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Extension of Chromatographic Method of Determination of Thermodynamic Properties

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Abstract

A gas-chromatographic method is proposed for the determination of the slope of the curve $\gamma = \gamma(x)$ for $x \to 0$. The values so obtained are compared with those calculated on the basis of liquid–liquid and liquid–vapor data.

INTRODUCTION

Gas–liquid chromatography is now an established method for determining the thermodynamic properties of a solution at infinite dilution of solutes in solvents (i.e., activity coefficients at infinite dilution) from measurement of the retention time.

The deviations of this quantity from its value at infinite dilution, when a finite concentration of the solute is considered, can be caused either by a variation of the partition coefficient or by a physical effect which can be derived from the theory of chromatography (*1*, *2*).

In the papers of Lenoir (*2*, *3*) these effects are considered and good agreement is obtained when experimental chromatographic data (retention time) are compared with those calculated on the basis of vapor–liquid equilibrium measurements on the same systems.

The present paper reports an attempt to study the variation of retention time from its infinite dilution value for the determination of the slope of

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the curve $\gamma = \gamma(x)$ for $x \rightarrow 0$. In this manner the gas–liquid chromatography would allow two thermodynamic parameters to be determined: activity coefficients at infinite dilution, and the activity coefficient slope for $x \rightarrow 0$.

THEORY

The equations relating the characteristic quantities of the elution process (retention time) to the thermodynamic parameters, as the equilibrium coefficient of the solute, are obtained by a material balance on the solute around an element of column of length dz:

$$\frac{\partial}{\partial z}(q\eta) + \frac{\varepsilon H}{v_g}\frac{\partial y}{\partial t} + Ka\left(\frac{y}{m} - x\right) = 0 \tag{1}$$

$$\frac{\varepsilon(1 - H)}{v_s}\frac{\partial x}{\partial t} - Ka\left(\frac{y}{m} - x\right) = 0 \tag{2}$$

(where $\eta = y/(1 - y)$ is the mole fraction of the solute in the vapor phase on a solute-free basis), with the boundary conditions:

$$\text{at } t = 0 \qquad y = x = 0$$

$$\text{at } z = 0 \qquad y(t) = y_e(t)$$

In these equations the axial diffusion is neglected and the overall mass transfer coefficient K is assumed constant. An equation in which the moments of the response impulse are the main variables is obtained from the Laplace transforms of Eqs. (1) and (2):

$$\frac{\partial}{\partial z}[q\eta]_1 - \frac{\varepsilon H}{v_g}[y]_0 + \frac{\varepsilon(1 - H)}{v_s}[x]_0 = 0 \tag{3}$$

The retention time is then calculated by

$$t_R = [\eta]_1/[\eta]_0 \tag{4}$$

Integration of Eq. (3) presents some difficulties in the finite concentration case: it can not be considered in the gas phase $y = \eta$ and also, what is the main difficulty, the partition coefficient m is not a constant but it is a function of the concentration of solute in the liquid phase. Its variations are ascribed to the corresponding variation of activity coefficient with concentration:

$$m/m_\infty = \gamma/\gamma_\infty \tag{5}$$

The liquid phase concentration, x, is obviously the variable within the activity coefficient and the distribution coefficient change, but in what follows, for mathematical facility, the development of m as a function of gas-phase concentration, y, is considered:

$$\frac{x}{y} = \frac{1}{m} = \frac{1}{m_\infty}\sum_{K=1}^{\infty} \alpha_{K+1} y^K \qquad \text{with } \alpha_1 = 1 \tag{6}$$

The calculation of $[\eta]_1$ by integration of Eq. (3) in which x is replaced by its value obtained from Eq. (6) yields the relation between $(\partial\delta/\partial\tau_s)_{\tau_s=0}$ and α_2; by dropping the terms of higher order in the development of $\delta(\tau_s)$ (derivation in Appendix A), where

$$\delta = \frac{t_R - t_{R\infty}}{t_R} \tag{7}$$

and

$$\tau_s = \frac{[\eta]_0}{\sqrt{2\pi}\sigma_s} \tag{8}$$

we obtained:

$$\alpha_2{}^2 = \left[\left(\frac{\partial\delta}{\partial\tau_s}\right)_{\tau_s=0} + \sqrt{2} - \frac{1}{\sqrt{2}}\frac{t_m}{t_{R\infty}}\right]\frac{1}{\sqrt{2}}\frac{t_{R\infty}{}^2}{(t_{R\infty} - t_m)^2} \tag{9}$$

