

Let

$$a = \frac{R}{\frac{1}{T_1} - \frac{1}{T_2}} \qquad (4.26)$$

$$u = \ln\gamma^{\infty}_{13(T_1)} \qquad (4.27)$$

and

$$v = \ln\gamma^{\infty}_{13(T_2)} \qquad (4.28)$$

Using equation 4.16, equation 4.25 becomes

$$\sigma_{H_1^{E\infty}} = a^2\sigma_u^{\,2} + a^2\sigma_v^{\,2} \qquad (4.29)$$

$$\sigma_{H_1^{E\infty}} = a\,[\sigma^2_{\ln\gamma^{\infty}_{13(T_1)}} - \sigma^2_{\ln\gamma^{\infty}_{13(T_2)}}] \qquad (4.30)$$

In order to determine the error in $H_1^{E\infty}$ the error in **ln** γ^{∞}_{13} has to be determined.

$$\sigma_{H_1^{E\infty}} = a^2[\frac{\sigma^2_{\gamma_{13(T_1)}}}{\gamma^{2\infty}_{13(T_2)}} - \frac{\sigma^2_{\gamma_{13(T_2)}}}{\gamma^{2\infty}_{13(T_2)}}] \qquad (4.31)$$

since

$$\sigma_{\ln x} = \frac{\sigma_x}{x} \qquad (4.32)$$

4.1.5. Sample Calculation

The following is a detailed calculation for the determination of γ_{13}^{∞}, $P_3^{\prime}$, $H_1^{E\infty}$ (together with the errors for each value) for n-pentane in trans-decalin at 298.15 K and 283.15 K.

STEP 1. The determination of γ_{13}^{∞}

T1 = 298.15 T2 = 283.15

From graphs 7 and 14 the intercepts $\boldsymbol{a}$ are obtained.

$a_{T1} = 0.02739$ $a_{T2} = 0.0465$

σa is obtained by equation 4.11. Thus

$a_{T1} = 0.02739 \pm 0.0003$ $a_{T2} = 0.0465 \pm 0.0003$

from equation 4.15

$$\gamma^{\infty}_{13(T1)} = \frac{8.134 \times 298.15}{0.02739 \times 68325.66} = 1.32 \qquad \gamma^{\infty}_{13(T2)} = \frac{8.314 \times 283.15}{0.0465 \times 37827.56} = 1.34$$

STEP 2. Determination of $\sigma\gamma^{\infty}_{13}$

$\sigma\gamma^{\infty}_{13}$ is determined by equation 4.19

At 298.15 K

$$\sigma\gamma^{\infty}_{13(T1)} = \frac{0.0003 \times 1.32^2 \times 68325.15}{8.314 \times 298.15} = 0.05$$

At 283.15

$$\sigma\gamma^{\infty}_{13(T2)} = \frac{0.0003 \times 1.33^2 \times 37827.56}{8.314 \times 283.15} = 0.01$$

STEP 3. The determination of P_3'

P_3' is obtained using the slope of graphs 7 and 14.

$b_{(T1)} = 0.0021 \pm 3.37\text{x}10^{-5}$ $\qquad$ $b_{(T2)} = 0.0015 \pm 0.0003$

The errors are obtained from equation 4.12.

To calculate P_3' the ratio of the slope to the intercept is used (equation 5.2).

Therefore

$$\frac{0.0021}{0.02739}\,(8.314\times298.15) = P'_{1(T1)}=189.1Pa$$

$$\frac{0.0015}{0.0465}.(8.314\times283.15)=P'_{1(T2)}=75.9Pa$$

STEP 4. The Determination of $\sigma P_3'$

$\sigma P_3'$ is determined from equation 4.23

At 298.15

$$\sigma_{P_3'} = 1.32 \times 68325.66\sqrt{(3.37x10^{-5})^2 - (\frac{189.1}{1.32^2 \times 68325.66})\,0.05^2} = 2.68$$

and at 283.15

$$\sigma_{P'_{1(T2)}} = 1.33 \times 37827.56 \sqrt{0.0003^2 - \frac{75.9}{1.33^2 \times 37827.56} \quad 0.01^2} = 15.19$$

STEP 5. The determination of $H_1^{E\infty}$

The calculated values for γ_{13}^{∞} at 298.15 K and 283.15 K are used to determine $H_1^{E\infty}$ using equation 4.25

$$\frac{8.314}{\frac{1}{298.15} - \frac{1}{283.15}} [\ln(1.32) - \ln(1.33)] = H_1^{E\infty} = 990 \, Jmol^{-1}$$

STEP 6. The determination of $\sigma H_1^{E\infty}$

$\sigma H_1^{E\infty}$ is determined using equation 4.31.

$$\sigma_{H_1^{E\infty}} = \sqrt{\left(\frac{8.314}{\frac{1}{298.15} - \frac{1}{283.15}}\right)^2 \left[\frac{0.01^2}{1.32^2} - \frac{0.01^2}{1.33^2}\right.} = 1500 \, J \, mol^{-1}$$