From Eqs. (5) and (6) and from the equilibrium relation

$$\left(\frac{\partial\gamma}{\partial x}\right)_{x=0} = -\alpha_2\gamma_\infty{}^2\frac{f^0}{P} \tag{10}$$

it follows that the evaluation of α_2 from experimental data of retention times by Eq. (9) gives the slope of the $\gamma = \gamma(x)$ curve for $x = 0$.

EXPERIMENTAL

The apparatus used and the experimental techniques for the preparation of the column, when volatile solvents are used, are described elsewhere (*4*).

In the case of nonvolatile solvents, the solid support (Chromosorb W) and the stationary phase in weighed proportions (25 wt-% stationary phase) were mixed with a volatile solvent, which was then evaporated in a stream of inert gas with continuous stirring. In this manmer a uniform film was obtained on the support.

Columns of various lengths (from 0.30 to 1 m) and 0.4 mm i.d. were used. We used *N*-methylpyrrolidone (NMP), β,β'-oxydipropionitrile, and hexadecane as the stationary phase.

The solutes were hydrocarbons (*n*-hexane, isooctane, *n*-heptane, cyclohexane, and benzene). They were chosen so as to change the γ-values in a range as large as possible.

Liquid–liquid equilibria were measured for the systems *n*-hexane–NMP, *n*-heptane–NMP, and isooctane–NMP, between 20 and 30°C by a modification of the cloud point method.

Liquid–vapor equilibrium data were also determined for the systems *n*-heptane–NMP and cyclohexane–NMP with a static apparatus presented elsewhere (*5*).

RESULTS AND DISCUSSION

According to Eq. (4), the retention times are calculated from the measured quantities with a computer program which calculates first and second moment from a transcription on punched cards of the peaks read on a recorder. The retention time at infinite dilution is evaluated by extrapolating the experimentally determined retention times which are also correlated with τ_s.

In Figs. 1 to 3 the experimental values of δ obtained are plotted as a function of τ_s for the different solutes in the solvents used. In these diagrams the dashed line represents the theoretical values of deviations calculated for $\gamma_\infty = 1$ and $\alpha_2 = \alpha_3 = 0$.

It can be noticed that the difference between the slopes of all experimental and the theoretical curves is always positive for solutes with negative and positive deviations from ideality; solutes in hexadecane present deviations which, as absolute values, are greater than the theoretical values; this occurs when the square term of Eq. (14A) is not negligible. This is a confirmation that the chromatographic behavior depends only on $\alpha_2{}^2$ and $\alpha_3{}^2$; consequently the curves have the same slope at the origin for the same absolute value of α_2 whatever the sign of α_2.

The $\alpha_2{}^2$ and $(\partial\gamma/\partial x)_{x=0}$ values obtained are reported in Table 1. The sign of $(\partial\gamma/\partial x)_{x=0}$ is given according to thermodynamic considerations: indeed, for these systems, if $\gamma_\infty > 1$ we have $(\partial\gamma/\partial x)_{x=0} < 0$, and if $\gamma_\infty < 1$ we have $(\partial\gamma/\partial x)_{x=0} > 0$.

An estimation was made of the error affecting the $(\partial\gamma/\partial x)_{x=0}$ values obtained. The error in $(\partial\gamma/\partial x)_{x=0}$ arises from the determination of $(\partial\delta/\partial\tau_s)_{\tau_s=0}$ and of the activity coefficients at infinite dilution. In Fig. 4, δ/τ_s values are reported as a function of τ_s. The value of the intercept