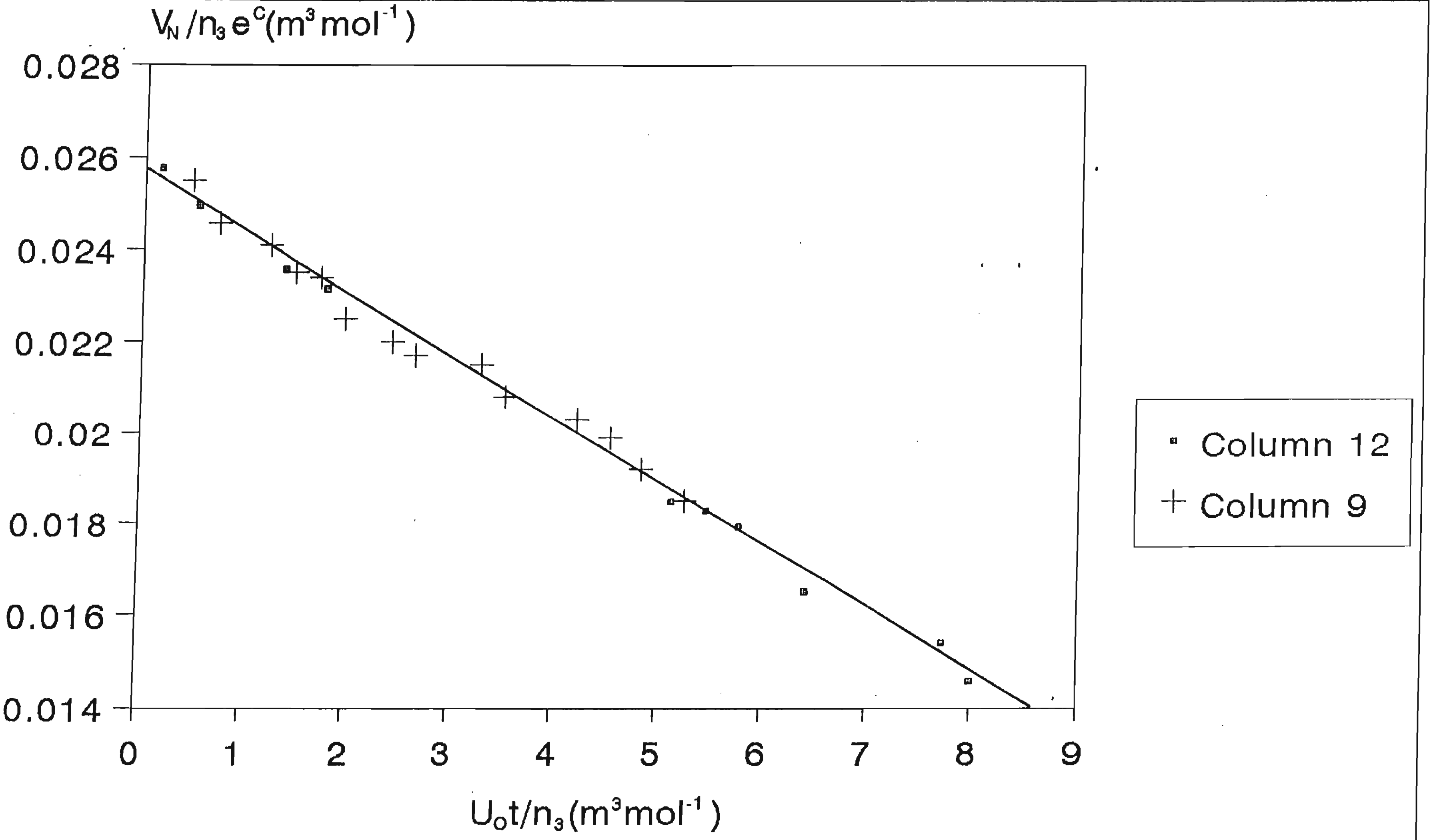


FIGURE 1. n-Pentane in cis-decalin at 298.15 K

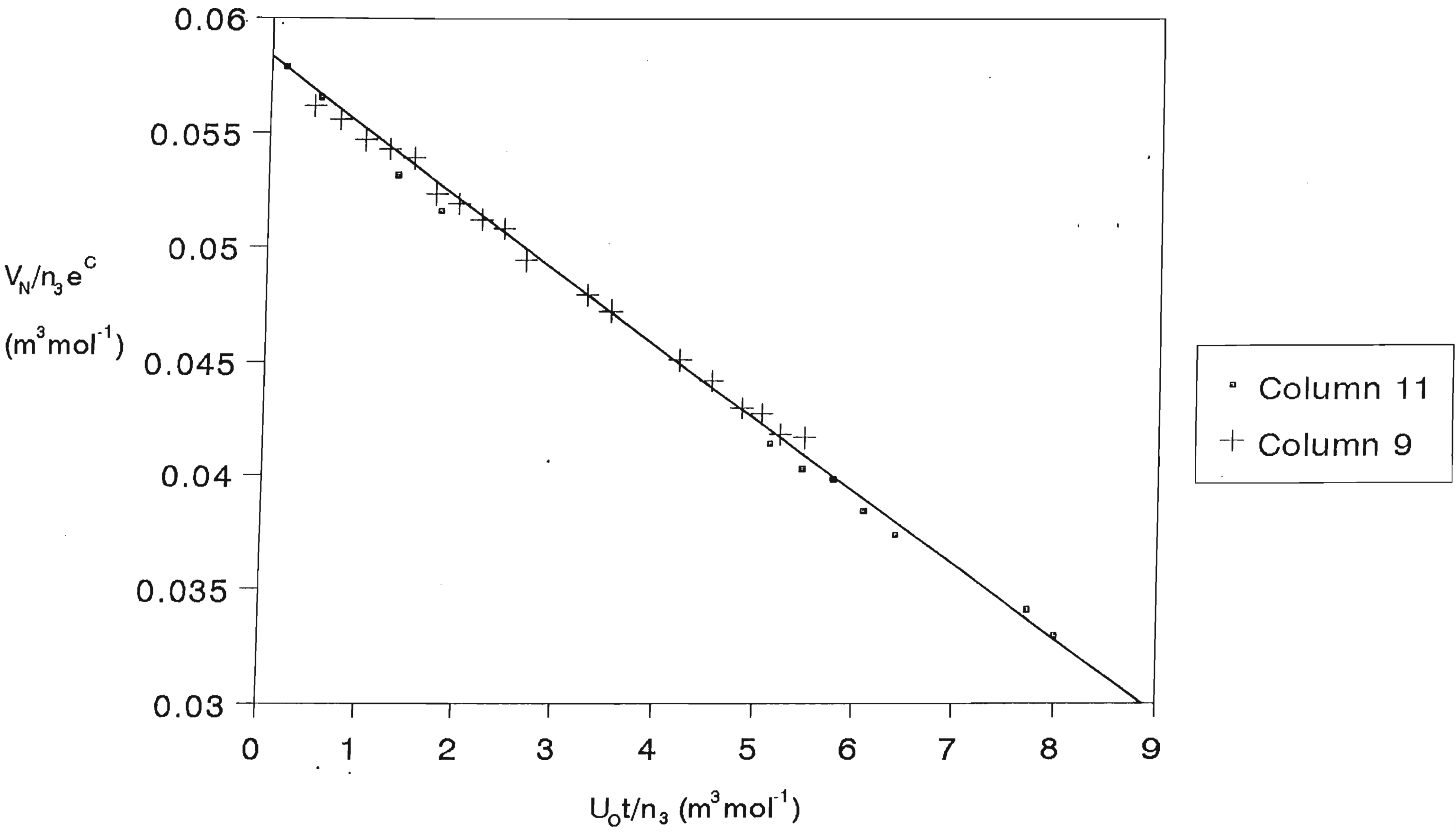


FIGURE 2. Cyclopentane in cis-decalin at 298.15 K

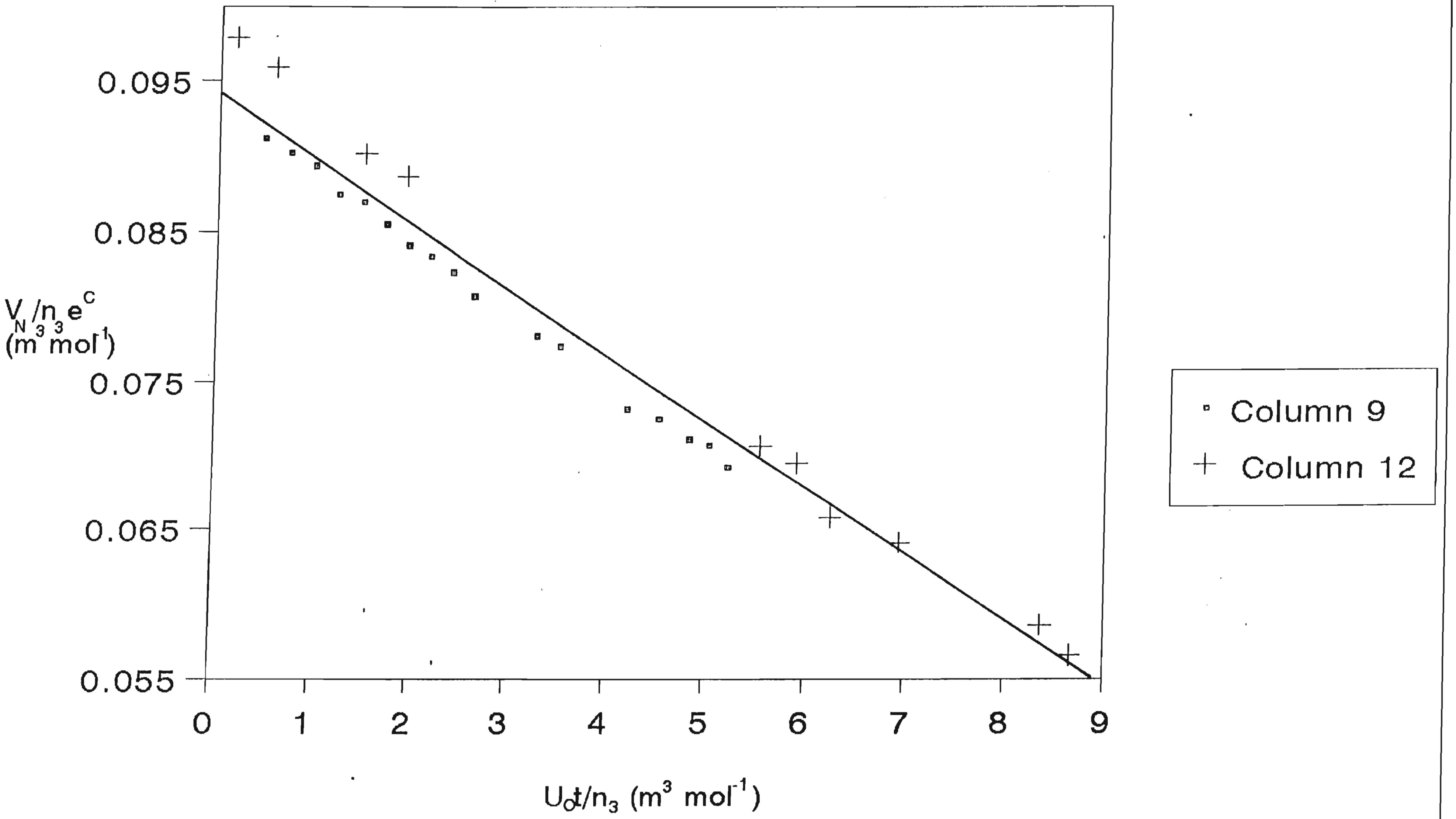


FIGURE 3. n-Hexane in cis-decalin at 298.15 K

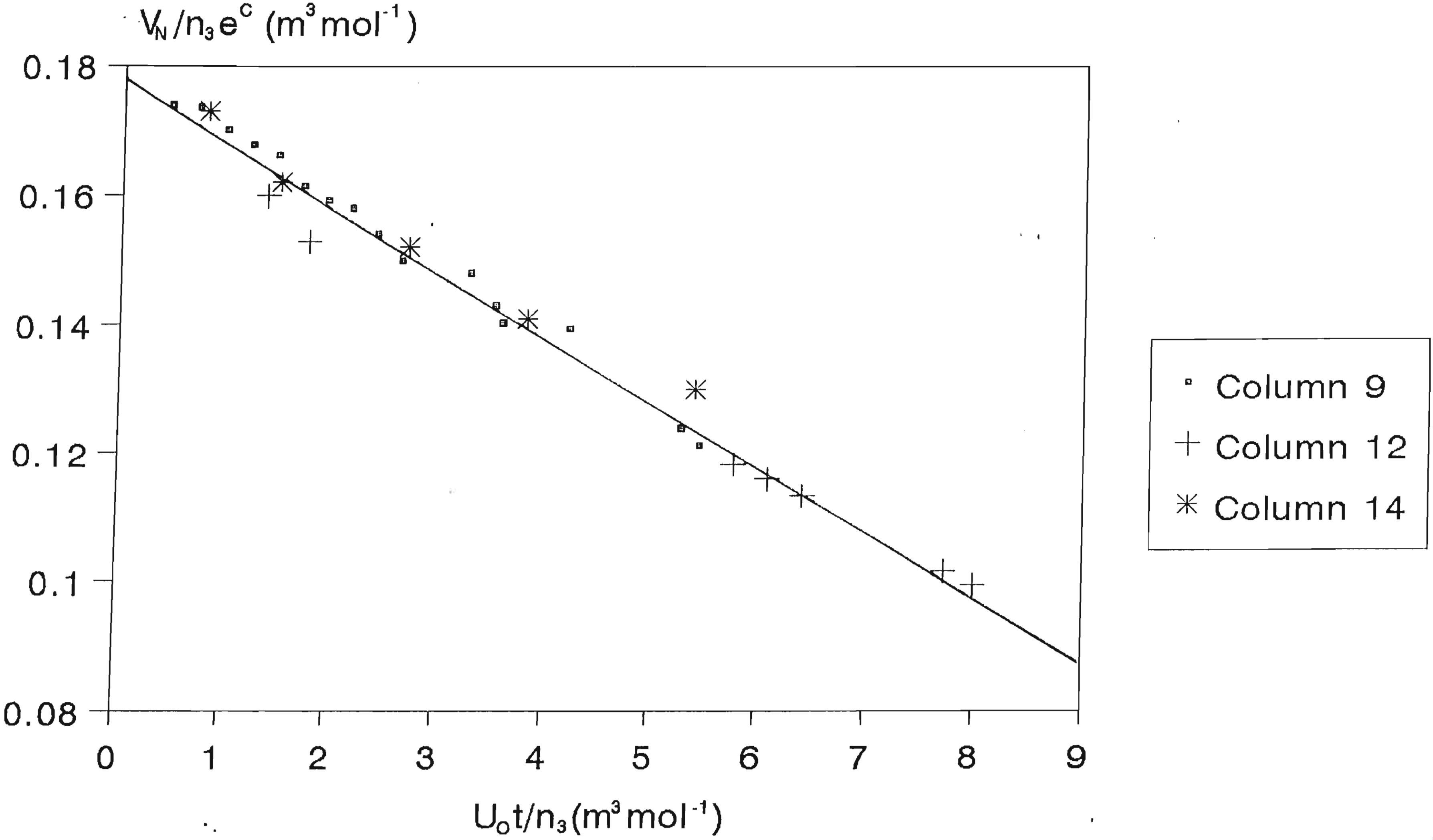


FIGURE 4. Cyclohexane in cis-decalin at 298.15 K

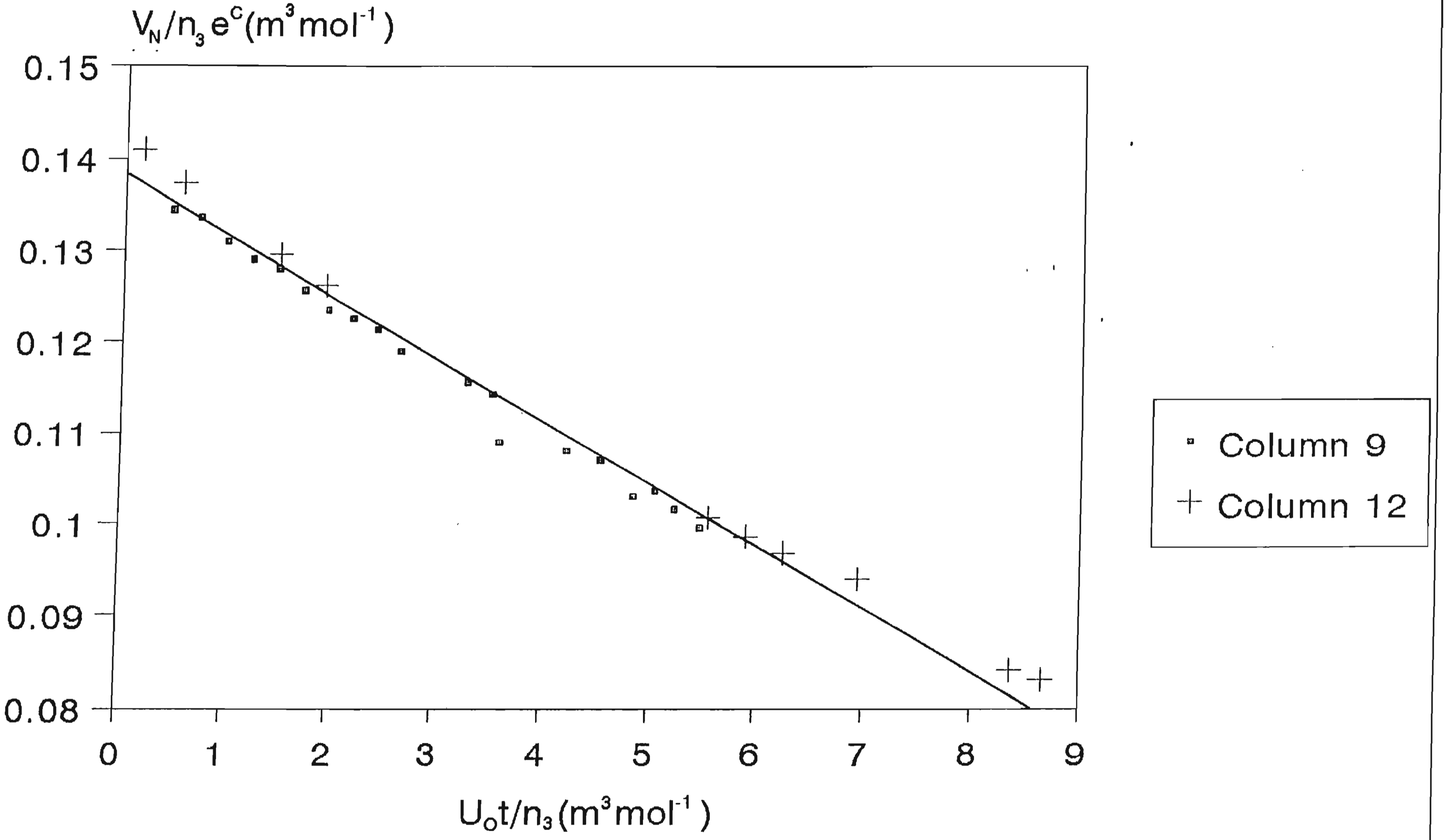


FIGURE 5. Benzene in cis-decalin at 298.15 K

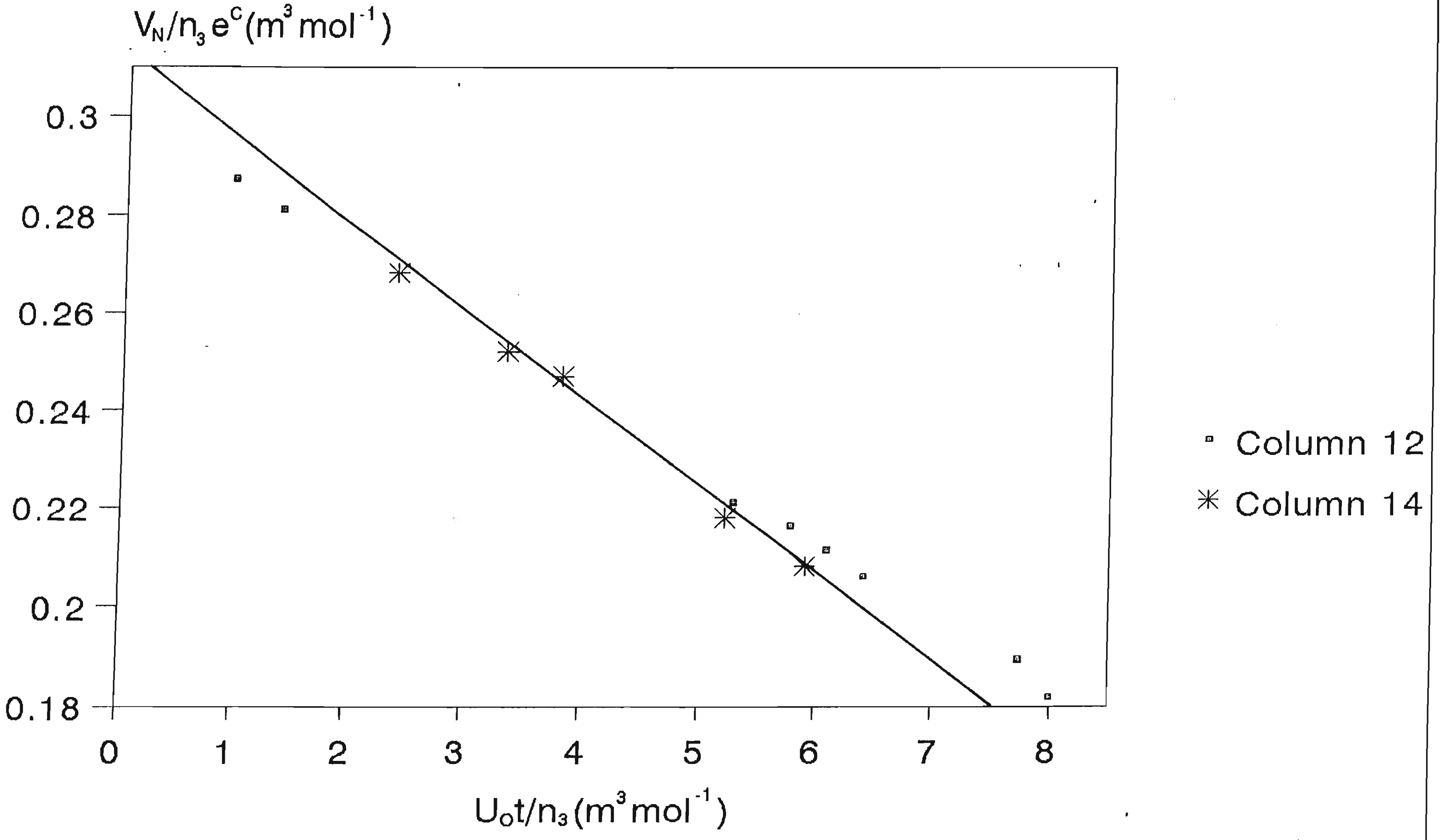


FIGURE 6. n-Heptane in cis-decalin at 298.15 K

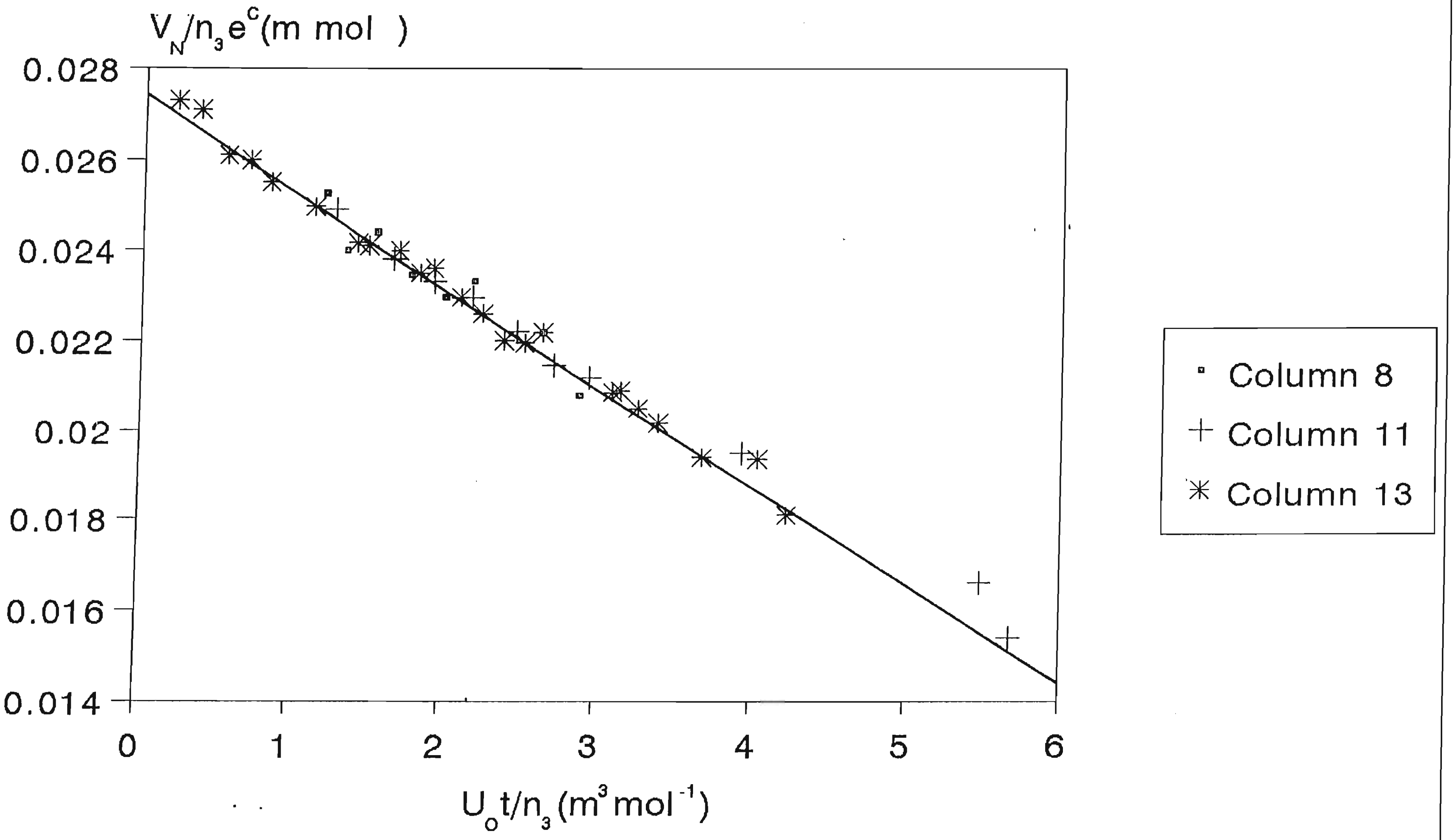


FIGURE 7. n-Pentane in trans-decalin at 298.15 K

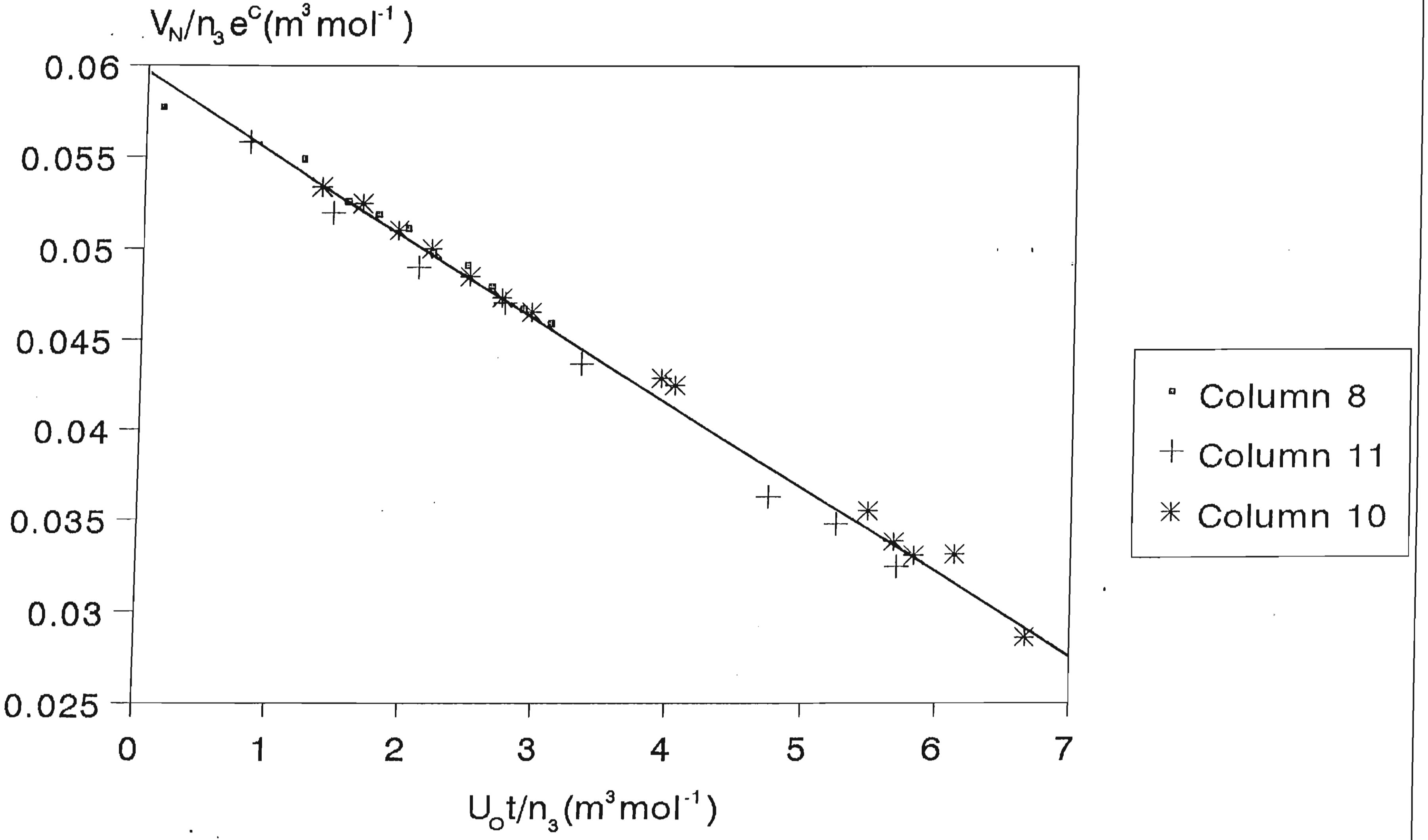


FIGURE 8. Cyclopentane in trans-decalin at 298.15 K

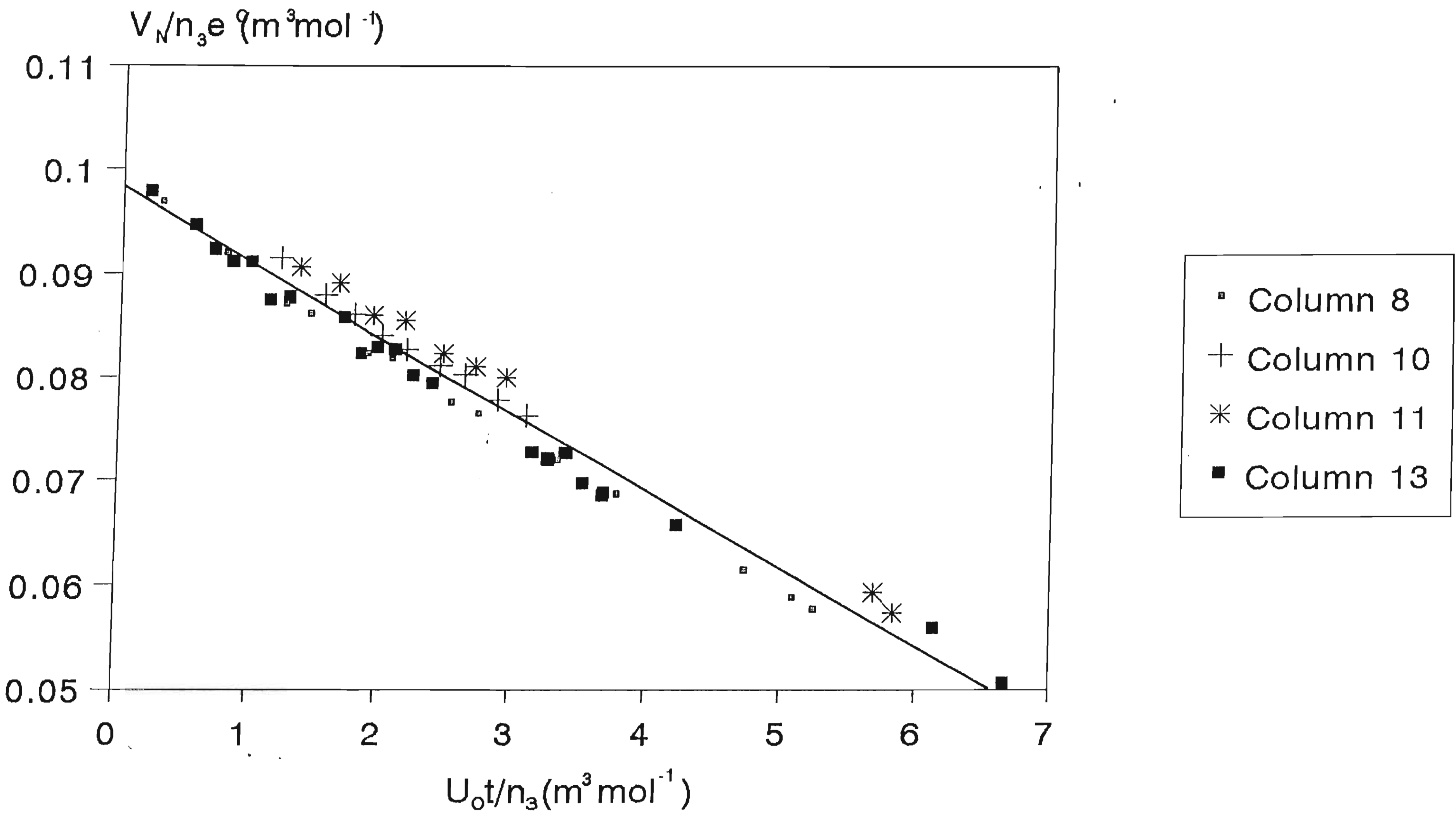


Figure 9. n-Hexane in trans-decalin at 298.15 K

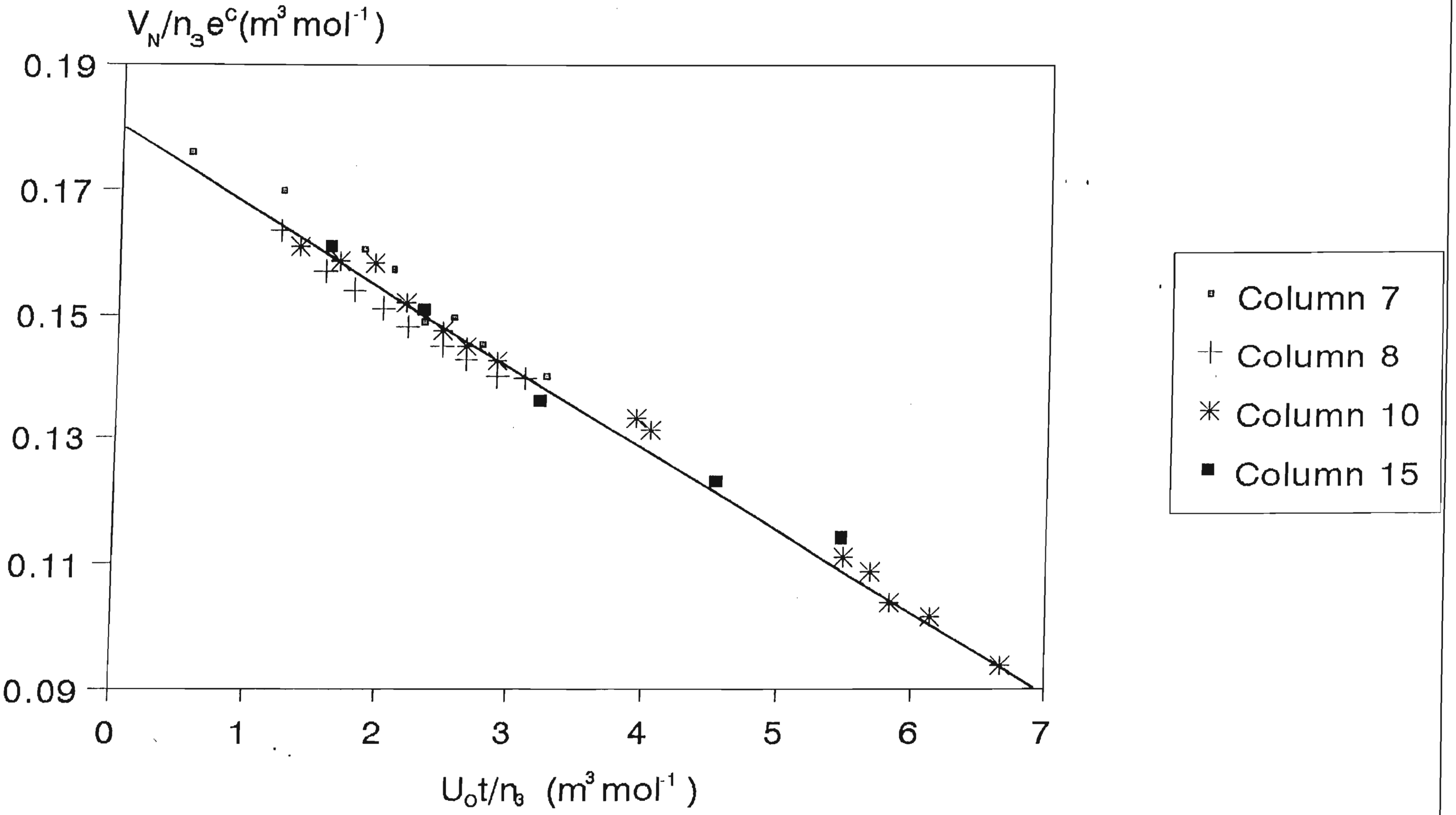


FIGURE 10. Cyclohexane in trans-decalin at 298.15 K

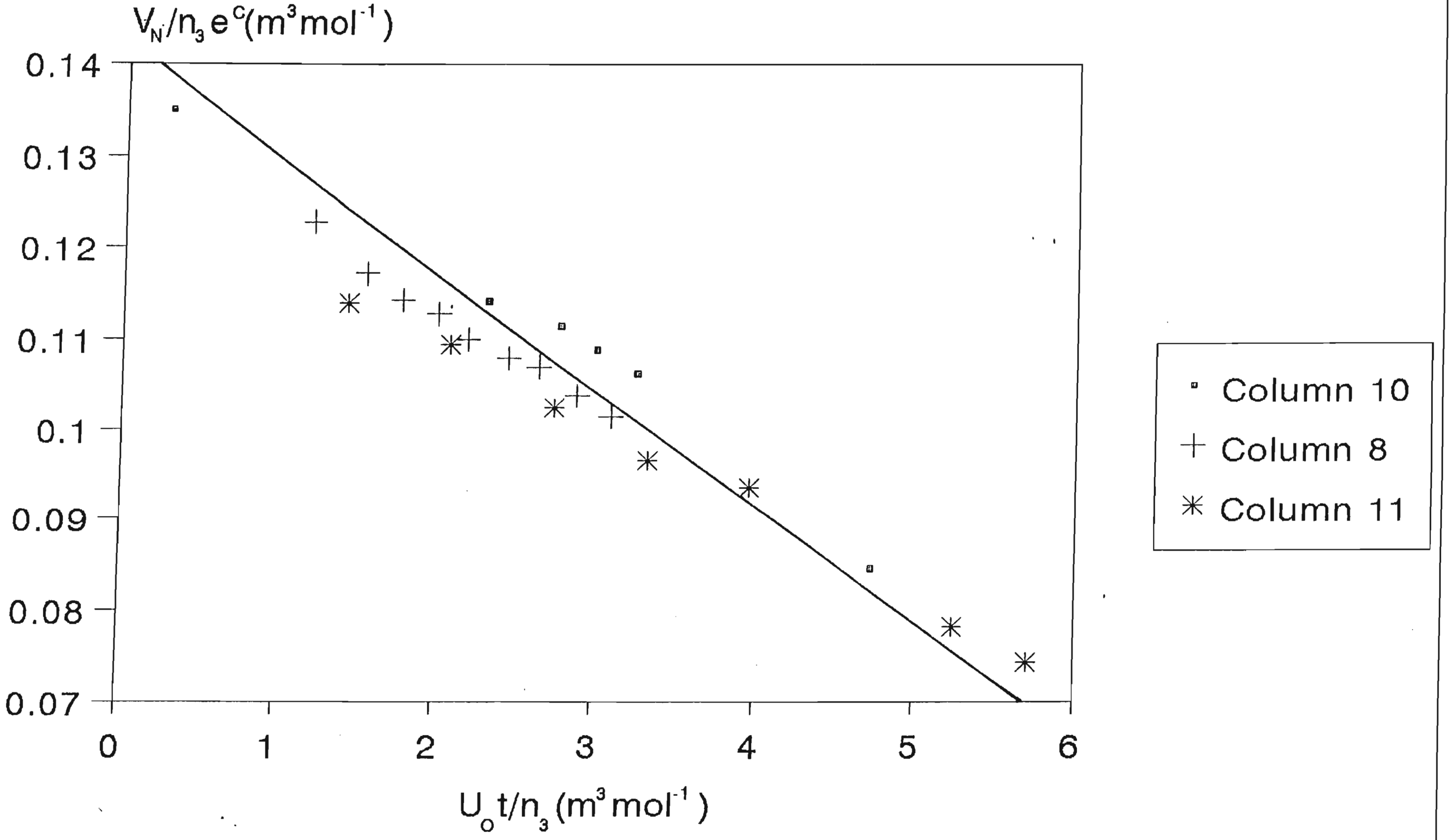


FIGURE 11. Benzene in trans-decalin at 298.15 K

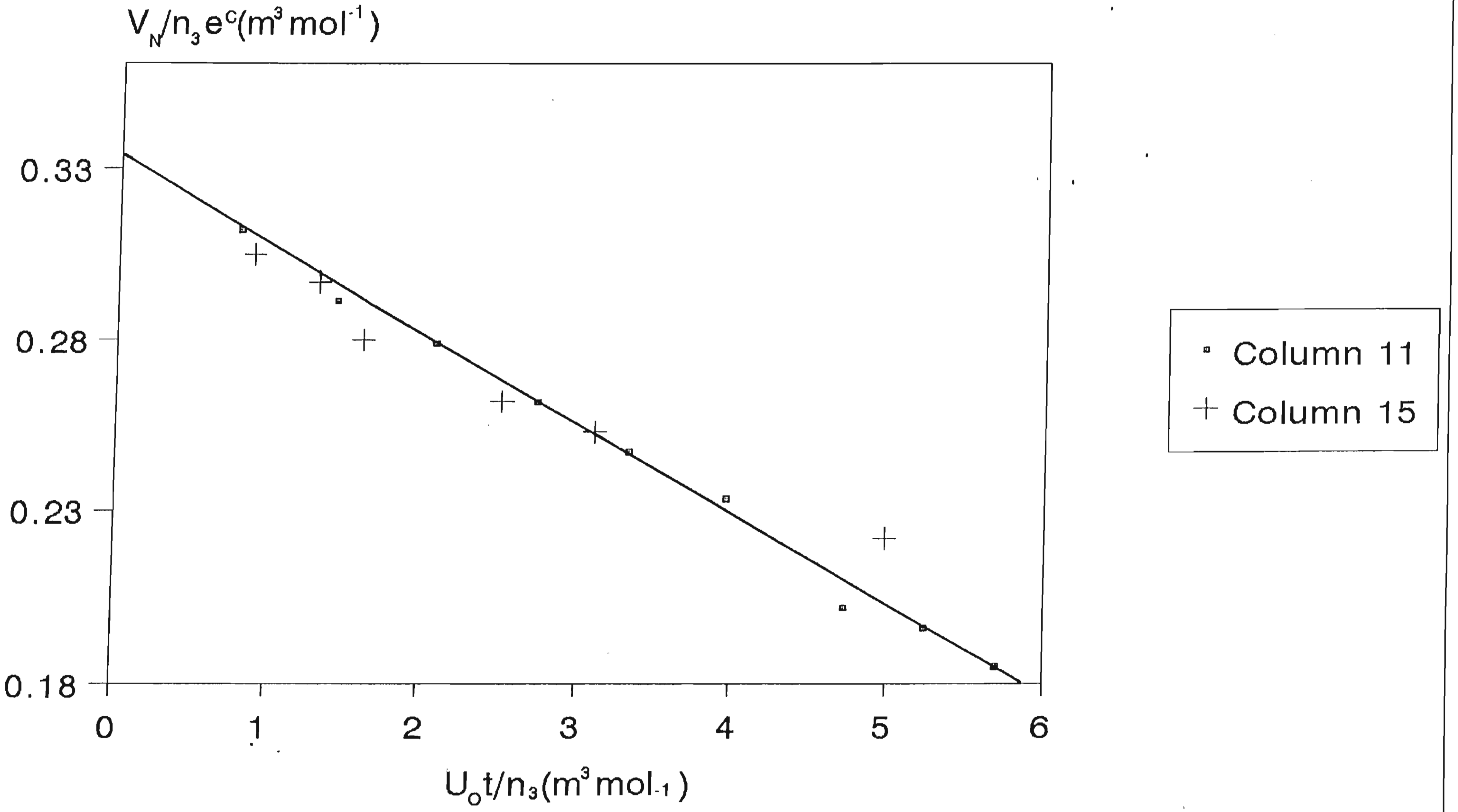


FIGURE 12. n-Heptane in trans-decalin at 298.15 K

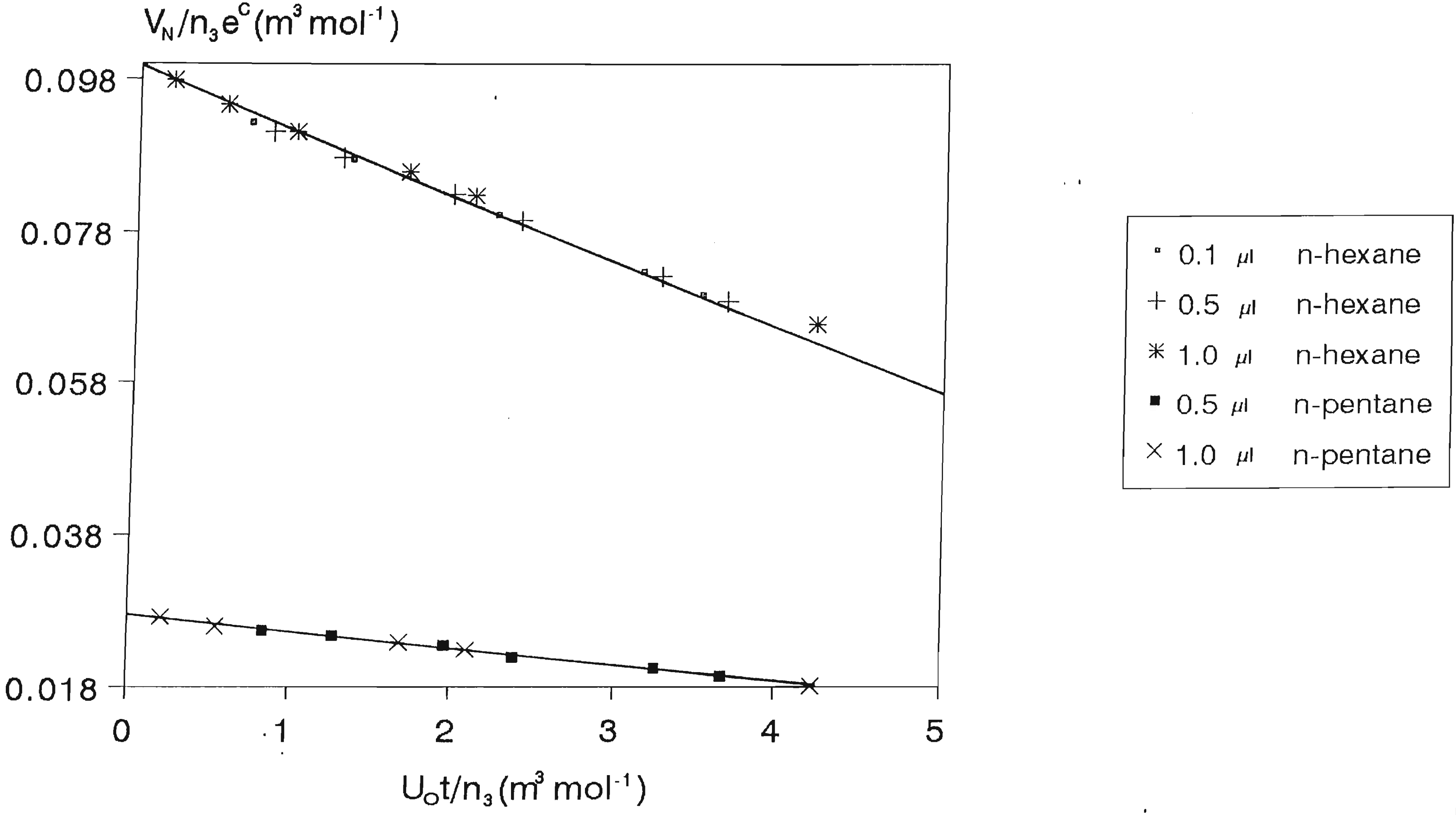