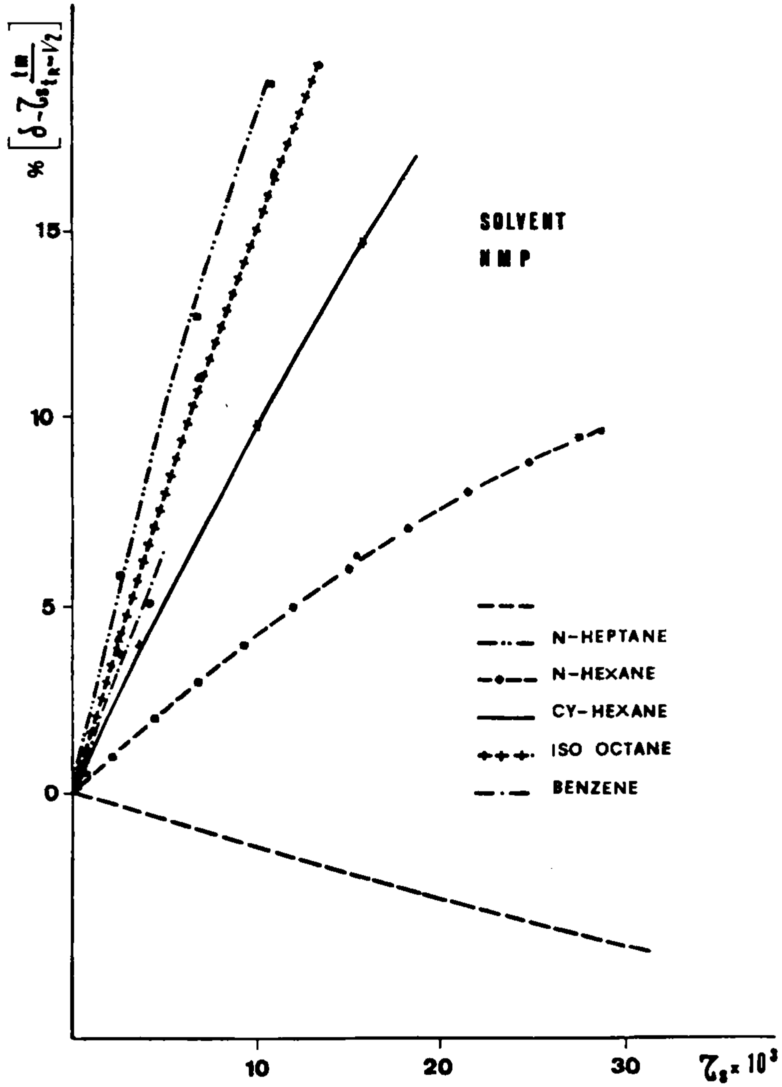

FIG. 1. Experimental values of δ for some solutes in NMP (the dashed line represents the theoretical values).