FIGURE 13. n-Pentane and n-Hexane in trans-decalin at 298.15 K

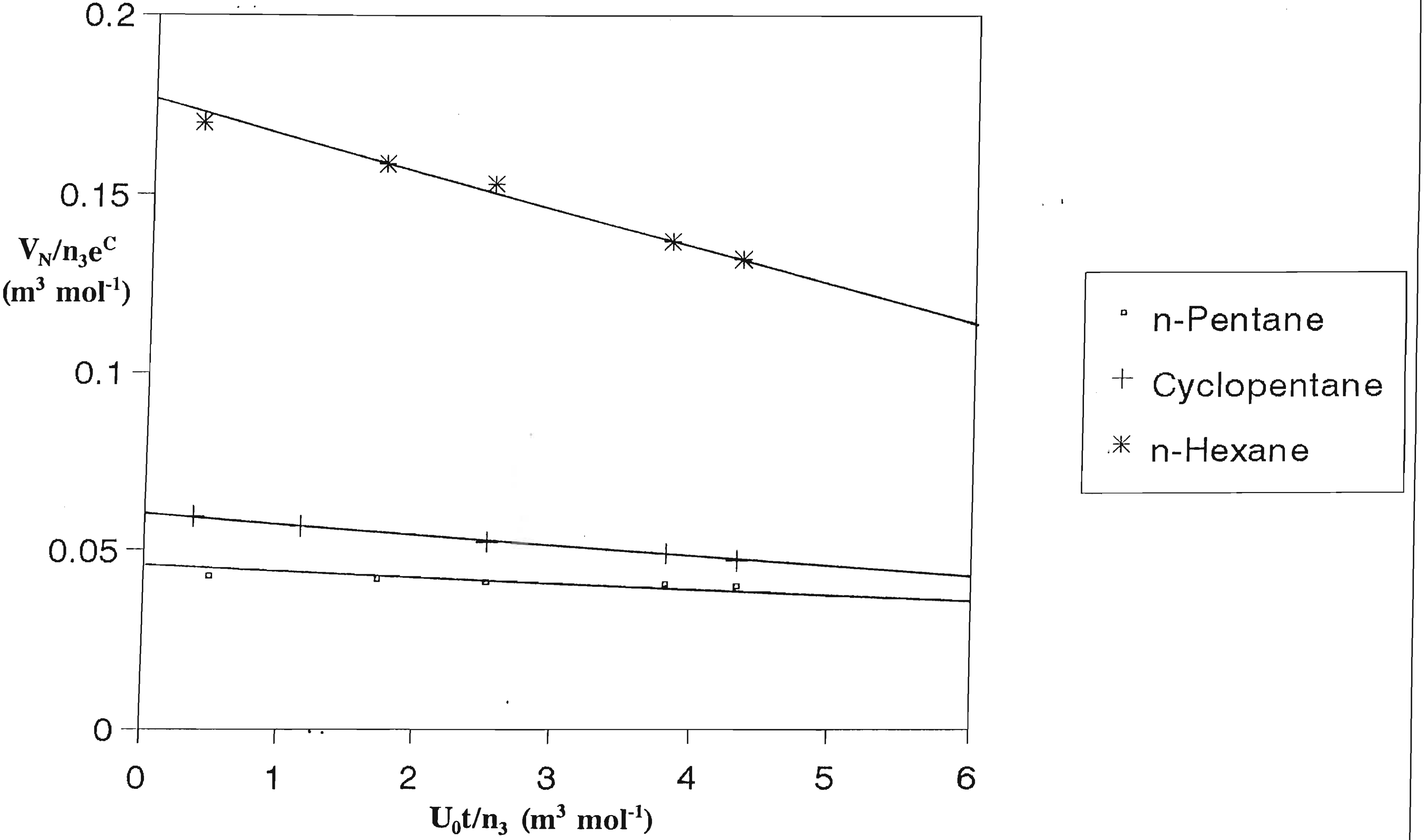


FIGURE 14. n-Pentane, cyclopentane and n-hexane in cis-decalin at 283.15 K

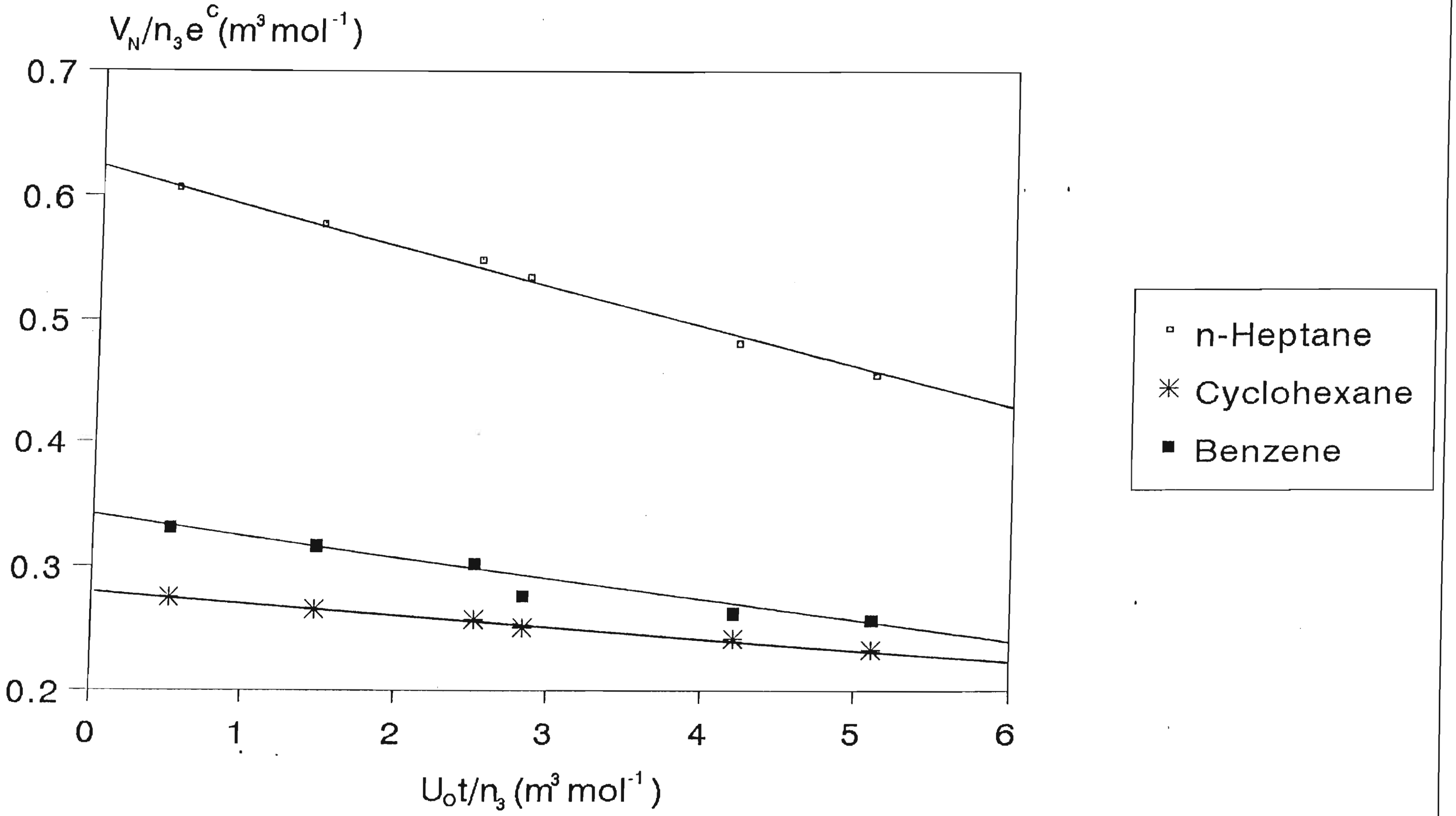


Figure 15. Cyclohexane, Benzene and n-Heptane in cis-decalin at 283.15 K

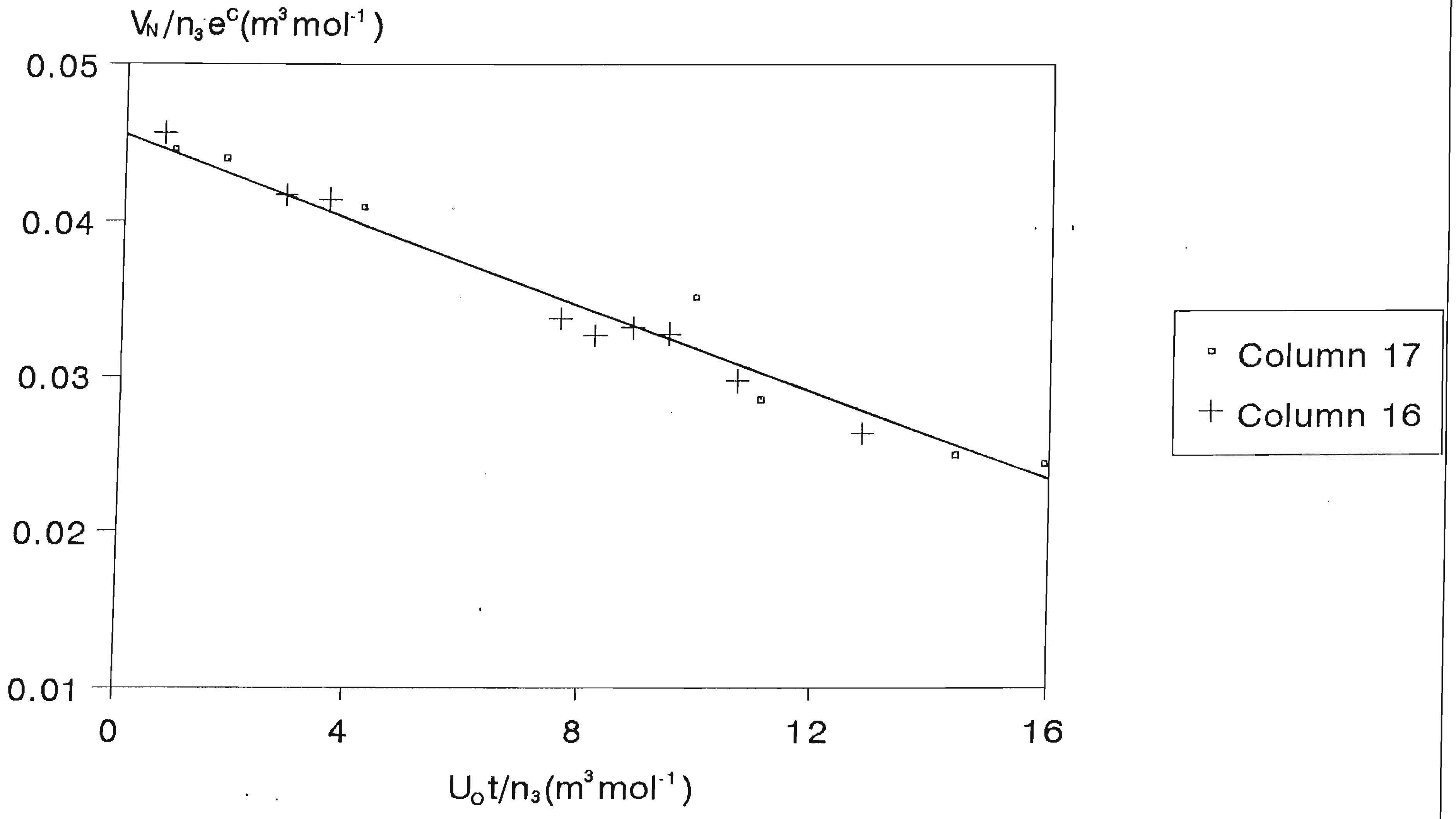


Figure 16. n-Pentane in trans-decalin at 283.15 K

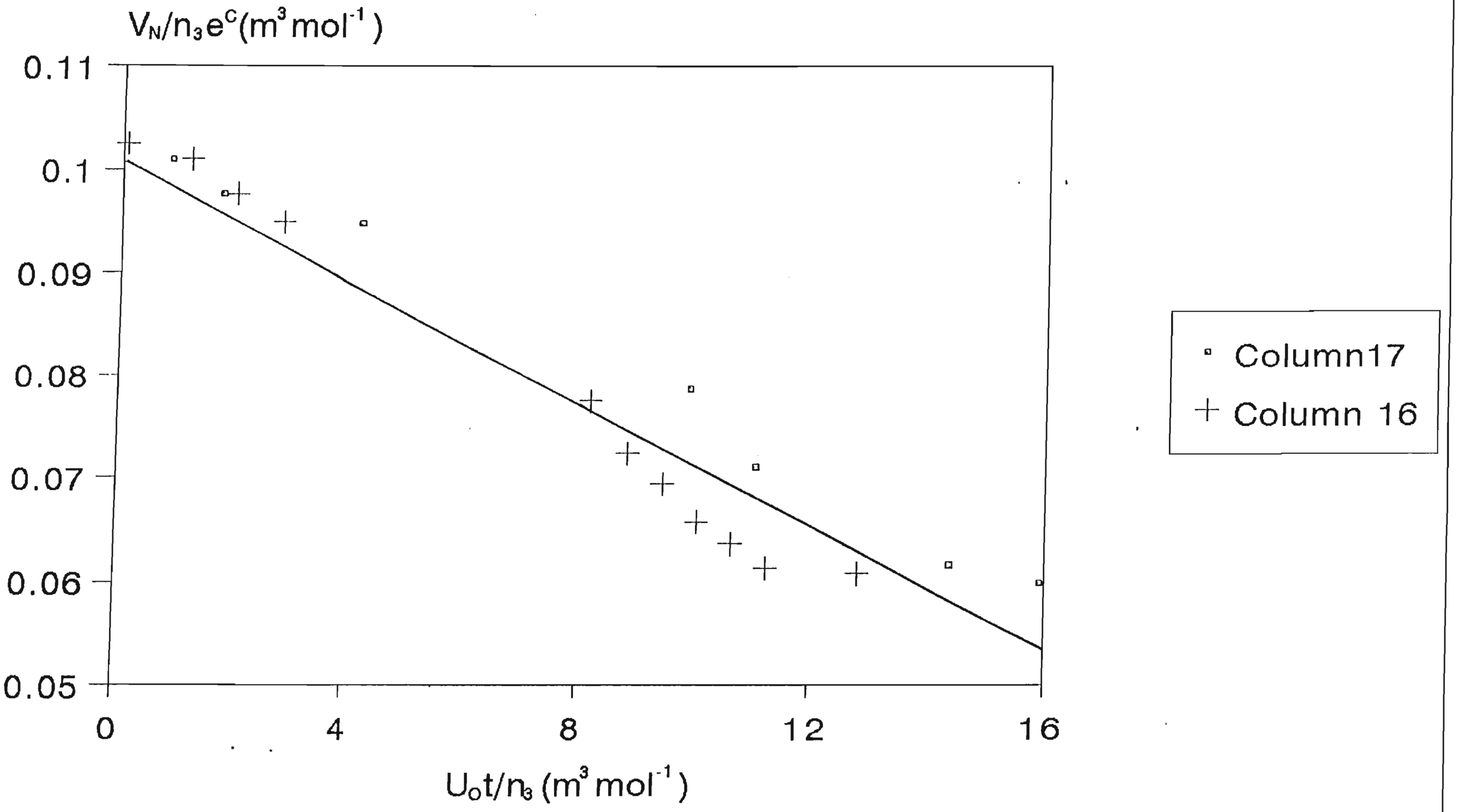


Figure 17. Cyclopentane in trans-decalin at 283.15 K

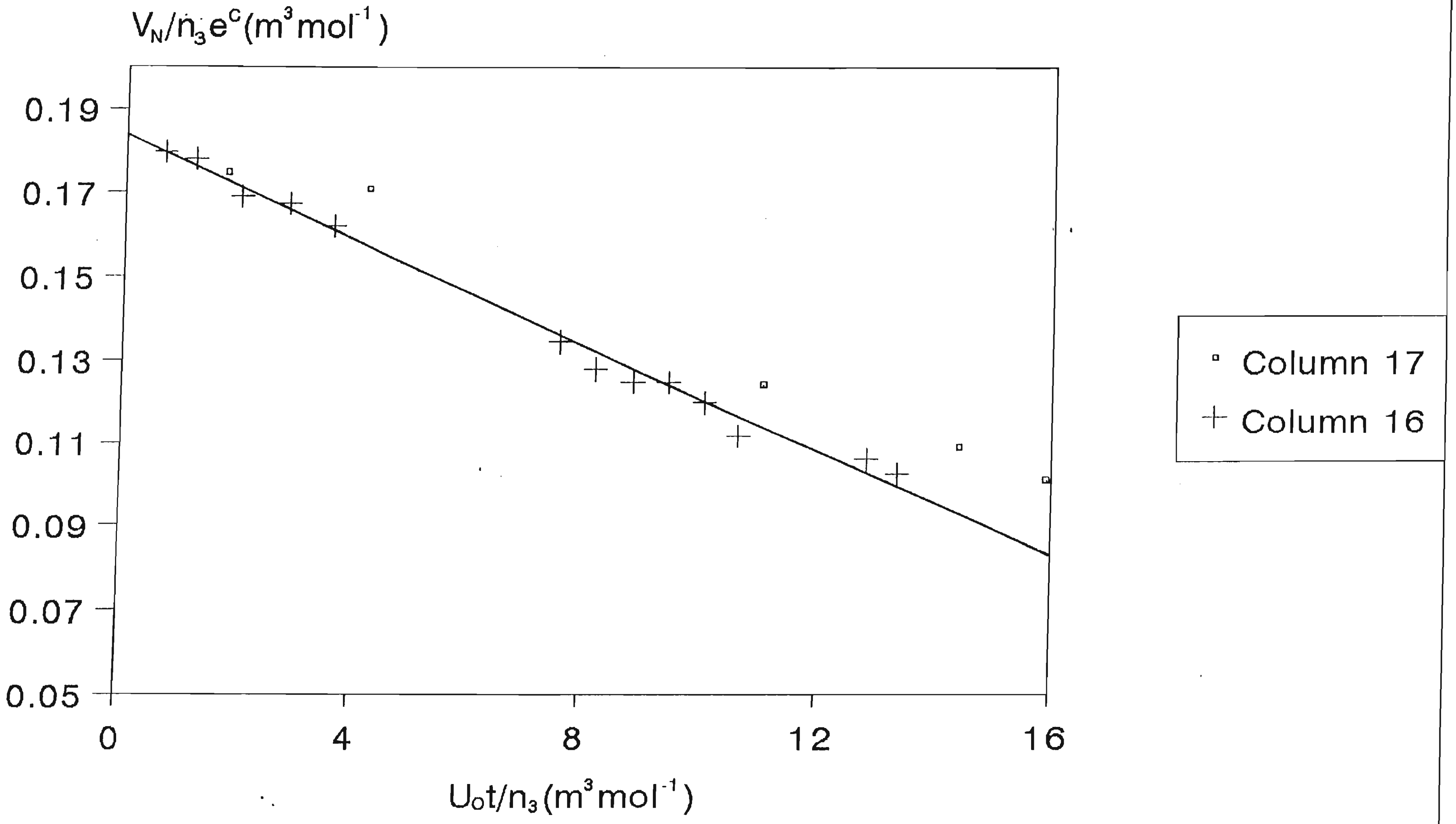


Figure 18. n-Hexane in trans-decalin at 283.15 K