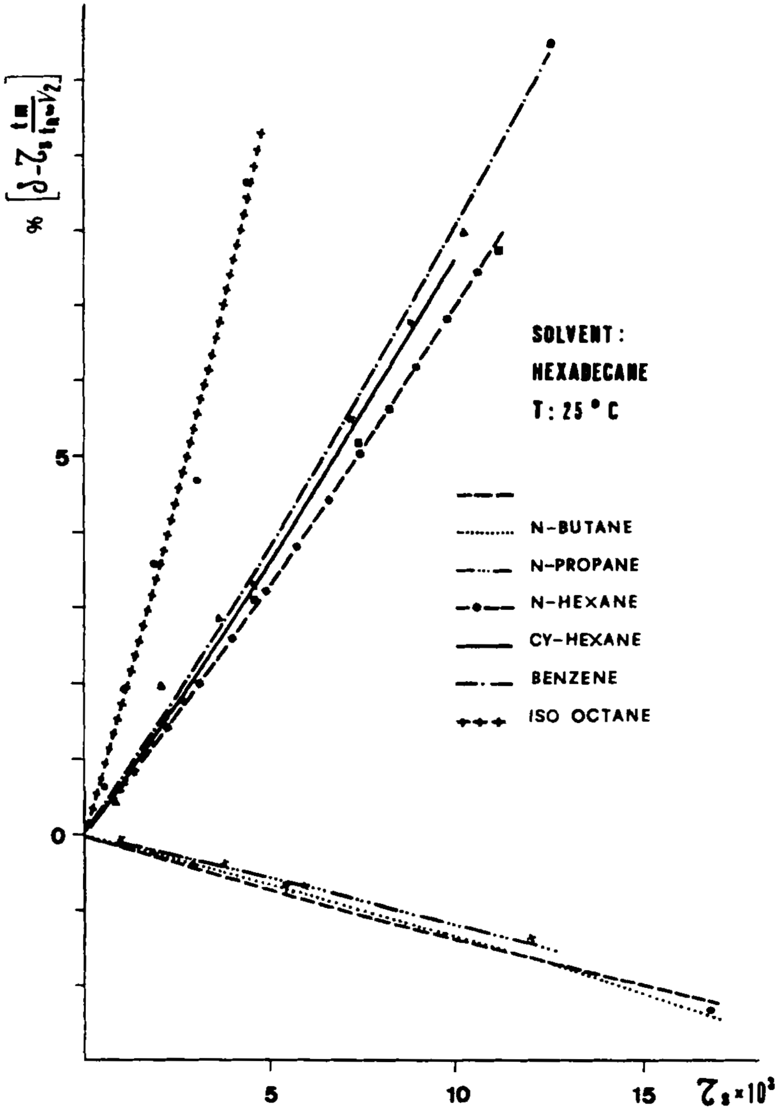

FIG. 2. Experimental values of δ for some solutes in hexadecane (the dashed line represents the theoretical values).

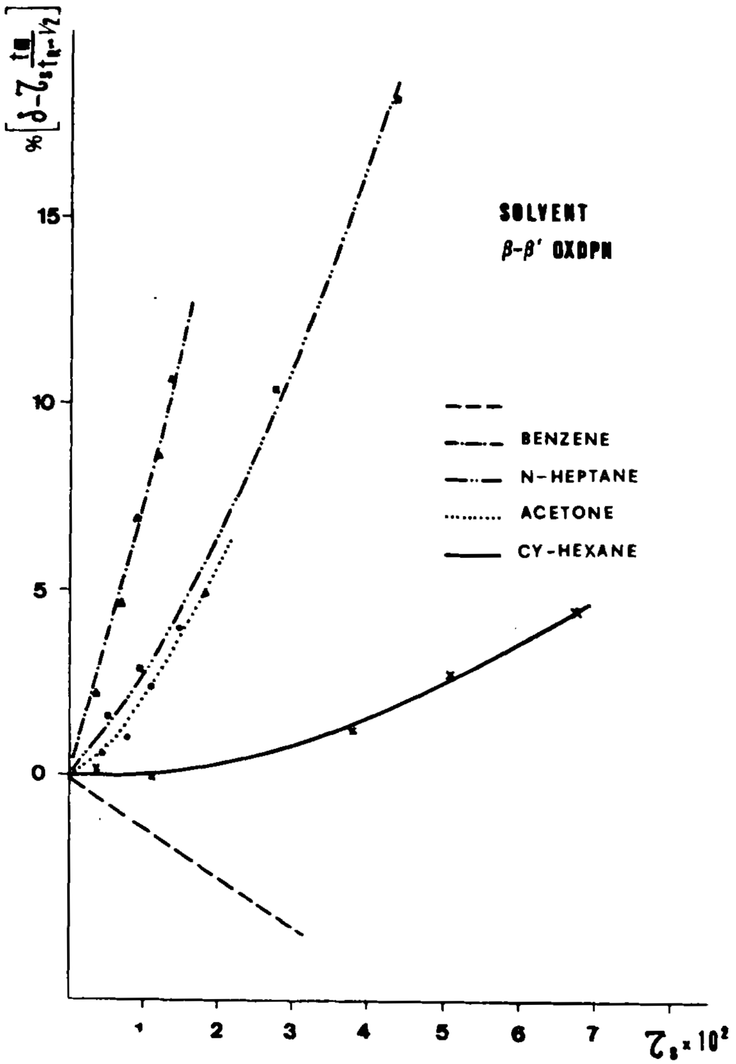

FIG. 3. Experimental values of δ for some solutes in β,β'-oxydipropionitrile (the dashed line represents the theoretical values).

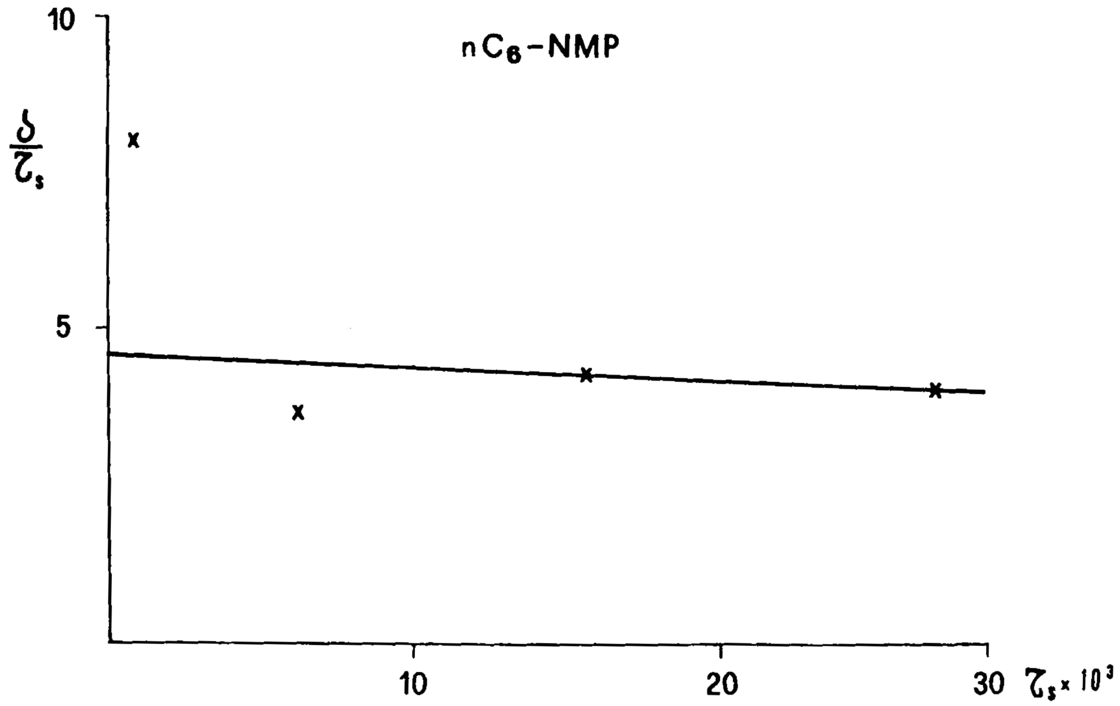

FIG. 4. δ/τ_s values as a function of τ_s for the system *n*-hexane-NMP.

TABLE 1

Experimental Values of α_2^2, $(\partial\gamma/\partial x)_{x=0}$, and γ_∞

Solute	Solvent	α_2^2	$(\partial\gamma/\partial x)_{x=0}$	γ_∞
n-Hexane	NMP	6.5516	−92.0	14.77
n-Heptane	NMP	20.215	−77.0	18.54
Isooctane	NMP	16.056	−86.5	20.07
Cyclohexane	NMP	10.469	−28.4	9.09
Benzene	NMP	15.398	−0.37	0.997
n-Hexane	Hexadecane	2.9856	−0.24	0.87
n-Heptane	Hexadecane	24.197	−0.23	0.907
n-Pentane	Hexadecane	0.7386	−0.41	0.926
n-Propane	Hexadecane	0.6693	−5.06	0.961
Isobutane	Hexadecane	0.2054	−1.29	1.051
Isooctane	Hexadecane	11.597	−0.20	0.972
Cyclohexane	Hexadecane	5.8062	−0.18	0.778
Benzene	Hexadecane	6.7086	−0.34	1.056
n-Heptane	β,β'-Oxydipropionitrile	7.46	−2218	120.6
Isooctane	β,β'-Oxydipropionitrile	3.584	−2120	136.6
Cyclohexane	β,β'-Oxydipropionitrile	1.872	−215.4	36.25
Benzene	β,β'-Oxydipropionitrile	6.006	−2.01	2.658
Acetone	β,β'-Oxydipropionitrile	1.524	−0.34	0.997