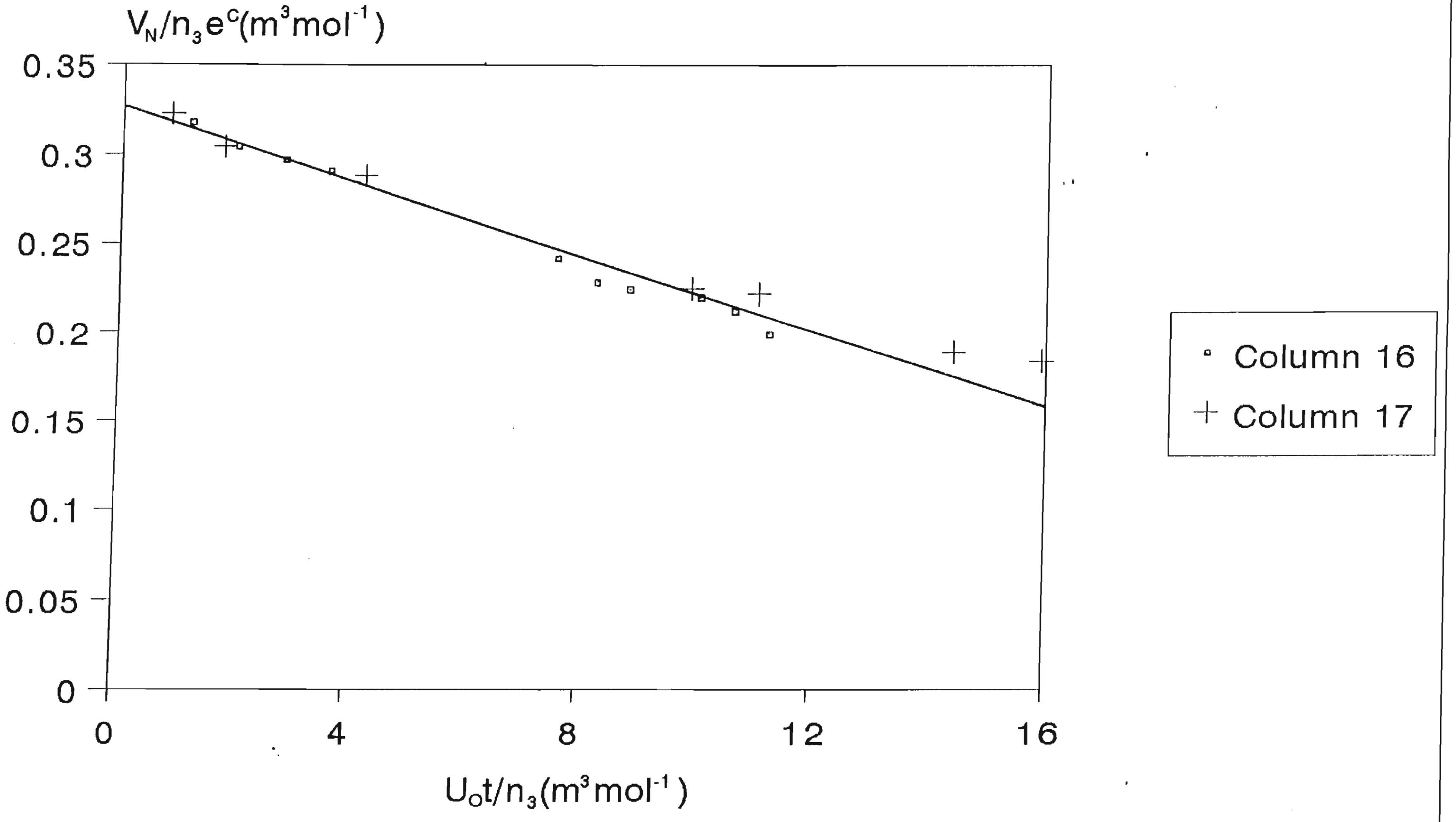


Figure 19. Cyclohexane in trans-decalin at 283.15 K

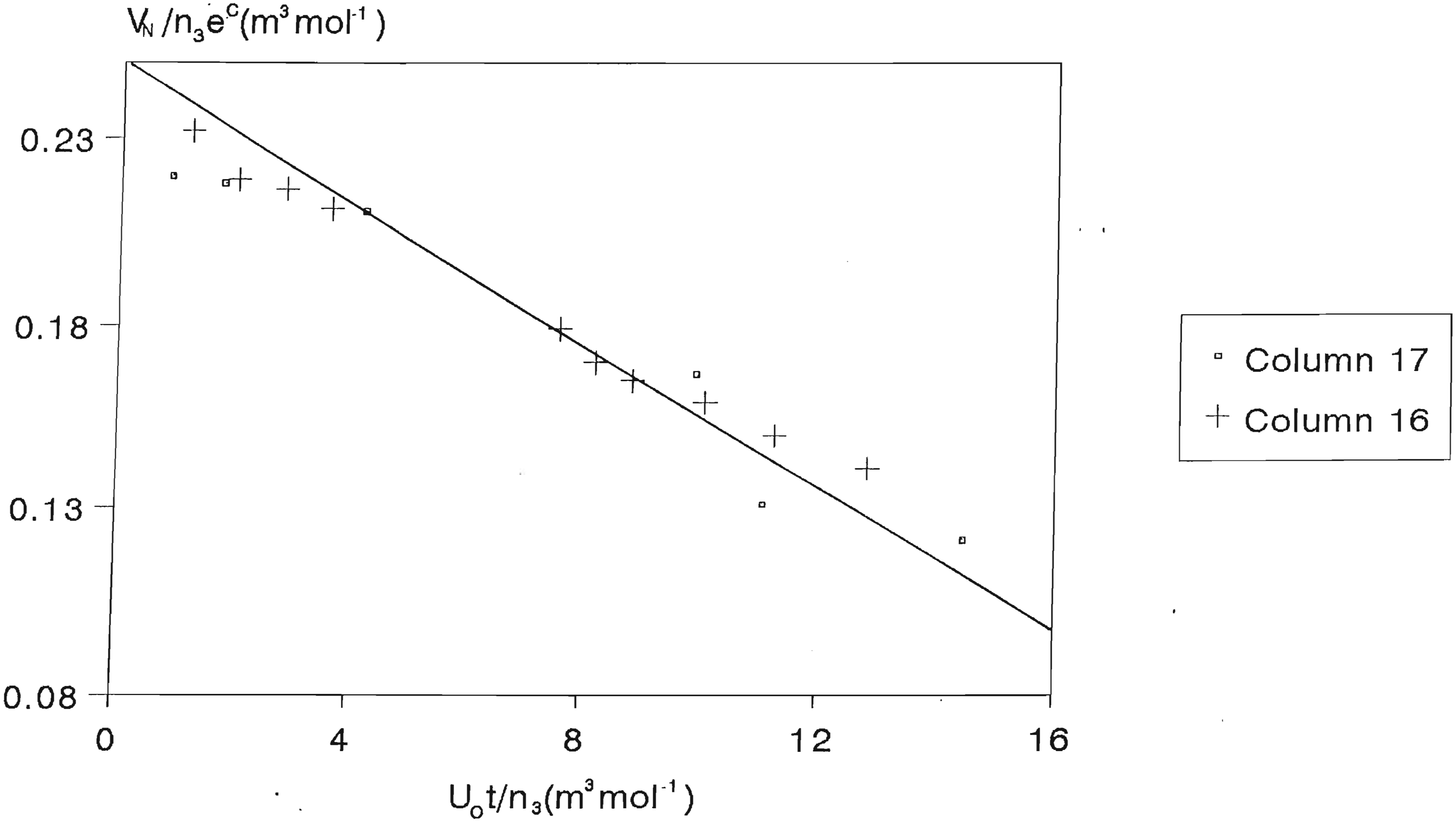


Figure 20. Benzene in trans-decalin at 283.15 K

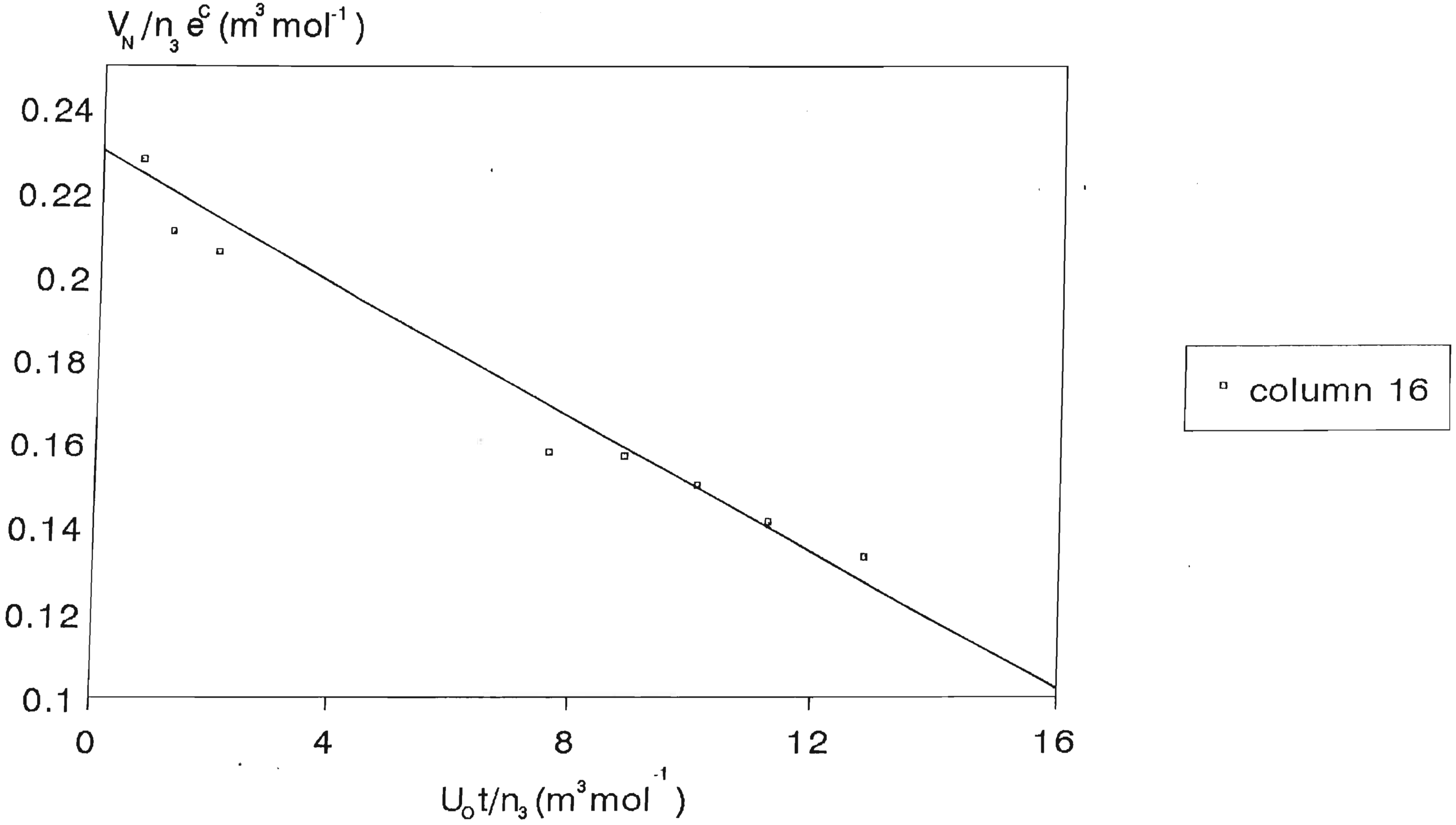


Figure 21. n-Heptane in trans-decalin at 283.15 K

5. DISCUSSION

The primary aim of this thesis was to develop a method to determine the activity coefficient at infinite dilution of solutes in volatile solvents at 298.15 K. The work was extended to include data at 283.15 K in order to test the possibility of determining the partial molar enthalpy at infinite dilution.