for $\tau_s = 0$ is $(\partial\delta/\partial\tau_s)_{\tau_s=0}$. It can be noticed that the spread of the values is greater at the lowest τ_s values when the quantities injected, and consequently the reproducibility of the measurements, are lower. From Eq. (9) it is possible to calculate the error in the evaluation of α_2^2, which is of the same order as $(\partial\delta/\partial\tau_s)_{\tau_s=0}$. Finally, from Eq. (10) and from the logarithmic derivative properties:

$$\frac{\Delta(\partial\gamma/\partial x)_{x=0}}{(\partial\gamma/\partial x)_{x=0}} = \frac{\Delta\alpha_2}{\alpha_2} + 2\frac{\Delta\gamma_\infty}{\gamma_\infty} + \frac{\Delta(f^0/P)}{f^0/P} \tag{11}$$

Since $\Delta\alpha_2/\alpha_2 \simeq 42\%$, $\Delta\gamma_\infty/\gamma_\infty$ is assumed (*6*) $\simeq 4\%$, and $\Delta[(f^0/P)/(f^0/P)]$ is 1 %, it follows that

$$\frac{\Delta(\partial\gamma/\partial x)_{x=0}}{(\partial\gamma/\partial x)_{x=0}} \simeq 50\% \tag{12}$$

The tests of the agreement of chromatographic measurement with direct measurement of equilibrium data were performed in three different ways:

(a) Predict liquid–liquid and liquid–vapor equilibria from chromatographic data only.

(b) Predict the thermodynamic behavior in the whole range of composition from chromatographic and other equilibrium data (i.e., one liquid–vapor point or solubility).

(c) Predict chromatographic data [γ_∞ and $(\partial\gamma/\partial x)_{x=0}$] from thermodynamic measurements.

The tests involve the use of an expression of $g^E(x)$ at the temperature of measurement with parameters which are calculated from experimental data and subsequently used to calculate other properties. The Redlich-Kister equation was used throughout with two or three parameters (in this case C = 0). Its expression is:

$$g^E(x) = RTx(1 - x)[A + B(2x - 1) + C(2x - 1)^2] \tag{13}$$

The results obtained for the systems tested are reported in Tables 2 to 6.

The first test was performed for the systems *n*-heptane–NMP, isooctane–NMP, *n*-hexane–NMP, cyclohexane–NMP, and benzene–NMP. The mutual solubilities for the immiscible systems were calculated from the values of two constants in the Redlich-Kister equation calculated from chromatographic data only. The error in the mutual solubilities is about 50%. The total pressure was also calculated for the systems *n*-heptane–NMP, cyclohexane–NMP, and benzene–NMP. The experimental values are in good agreement with the calculated values for the systems cyclohexane–NMP and benzene–NMP.

The second test was performed using γ_∞ and mutual solubility, equal activity of one component in the two liquid phases (b1), or γ_∞ and mutual solubilities with 3 parameters (b2). The estimation of $(\partial\gamma/\partial x)_{x=0}$ is not always good in the first case and is not improved in the second.

The third test (c1) was performed for immiscible systems using mutual solubilities to calculate two parameters. The prediction of both γ_∞ and $(\partial\gamma/\partial x)_{x=0}$ is poor.

For miscible systems (cyclohexane–NMP) the third test (c2) was performed using liquid–vapor data for the determination of the constants of the Redlich-Kister equation. In this case a good agreement is obtained in the prediction of the activity coefficients at infinite dilution as well as in the prediction of the slope.