5.1. Experimental Error in γ_{13}^{∞}

Table 5.1 shows the values obtained for γ_{13}^{∞} for the solutes investigated in cis-and trans-decalin at 283.15 K and 298.15K. The experimental error for γ_{13}^{∞} was determined using equation 4.19.

TABLE 5.1. Calculated values of activity coefficients at infinite dilution (γ_{13}^{∞}) for solutes n-pentane, cyclopentane, n-hexane, cyclohexane, benzene and heptane at 283.15 K and 298.15 K in cis- and trans-decalin.

Solute	trans-decalin γ_{13}^{∞}(298.15K)	cis-decalin γ_{13}^{∞}(298.15 K)	trans-decalin γ_{13}^{∞}(283.15 K)	cis-decalin γ_{13}^{∞}(283.15 K)
n-pentane	1.32±0.05	1.41±0.07	1.33±0.01	1.44±0.03
C_5H_{10}	0.98±0.02	1.01±0.07	0.97±0.07	1.01±0.03
n-hexane	1.28±0.02	1.31±0.03	1.27±0.03	1.29±0.01
C_6H_{12}	1.06±0.08	1.07±0.10	1.14±0.10	1.09±0.02
benzene	1.45±0.02	1.42±0.01	1.63±0.01	1.39±0.03
n-heptane	1.22±0.04	1.35±0.02	1.22±0.02	1.36±0.04

The experimental errors range from 0.01 to 0.1 with most of the $\sigma(\gamma_{13}^{\infty})$ values at about 0.04. The error obtained at 283.15 K is similar to that obtained at 298.15 K.

Cruickshank(39) obtained an error for γ_{13}^{∞} of 0.03 for various hydrocarbons in n-octadecane at 315.15 K. Everett(40) obtained an error for γ_{13}^{∞} of 0.02 for various hydrocarbons using squalene as the stationary phase.
Although the errors obtained by these workers are lower than those obtained in this work it must be noted that the stationary phases used in both cases by Cruickshank and Everett were involatile. This was not the case with cis- and trans-decalin used in this work.

5.1.1. Precision of γ_{13}^{∞}

Precision is a measure of the internal consistency of results obtained and describes the reproducibility of repeated determinations.
Using the values of γ_{13}^{∞} (for each solute) calculated for each column, given in table 4.22, the precision of γ_{13}^{∞} is calculated from the following equation

$$s^2 = \frac{1}{N-1}\sum(x_i - \bar{x})^2 \qquad (5.1)$$

The precision for γ_{13}^{∞} at 298.15 K (table 5.2) for both cis-and trans-decalin ranges from 0.5 to 2 %, whereas at 283.15 K the precision ranges from 1.0 to 0.05 %. Some investigators have managed to reduce the standard deviation to the 0.02 - 0.05% region. However this high precision was obtained from a single column(41) unlike in this work where γ_{13}^{∞} is calculated from a number of columns differing in the amount of solvent on the column and in the flow-rate.

TABLE 5.2. Calculated values for the precision (as a percentage) of γ_{13}^{∞} for cis- and trans-decalin at 298.15 K and 283.15 K.

Solute	T/ 298.15 K		T/ 283.15 K trans-decalin
	trans-decalin %	cis-decalin %	%
n-pentane	2.0	0.5	0.05
cyclopentane	0.5	0.1	0.2
n-hexane	1.0	2.0	1.0
cyclohexane	1.5	2.0	0.2
benzene	1.0	1.5	1.0
n-heptane	0.5	2.0	0.5

5.2. Activity coefficient data at 298.15 K.

Due to the volatility of the stationary phase very little work has been done by other workers by the G.L.C. method for determining activity coefficients for the systems studied in this thesis. However Letcher and Baxter$^{(41)}$ have attempted the determination of γ_{13}^{∞} of various solutes in decalin by G.L.C. using a method outlined in chapter 2 with n-hexane as the reference solute. Letcher's results were calculated from data which was more empirical and little was known about the rate at which solvent loss occurred.

Letcher(42) has also successfully predicted γ_{13}^{∞} using an application of the Prigogine-Flory-Patterson theory. The γ_{13}^{∞} results obtained in this work compare favourably with Letcher's results. The only other literature values of measured γ_{13}^{∞} reported here have been conducted by Vernier et al.(43) However loss of solvent from the column was not taken into consideration by Vernier. It is difficult to asses Vernier's results because we do not have a detailed description of his method. His results are however well within our experimental error. His results together with Letcher's results and the results obtained in this thesis are given in table 5.3.

TABLE 5.3. Comparison of results for the activity coefficient at infinite dilution for trans-decalin at 298.15 K with literature values. The standard deviation σ, is given for the work presented in this thesis.(see Error Analysis, Chapter 4)

Solute	γ_{13}^{∞} This work	$\gamma_{13}^{\infty\,a}$	$\gamma_{13}^{\infty\,b}$	$\gamma_{13}^{\infty\,c}$	$\gamma_{13}^{\infty\,d}$
n-heptane	1.22 $\sigma = 0.04$	1.27	1.26	1.27	
n-hexane	1.28 $\sigma = 0.02$	1.32	1.31	1.32	1.26
benzene	1.45 $\sigma = 0.02$	1.40	2.17	2.09	1.47
Cyclohexane	1.06 $\sigma = 0.08$	1.10	1.09	0.96	1.06

[a] Experimental values of Letcher by G.L.C.(41) [b] and [c] Predicted values by Letcher using Prigogine-Flory-Patterson theory.(42) [d] Experimental values of Vernier by G.L.C.(43)

5.2.1. Comparison of γ_{13}^{∞} for cis- and trans-decalin

From table 5.1 (comparing γ_{13}^{∞} for cis- and trans-decalin at 298.15 K) it is clear that cis-decalin has a higher γ_{13}^{∞} value than trans for every solute, the largest difference in γ_{13}^{∞} being for the solute n-heptane and the smallest for cyclopentane. At 283.15 K all the solutes show the same behaviour as at 298.15 K, except for the two six sided cyclic molecules (cyclohexane and benzene) where the effect is reversed and the γ_{13}^{∞} value for cis-decalin is lower than for trans-decalin.

5.2.2. Infinite Dilution Conditions

The volume of the solute required to satisfy infinite dilution conditions is investigated by injecting varying volumes of n-hexane (1.0 μl, 0.5μl and 0.1μl) and n-pentane (1.0μl and 0.1μl) on to the same column. γ_{13}^{∞} is calculated for each volume. These values are given in Table 5.4.

Table 5.4. γ_{13}^{∞} of n-hexane and n-pentane for different injection volumes.

	1.0μl n-hexane	0.1μl n-hexane	0.5μl n-hexane	1.0μl n-pentane	0.1μl pentane
γ_{13}^{∞}	1.27	1.28	1.28	1.31	1.32

From table 5.4 it is clear that a volume between 1.0μl and 0.1μl of solute is required to satisfy infinite dilution conditions. The minimum detectable volume was 0.1 μl.

5.3. The Significance and Calculation of P_3^l

Table 5.5. shows the values obtained for P_3^l (partial pressure of the solute in cis- and trans-decalin) at 298.15 K and 283.15 K. obtained from equation 4.6. From the equation the intercept $a = RT/\gamma_{13}^{\infty} P_1^*$ and the slope $b = P_3^l / \gamma_{13}^{\infty} P_1^*$. dividing b by a

$$\frac{b}{a} = \frac{P_3^l}{RT} \qquad (5.2)$$

from which P_3^l may be calculated. σ (P_3^l) is determined using eq. 4.31.

TABLE 5.5. Experimental and Literature values of the average P_3^l at temperatures 298.15 K and 283.15 K for cis- and trans-decalin.

	T/ 298.15 K		T/ 283.15 K	
	trans-decalin / Pa	cis-decalin / Pa	trans-decalin / Pa	cis-decalin / Pa
Experimental values	189.0±8.1	127.3±6.4	75.9±2.6	100.8±38.9
Literature values(44)	164.4	104.3	55.7	33.7

Assuming equilibrium conditions are satisfied in the column, this method should be capable of predicting the vapour pressure of the solvent. Data for the vapour pressure of trans-decalin and cis-decalin have been reported by Camin and Rossini(44), and fitted to an Antoine equation over the temperature range 372.95 K to 469.55 K for cis-decalin and 365.45 K to 461.05 K for trans-decalin. An extrapolation to 298.15 K using this equation gives values for the saturated vapour pressure of 104.3 Pa for cis-decalin and 164.4 Pa for trans-decalin at 298.15 K, and 33.7 Pa and 55.7 Pa for cis- and trans-decalin respectively at 283.15 K. In view of the length of the extrapolation involved it is quite probable that P_3^l obtained in this work at 298.15 K, (189.0±8.1 Pa and 127.3 ± 6.4 Pa for trans- and cis-decalin respectively) is a good estimate for the saturated vapour pressure, but further work is required in order to establish whether the solvent is actually in equilibrium along the column.

The P_3^l results determined by G.L.C. at 283.15 K are very different from the extrapolated data using the Antoine equation. This could be due to the unreliability of the extrapolation and it is also possible that equilibrium is not as good at 283.15 K as it is at 298.15 K.

P_3^l is dependent on the slope, and is therefore very sensitive to experimental error. The precision, calculated from equation 5.1, depends on how far the range of the controlled variable (time) can be extended, to reduce the effect of data point scatter, before the uncertainty in the slope due to curvature becomes commensurate with scatter.(41)

It is possible that the large scatter in P_3^l is largely due to the problem associated with the drawing of the correct slope for the line U_0t/n_3 versus V_N/n_3e^C. This effect can be explained with reference to figure 5.1. where + refers to the data points of any column allowed to operate for a short time and □ refers to the data points of a column allowed to operate for a longer time. It is clear that the slope is affected by points further along the x axis. Thus two different values for P_3^l could be obtained. This explanation can be directly associated with some of the work presented in this thesis where there are columns containing different amounts of decalin (eg. a 3 % and

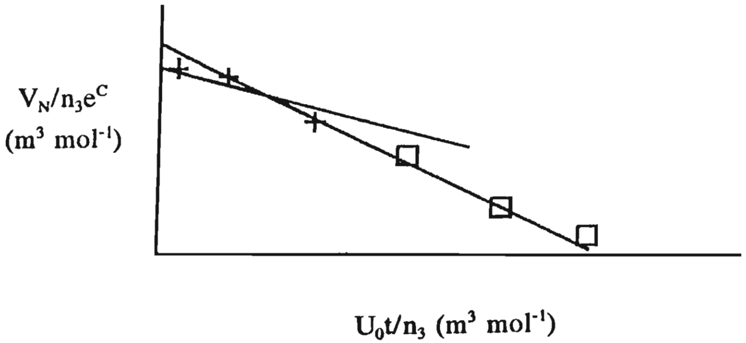


Figure 5.1. Diagramatic representation of the difficulty associated with obtaining the correct slope.

15 % column), where + could refer to the 3 % column and ☐ to the 15 % column since under normal circumstances the 15% column will be in operation for a longer time than the 3 % column and therefore contain more data points further along the x axis.

The error in P_3' then depends on the difficulty associated in obtaining the same slope from different columns.

5.4.Determination of $H_1^{E\infty}$

5.4.1 Theory

5.4.1.1.$H_1^{E\infty}$ from γ_{13}^{∞} Values

The activity coefficient at infinite dilution γ_{13}^{∞}, based on the pure component standard state is related to the partial molar excess free energy by

$$\ln\gamma_{13}^{\infty} = \frac{G_1^{E\infty}}{RT} \tag{5.3}$$

Applying the Gibbs-Helmholtz equation directly to equation 5.3

$$\left(\frac{\partial \ln\gamma_{13}^{\infty}}{\partial T}\right)_P = \left[\frac{\partial\left(\frac{G_1^{E\infty}}{RT}\right)}{\partial T}\right]_P = \frac{-\Delta H_1^{E\infty}}{RT^2} \qquad (5.4)$$

Integrating from some reference temperature

$$\ln\gamma_{13(T_1)}^{\infty} - \ln\gamma_{13(T_2)}^{\infty} = \int_{\frac{1}{T_2}}^{\frac{1}{T_1}} \frac{H_1^{E\infty}}{R}\, d\left(\frac{1}{T}\right) \qquad (5.5)$$

$$\ln\gamma_{13(T_1)}^{\infty} - \ln\gamma_{13(T_2)}^{\infty} = \frac{H_1^{E\infty}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (5.6)$$

5.4.1.2. $H_1^{E\infty}$ from H^E data using the Redlich Kister equation.

Finite concentration enthalpies of mixing are usually expressed in the form :

$$H^E = x_1(1-x_1)[A+B(1-2x_1)+C(1-2x_1)^2] \qquad (5.7)$$

Equation 5.7 is known as the Redlich Kister equation.

The partial molar enthalpy of mixing at mole fraction

$$x_1 = \frac{n_1}{(n_1+n_2)} \qquad (5.8)$$

is given by:

$$H_1^E = \left(\frac{\partial H^E}{\partial n_1}\right)_{n_2} = (1-x_1)\frac{dH^E}{dx_1} + H^E \qquad (5.9)$$

At infinite dilution ($x_1 = 0$) this becomes:

$$H_1^{E\infty} = \frac{dH^E}{dx_1} = A + B + C \qquad (5.10)$$

Errors for $H_1^{E\infty}$ are in the order of 300-400 J mol^{-1} for an error of 5 J mol $^{-1}$ in H^E.

5.4.1.3. The Tangent to Intercept Method (Rhizobium method)(45) of determining $H_1^{E\infty}$

The molar excess enthalpy of a solution is given by

$$H_m^E = \frac{H^E}{n_a + n_B} \qquad (5.11)$$

Then

$$H_1^{E\infty} = \left(\frac{\partial H^E}{\partial n_a}\right)_{n_b} = H_m^E + (n_a + n_b)\left(\frac{\partial H_m^E}{\partial n_a}\right)_{n_b} \qquad (5.12)$$

Now the derivative with respect to mole number of A, n_A, is transformed into a derivative with respect to mole fraction B, X_B ,

$$\left(\frac{\partial H_m^E}{\partial n_A}\right)_{n_B} = \frac{dH_m^E}{dX_B}\left(\frac{\partial X_B}{\partial n_a}\right)_{n_B} \qquad (5.13)$$

since

$$X_B = \frac{n_B}{n_A + n_B} \qquad (5.14)$$

and

$$\left(\frac{\partial X_B}{\partial n_A}\right)_{n_B} = -\frac{n_B}{(n_A + n_B)^2} \qquad (5.15)$$

Thus eq. 5.12 becomes

$$H_1^E = H_m^E - \frac{n_B}{n_A + n_B} \cdot \frac{dH_m^E}{dX_B} \qquad (5.16)$$

$$H_1^E = H_m^E - X_B \frac{dH_m^E}{dX_B} \qquad (5.17)$$

The application of this equation is illustrated in figure 5.2. where H^E is plotted against mole fraction. From the figure the distance S_1A_1 is equal to the slope at X_{B1} multiplied by X_{B1} ie. $X_B(dH_m^E/dX_B)$ (see equation 5.17). It follows that $O_1S_1 = O_1A_1 - S_1A_1$ equals H_1^E (partial molar excess enthalpy) since O_1A_1 equals the molar excess enthalpy (H_m^E).

Therefore drawing a tangent to the curve, the intercepts at $x = 0$ and $x = 1$ yields the values for the partial molar enthalpies of both components at the specified mixture composition. To determine the partial molar excess enthalpy at infinite dilution a tangent has to be drawn at $x = 0$ and extrapolated to the $x = 1$ axis. This intercept on the $x = 1$ axis is $H_1^{E\infty}$. For the best results, values of H^E as close to $x_1 = 0$ as possible should be used, otherwise the tangent method will produce large errors in determining $H_1^{E\infty}$, in the region of 300-400 J. This is true in this work as the value of H^E (from the literature)$^{(46)}$ were taken from the whole concentration range and not particulary close to $x = 0$. No data was available in the literature in the concentration range $0.1 > x_1 > 0.05$ mole fraction. $H_1^{E\infty}$ values were calculated from γ_{13}^∞ (T_1 =298.15 K and T_2 = 283.15 K) and are given in table 5.6. together with errors calculated using equation 4.32. These values are compared with extrapolated enthalpy data from the literature using equation 5.7.

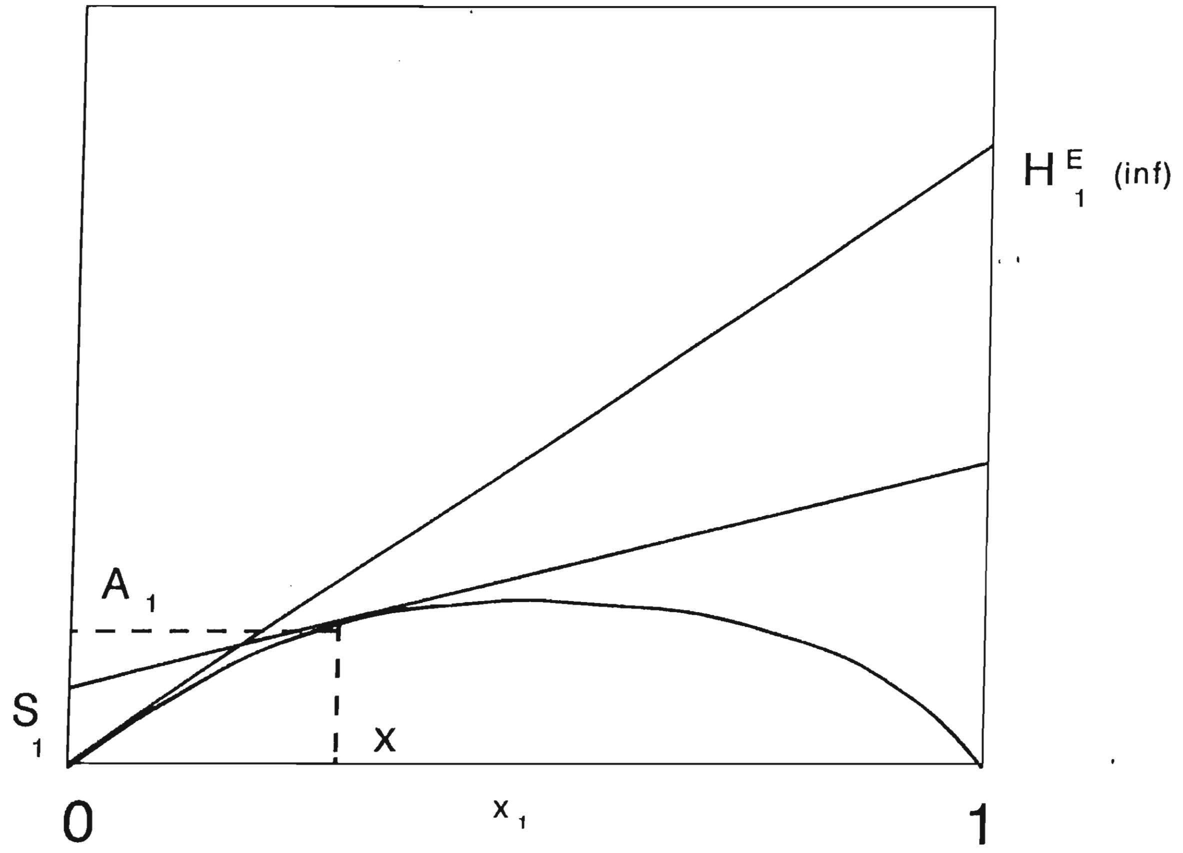


Figure 5.2. Graphical construction to obtain partial molar entalpies at infinite dilution showing the error incurred in the extrapolation

TABLE 5.6. Partial molar excess enthalpy at infinite dilution for cis- and trans-decalin with various solutes at 298.15 K.

Solute	trans-decalin		cis-decalin	
	$H_1^{E\infty}$ / J mol^{-1}	$H_1^{E\infty}$ § / J mol^{-1}	$H_1^{E\infty}$ / J mol^{-1}	$H_1^{E\infty}$ § / J mol^{-1}
n-Pentane	350±1700		990± 1500	
Cyclopentane	-500± 700	-1100 ± 400	0± 140	
n-Hexane	-700± 660	-110 ± 300	-366± 800	600± 300
Cyclohexane	870± 2000	100 ± 300	3400± 1000	260± 300
Benzene	-5470± 1400	2700± 500	-1000± 800	
n-heptane	0 ± 40	-70 ± 300	450± 1400	600± 300

§ the enthalpy values in these columns have been determined from finite concentration data.(46)

The errors in determining $H_1^{E\infty}$ from G.L.C. are very large, ranging between 450 J mol^{-1} and 2000 J mol^{-1}. The error in determining $H_1^{E\infty}$ from finite concentration H^E measurements is also large in the range 300-500 J mol^{-1}. From the table it can be seen that only the values obtained for $H_1^{E\infty}$ (using the temperature dependence of γ_{13}^{∞}) for n-heptane (in solvents cis- and trans-decalin) and n-hexane (in solvents trans-decalin), compare favourably with the values from literature. It is apparent that due to the large errors in determining γ_{13}^{∞} from G.L.C. the accurate calculation of $H_1^{E\infty}$ is impossible. When an excess partial molar enthalpy of mixing is determined from retention measurements at two different temperatures, T_1 and T_2, there is an optimum temperature difference which should be employed to maximise precision.(47) If the difference is too small the error in measuring retention is large in relation to the difference in retention. Young(47) states that the larger the difference in temperature the smaller the error in $H_1^{E\infty}$

Letcher and Marsicano(27) attempted to extract entropy from the temperature dependence of $\log_{10} \gamma_{13}^{\infty}$ at 308.15 K and 328.15 K using short chain (C_5 and C_6) saturated and unsaturated hydrocarbons in longer chain (C_{16} and C_{18}) saturated and unsaturated liquid hydrocarbons . However this too proved unsuccessful since the difference in $\log_{10}\gamma_{13}^{\infty}$ at 308.15 and 328.15 K was of the order of the experimental scatter.

The activity coefficients of most systems which have been studied accurately by G.L.C., exhibit small or medium temperature dependence ie. γ_{13}^{∞} does not change by more than 0.002 per K.(47) Since the experimental precision of γ_{13}^{∞} is usually of the order of 0.03, estimation of $H_1^{E\infty}$ requires measurements of γ_{13}^{∞} over a 30-40 K temperature range. Alternatively more precise values of γ_{13}^{∞} must be determined.

Martire(48) suggested that due to the above difficulties it was probably not possible to obtain meaningful $H_1^{E\infty}$ results from chromatographic data. Moreover $H_1^{E\infty}$ of systems for which γ_{13}^{∞} have a low temperature dependence are greatly affected by gas phase imperfections. A substantial part of $H_1^{E\infty}$ obtained in cases for which $H_1^{E\infty}$ is small may actually be due to the correction for gas phase imperfections.(47)

Young(47) states that the gas chromatographic method (or indeed any method that measures free energies as a function of temperature, and hence $H_1^{E\infty}$), will never provide as accurate or as convenient an alternative as the calorimetric techniques.

5.6. Conclusion

From the comparison of γ_{13}^{∞} with the literature data obtained it can be concluded that the method developed in this work for determining activity coefficients of solutes in volatile solvents is a reliable one.

However the attempt at determining $H_1^{E\infty}$ proved not to be conclusive. Due to the small range of temperatures involved the experimental errors were usually larger than the property being determined, $H_1^{E\infty}$.

The method does 'however' appear to be a good one for measuring vapour pressures of moderately volatile solvents.

5.7. Future Work

There are many moderately volatile solvents which can be used as stationary phases (bicyclohexyl, tetralin, decane, etc.) which will be studied to test the new technique. The technique could prove to be valuable in determining the vapour pressure of liquids in the range 10 to 1000 Pa ie., between 10^{-4} atms. and 10^{-2} atms.

APPENDIX I

Computer Program (GAMMA) for the calculation of V_N and γ_{13}^{∞}

```
10  PRINT " Calculation of activity coefficient at infinite dilution using G.L.C. data"
20  INPUT " INPUT THE RETENTION TIME OF THE UNRETAINED GAS"; t_g
30  INPUT " INPUT THE FLOW RATE"; U_o
40  V_D = t_g * U_o
50  PRINT " THE DEAD SPACE IS "; V_d : PRINT
60  INPUT " INPUT THE RETENTION TIME OF THE SOLUTE"; t_r
70  V_r = t_r * U_o
80  PRINT " THE RETENTION VOLUME IS "; V_R
90  INPUT " THE OUTLET PRESSURE "; P_i
100 INPUT " THE INLET PRESSURE"; P_o
110 A = (P_i/P_o)^2 -1
120 B = (P_i/P_o)^3 -1
130 J_2^3 = 3/2 * (A/B)
140 PRINT " THE NET RETENTION VOLUME IS " V_N
180 R = 8.314
190 INPUT " INPUT THE MOLES OF SOLVENT "; n_3
200 INPUT " INPUT THE TEMPERATURE"; T
210 INPUT " INPUT THE VAPOUR PRESSURE OF THE SOLUTE"; P_1^*
220 GAMMA = (N*R*T)/(V_N P_1^*)
230 PRINT  "THE UNCORRECTED ACTIVITY COEFFICIENT IS "; GAMMA
240 INPUT " INPUT THE FIRST VIRIAL COEFFICIENT"; B_11
250 INPUT " INPUT THE MOLAR VOLUME OF THE SOLUTE"; V_1^*
260 C = ((B_11 - V_1^*)/RT)*P_1^*
270 INPUT " INPUT THE MIXED VIRIAL COEFFICIENT"; B_12
280 D = ({(2*B_12 - V_1^*)/RT} *P_o*J}
290 G = GAMMA - C + D
310 PRINT " THE CORRECTED ACTIVITY COEFFICIENT IS"; G
```

APPENDIX II

In the theoretical plate model, the column is regarded as divided up into large number of theoretical plates small enough so that the concentration of sample in both mobile and stationary phases can be regarded as uniform.

Each plate consists of 2 volumes, ie. the volume of free gas (ΔV_G) and of liquid (ΔV_L); the sum of the volumes being the total plate volume Δx, thus

$$\Delta x = \Delta V_G + \Delta V_L \qquad (1)$$

The solute sample in the first theoretical plate is distributed between the stationary and mobile phase according to a partition coefficient, such that at equilibrium a fraction z of solute exists in the gas phase and a fraction y in the liquid phase.(17)

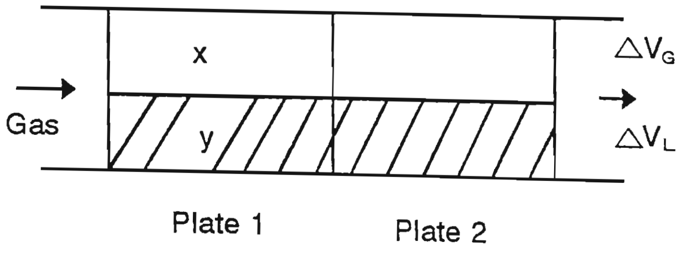
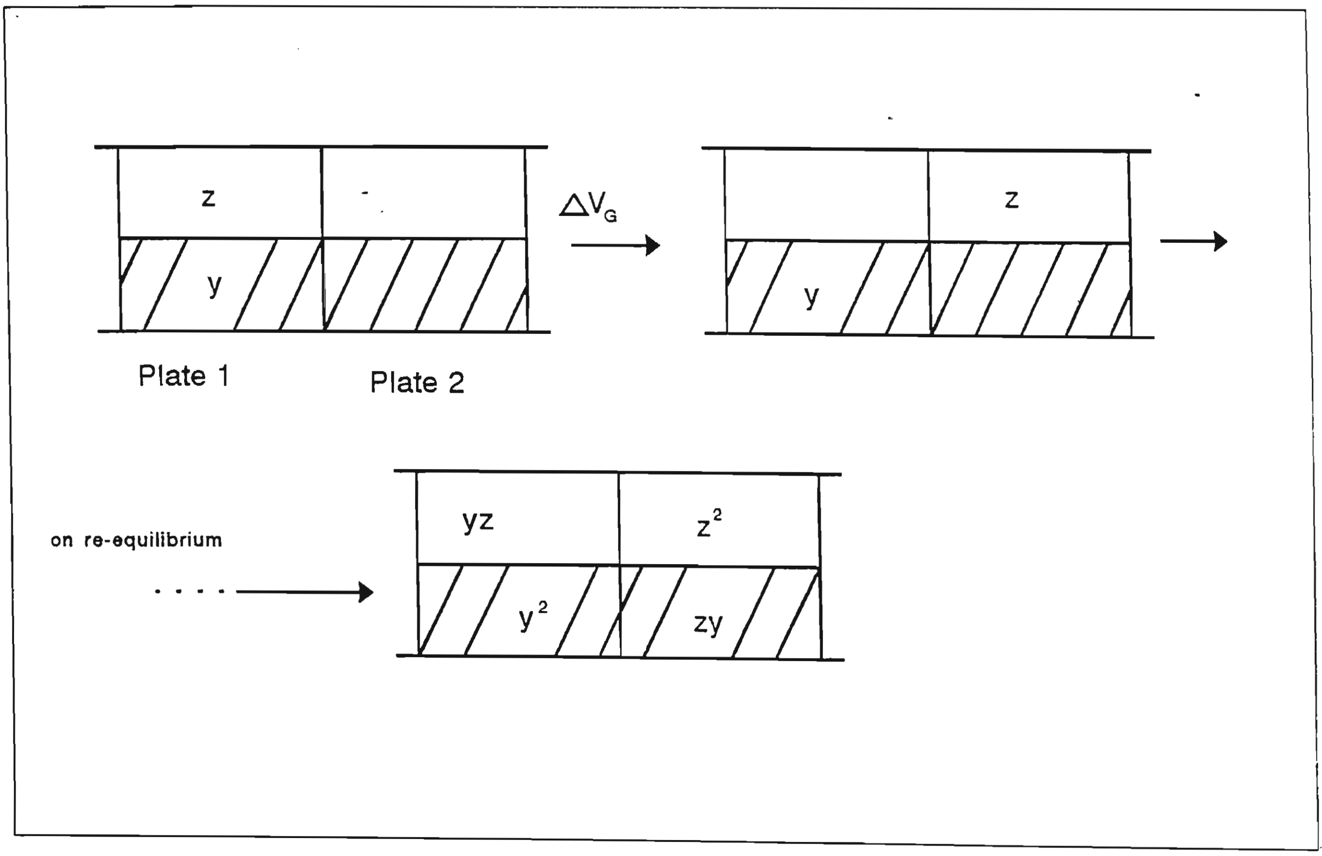


Diagram 1. Diagramatic view of a packed column according to the plate theory

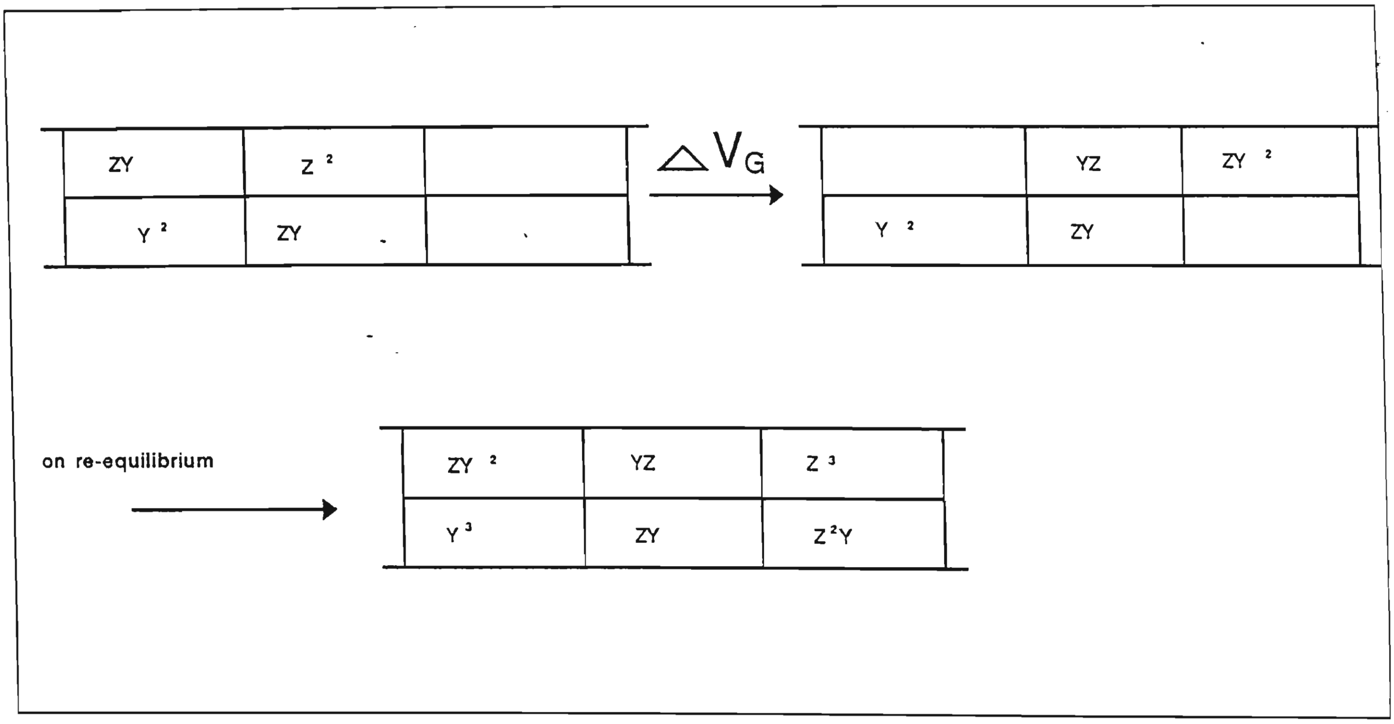
The addition of ΔV_G of mobile phase carrier gas to the first plate causes an equal movement of carrier through every plate in the column, the z ml of solute in the gas phase in plate 1 being swept to plate 2. When the movement of carrier gas ceases, reequilibrium occurs in plate 1 and 2. In plate 1 a volume yz ml of solute enters the gas phase while y^2 ml of solute remains in the liquid phase. In plate 2 a volume zy ml enters the liquid phase while z^2 remains in the gas phase.



The distribution of solute between the 2 plates after equilibrium is established is

$$y^2 + yz\ (plate1) + z^2 + zy\ (plate2) = y^2 + 2yz + z^2 = (y + z)^2 \qquad (2)$$

At this point a further volume of carrier gas is added (ΔV_G) to the column and the process is repeated with solute being transported into plate 3.



the distribution of solute being

$$y^3 + zy^2 + 2zy + z^2y + z^3 \qquad (3)$$

but

$$zy = zy^2 + z^2y \qquad (4)$$

$$eq.3 = y^3 + 3zy^2 + 3yz^2 + z^3 = (y+z)^3 \qquad (5)$$

Likewise after the addition of 4 volumes of carrier gas the solute distribution is

$$(y + z)^4 \qquad (6)$$

TABLE 1.

Number of volumes of carrier gas	Number of plates					Distribution
1	y	z				$(y + z)$
2	y^2	$2yz$	y^2			$(y + z)^2$
3	y^3	$3y^2z$	$3z^2y$	z^3		$(y + z)^3$
4	y^4	$4y^3z$	$6y^2z^2$	$4z^3y$	z^4	$(y + z)^4$

Clearly in each plate, the quantity of solute corresponds to a term in a binomial expansion. This implies that if r volumes of carrier gas is added to the column and we designate the number of any plate by N, the quantity of solute in any plate is given by

$$Q_{N+1} = \frac{r!\ (y)^{r-N}\ (z)^N}{N!\ (r-N)!} \qquad (7)$$

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The determination of activity coefficients at infinite dilution using g.l.c. with moderately volatile solvents

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A novel method for determining activity coefficients at infinite dilution by g.l.c. is presented for solutions involving a moderately volatile solvent. The loss of solvent in the column is related to its partial pressure. In this work the activity coefficients for hexane in *cis*- and *trans*-decahydronaphthalene (decalin) have been investigated at the temperature 298.15 K. The method can be used for any solvent of low volatility such as decane, tetrahydronaphthalene, cyclohexylbenzene, or bicyclohexyl.

1. Introduction

The usual method for determining activity coefficients at infinite dilutions developed by Everett[1] and Cruickshank *et al.*[2] is restricted to volatile solutes (*e.g.* pentane, hexane, and heptane) and involatile solvents (*e.g.* dotricontane, squalane, and dinonylphthalate). In the present work this method has been extended to accommodate a solvent of low volatility.

2. Experimental

The g.l.c. apparatus has been described previously.[3] The columns used were stainless-steel tubes (4.2 mm bore; length 1 m to 1.5 m). The support was celite (Manville 80/100 mesh). A catharometer detector was used with helium as the carrier gas, the flow rate of which was maintained constant for each set of runs on a column. This rate was measured using a calibrated bubble meter and corrected for water vapour. The column temperature was controlled to within 0.01 K.

Solvents: *cis*-decalin and *trans*-decalin, of purity 99 moles per cent, and supplied by Aldrich, were used without further purification at a column loading of (3 to 15) mass per cent. The solute used was hexane and was also supplied by Aldrich. It was unnecessary to purify the solute further because of the nature of the experiment.

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3. Theory: treatment of a volatile solute

Everett and Cruickshank developed the equation:

$$\ln \gamma_{13}^{\infty} = \ln(n_3 RT/V_N p_1^*) - (B_{11} - V_1^*)p_1^*/RT + (2B_{12} - V_1^{\infty})J_2^3 p_o/RT, \qquad (1)$$

for obtaining activity coefficients γ_{13}^{∞}, at infinite dilution of solutes in an involatile solvent from g.l.c. results. Here V_N denotes the net retention volume of the solvent, p_0 the outlet pressure, $J_2^3 p_o$ the mean column pressure, n_3 the amount of liquid solvent on the column, T the column temperature, p_1^* the saturated vapour pressure of the solute at temperature T, B_{11} the second virial coefficient of pure solute, V_1^* the molar volume of the solute as liquid, V_1^{∞} the partial molar volume of the solute at infinite dilution in the solvent, and B_{12} the mixed second virial coefficient of the solute and carrier gas.

The net solute retention volume V_N is given by

$$V_N = J_3^2 U_o(t_R - t_G), \qquad (2)$$

where

$$J_3^2 = (3/2)\{(p_i/p_o)^2 - 1\}/\{(p_i/p_o)^3 - 1\}, \qquad (3)$$

and

$$J_2^3 = (J_3^2)^{-1}, \qquad (4)$$

where U_o is the volumetric flow rate of the carrier gas at the column outlet expressed at column temperature and corrected for vapour pressure and t_G and t_R the retention times for an unretained gas (nitrogen) and the solute respectively.

During its passage through the column, the carrier gas becomes charged with solvent vapour. The total amount of solvent n'_3 lost from the column may be expressed in terms of the total volume of gas which has passed through the column, the partial pressure p'_3 of the solvent in the gas at the column outlet, and the time t elapsed from the start of the carrier gas passing through the column. We assume that the observed retention times are negligible compared with the total flow time through the column. The gas flow rate U_o measured at the outlet is maintained constant during the whole experiment. The expression for n'_3 is

$$n'_3 = p'_3 U_o t/RT. \qquad (5)$$

In this work we found the partial pressure of the solvent in the carrier gas to be <0.01 of the total. It is probably further reduced in the flowmeter. Therefore no correction was applied to the flow rate for the presence of the solvent and ideal-gas behaviour was assumed.

Equation (1) becomes

$$\ln \gamma_{13}^{\infty} = \ln\{(n_3 RT - p'_3 \cancel{U}_o t)/V_N p_1^*\} + C, \qquad (6)$$

U

where

$$C = -(B_{11} - V_1^*)p_1^*/RT + (2B_{12} - V_1^{\infty})J_2^3 p_o/RT. \qquad (7)$$

Hence

$$V_N \cdot \exp(-C)/n_3 = RT/\gamma_{13}^{\infty} p_1^* - (p_3'/\gamma_{13}^{\infty} p_1^*)(U_o t/n_3) = a - b(U_o t/n_3). \qquad (8)$$

The values of γ_{13}^{∞} and p_3' are obtained graphically from this linear relation.

4. Results

Results were collected for five columns loaded with *trans*-decalin and two with *cis*-decalin using hexane as solute and helium as the carrier gas. Detailed results obtained for hexane (15.02 mass per cent) are given in table 1. The retention time t_G was determined using nitrogen.

Table 2 summarizes all the results obtained showing those from table 1 as the first entry and lists the values obtained for γ_{13}^{∞} and p_3'.

The mixed virial coefficient B_{12} for hexane was calculated (equation (9)) from McGlashan and Potter's equation[4] and Hudson and McCoubrey's combining rules[5, 6] following Letcher *et al.*[7]

$$B_{12}/V_{c,12} = 0.43 - 0.886(T_{c,12}/T) - 0.694(T_{c,12}/T)^2 - 0.0375(n_{12} - 1)(T_{c,12}/T)^{4.5}, \qquad (9)$$

TABLE 1. Experimental results for the determination of γ_{13}^{∞} for hexane in *trans*-decalin (15.02 moles per cent) at $T = 298.15$ K. The symbols are as defined for equations (1) and (2). For this experiment $U_o = 8.87 \cdot 10^{-7}\ m^3 \cdot s^{-1}$, $n_3 = 3.393 \cdot 10^{-3}$ mol, $J_2^3 = 0.914$, and $t_G = 20.3$ s

$\frac{t}{s}$	$\frac{t_R}{s}$	$\frac{10^4 \cdot V_N}{m^3}$	$\frac{V_N/n_3}{m^3 \cdot mol^{-1}}$	$\frac{U_o t/n_3}{m^3 \cdot mol^{-1}}$
1200	428.8	3.312	0.0975	0.314
2400	419.2	3.348	0.09532	0.627
4800	413.9	3.191	0.0904	1.255
5700	413.3	3.183	0.09378	1.490
6600	401.8	3.089	0.09102	1.725
7200	401.1	3.088	0.09098	1.882
9000	399.7	3.076	0.09064	2.353
9600	396.1	3.047	0.08979	2.510

TABLE 2. Summary of operating conditions for hexane in *cis*-decalin and *trans*-decalin at $T = 298.15$ K for six different columns. The first row relates to table 1

solvent: decalin isomer	$\frac{n_3}{mmol}$	$10^2 \cdot \frac{n_1}{n_1 + n_3}$	$\frac{10^7 \cdot U_o}{m^3 \cdot s^{-1}}$
trans	3.393	15.02	8.872
trans	2.124	10.01	9.542
trans	2.239	7.99	8.373
trans	3.693	10.00	9.543
cis	1.786	3.03	5.715
cis	1.790	9.97	9.828

where

$$T_{c,12} = 128(T_{c,11}T_{c,22})^{1/2}(I_{c,11}I_{c,22})^{1/2}V_{c,11}V_{c,22}/I_{c,12}, \tag{10}$$

$$V_{c,12} = (V_{c,11}^{1/3} + V_{c,22}^{1/3})^3/8, \tag{11}$$

$$I_{c,12} = (I_{11} + I_{12})(V_{c,11}^{1/3} + V_{c,22}^{1/3})^6, \tag{12}$$

and

$$n_{12} = (n_1 + n_2)/2. \tag{13}$$

The critical quantities and ionization energies used in the calculation of B_{12} are given in table 3 using $n_1 = 6$ (hexane) and $n_2 = 1$ (helium). The value for B_{12} was found to be $29\ \mathrm{cm^3 \cdot mol^{-1}}$. The value of B_{11} for hexane used in the calculation was $-1984\ \mathrm{cm^3 \cdot mol^{-1}}$.(8)

5. Discussion

From table 2 it can be seen that results have been collected from experiments in which the flow rates changed by approximately 50 per cent and the column loadings five-fold. These measurements fit a single linear relation (equation 8) shown in figures 1 and 2 to within experimental accuracy.

The points from figure 1 (*trans*-decalin) have been fitted to equation (8) giving $a = (0.975 \pm 0.0012)\ \mathrm{m^3 \cdot mol^{-1}}$, $b = -(0.00336 \pm 0.00017)\ \mathrm{m^3 \cdot mol^{-1}}$, $\gamma_{13}^{\infty} = (1.28 \pm 0.01)$, and $p_3' = (85.4 \pm 4.4)$ Pa. Similarly from figure 2 (*cis*-decalin) $a = (0.0977 \pm 0.0024)\ \mathrm{m^3 \cdot mol^{-1}}$, $b = -(0.00262 \pm 0.00032)\ \mathrm{m^3 \cdot mol^{-1}}$, $\gamma_{13}^{\infty} = (1.28 \pm 0.03)$, and $p_3' = (67.2 \pm 8.2)$ Pa.

The values obtained for γ_{13}^{∞} for both *cis*-decalin and *trans*-decalin are within 0.02 of the value predicted by Letcher and Baxter(10) using the Prigogine-Flory-Patterson theory. Vernier *et al.*(11) obtained a value for γ_{13}^{∞} of 1.260 for hexane in decalin at $T = 298.15$ K. However vapour-phase imperfections and solvent loss were not taken into consideration by them.

Assuming that equilibrium conditions are satisfied in the column, the method should be capable of predicting the vapour pressure of the solvent. The saturated vapour pressure of *trans*-decalin and *cis*-decalin have been reported(12) and fitted to an Antoine equation over the temperature range 363.45 K to 467.55 K. An extrapolation to 298.15 K using this equation gives a value of 104.4 Pa for *cis*-decalin and 164.35 Pa for *trans*-decalin. This places an upper bound on the acceptable values for p_3'. In view of the length of the extrapolation involved it is quite probable that p_3' obtained in this work is a good estimate for the saturated vapour pressure at

TABLE 3. The critical constants and molar ionization energies I used in the calculation of mixed second virial coefficients B_{12}(13)

Compound	$V_{c,m}/\mathrm{cm^3 \cdot mol^{-1}}$	T_c/K	$I/\mathrm{kJ \cdot mol^{-1}}$
Hexane	370.0	507.3	0.9822
Helium	5.20	57.76	5.2487

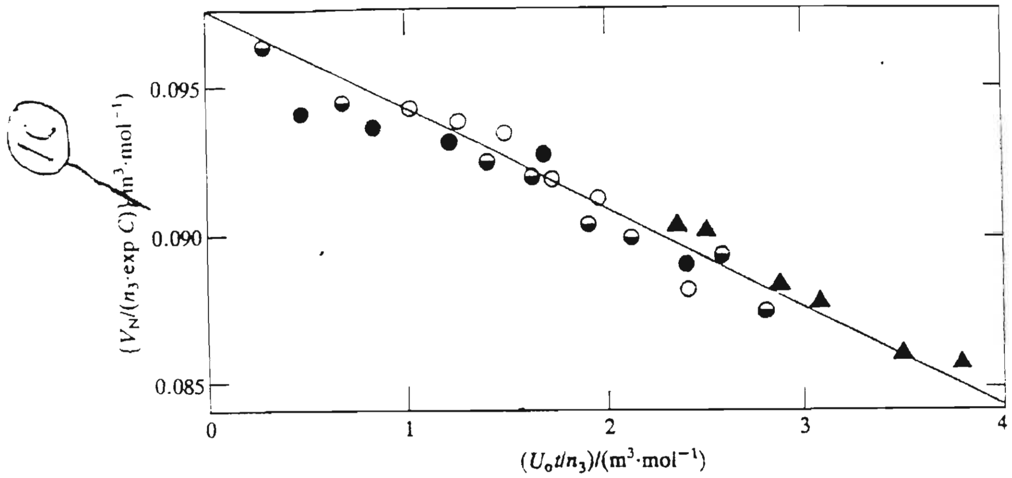

FIGURE 1. A plot of V_N/n_3 against U_0t/n_3 for *trans*-decalin at $T = 298.15$ K. Column loadings: ●, 10.00 moles per cent; ▲, 10.01 moles per cent; ○, 7.99 moles per cent; ⊖, 15.02 moles per cent.

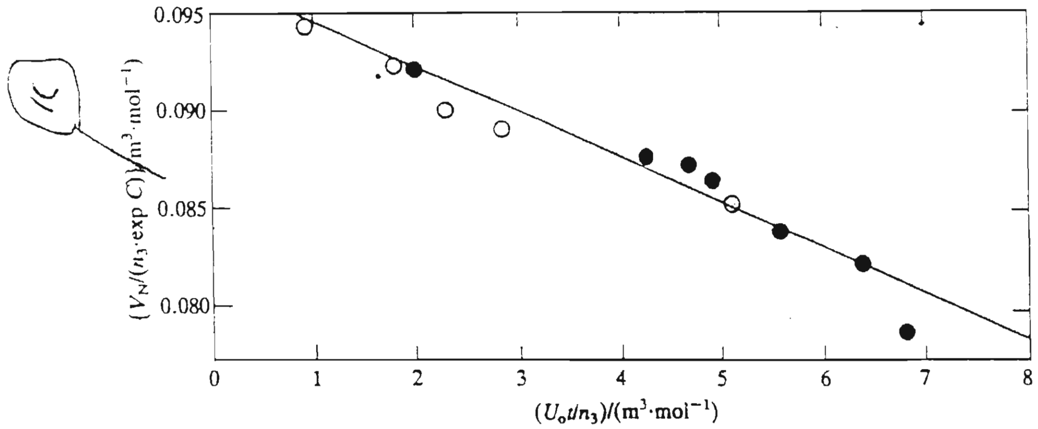

FIGURE 2. A plot of V_N/n_3 against U_0t/n_3 for *cis*-decalin at $T = 298.15$ K. Column loadings: ○, 9.97 moles per cent; ●, 3.03 moles per cent.

$T = 298.15$ K, but further work is required to establish whether the solvent is actually in equilibrium along the column.

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