Unfortunately, these tests are not very significant because they rely, most of the time, upon solubility data, and these data are very sensitive to the slope of the $g^E(x)$ curve. The choice of the Redlich-Kister equation is probably not appropriate because it leads to great errors in γ_∞ predicted from solubility data (test c1). The results are better for vapor–liquid

TABLE 2

Data for the System *n*-Heptane–NMP

Test	Data utilized	Parameter values	Comparison between calculated and experimental values of			
			x'_{exptl}	x'_{calc}	x''_{exptl}	x''_{calc}
a	γ_∞ and $(\partial\gamma/\partial x)_{x=0}$	$A = 3.3416$ $B = 0.4217$	0.144	0.07	0.917	0.97
			P_{exptl} (mmHg)	P_{calc} (mmHg)	$[(\partial\gamma/\partial x)_{x=0}]_{\text{exptl}}$	$[(\partial\gamma/\partial x)_{x=0}]_{\text{calc}}$
b1	γ_∞ and mutual solubilities	$A = 2.2456$ $B = -0.674$	43.73 43.7	42.4 43.2	−77.0	−158
			$\gamma_{\infty\ \text{exptl}}$	$\gamma_{\infty\ \text{calc}}$	$[(\partial\gamma/\partial x)_{x=0}]_{\text{exptl}}$	$[(\partial\gamma/\partial x)_{x=0}]_{\text{calc}}$
c1	Mutual solubilities	$A = 2.6629$ $B = 0.2442$	18.54	11.23	−77.0	−45.38
			$[(\partial\gamma/\partial x)_{x=0}]_{\text{exptl}}$	$[(\partial\gamma/\partial x)_{x=0}]_{\text{calc}}$		
b2	γ_∞ and mutual solubilities	$A = 2.5810$ $B = 0.1308$ $C = 0.4696$	−77.0	−168		

TABLE 3

Data for the System Isooctane–NMP

Test	Data utilized	Parameter values	x_{exptl}	x_{calc}		
a	γ_∞ and $(\partial\gamma/\partial x)_{x=0}$	$A = 3.42113$	0.129	0.052		
		$B = 0.4219$	0.909	0.970		
			$[(\partial\gamma/\partial x)_{x=0}]_{\text{exptl}}$	$[(\partial\gamma/\partial x)_{x=0}]_{\text{calc}}$		
b1	γ_∞ and mutual solubilities	$A = 2.7283$	−86.5	−142.2		
		$B = -0.2719$				
			$\gamma_{\infty\ \text{exptl}}$	$\gamma_{\infty\ \text{calc}}$	$[(\partial\gamma/\partial x)_{x=0}]_{\text{exptl}}$	$[(\partial\gamma/\partial x)_{x=0}]_{\text{calc}}$
c1	Mutual solubilities	$A = 2.2419$	20.07	4.303	−86.5	0.92
		$B = 0.7826$				
			$[(\partial\gamma/\partial x)_{x=0}]_{\text{exptl}}$	$[(\partial\gamma/\partial x)_{x=0}]_{\text{calc}}$		
b2	γ_∞ and mutual solubilities	$A = 1.8208$	−86.5	−356		
		$B = 0.5896$				
		$C = 1.7680$				

TABLE 4

Data for the System *n*-Hexane–NMP

Test	Data utilized	Parameter values	x_{exptl}	x_{calc}		
a	γ_∞ and $(\partial\gamma/\partial x)_{x=0}$	$A = 2.4823$	0.185	0.140		
		$B = -0.2105$	0.927	0.845		
			$[(\partial\gamma/\partial x)_{x=0}]_{\text{exptl}}$	$[(\partial\gamma/\partial x)_{x=0}]_{\text{calc}}$		
b1	γ_∞ and solubility	$A = 2.3480$	−92.0	−99.94		
		$B = -0.3448$				
			$\gamma_{\infty\ \text{exp}}$	$\gamma_{\infty\ \text{calc}}$	$[(\partial\gamma/\partial x)_{x=0}]_{\text{exptl}}$	$[(\partial\gamma/\partial x)_{x=0}]_{\text{calc}}$
c1	Mutual solubilities	$A = 2.5677$	14.77	8.489	−92.0	−21.75
		$B = 0.4289$				
			$[(\partial\gamma/\partial x)_{x=0}]_{\text{exptl}}$	$[(\partial\gamma/\partial x)_{x=0}]_{\text{calc}}$		
b2	γ_∞ and mutual solubilities	$A = 2.0111$	−92.0	−104.4		
		$B = 0.7401$				
		$C = 0.7481$				

TABLE 5

Data for the System Cyclohexane–NMP

Test	Data utilized	Parameter values	P_{exptl} (mmHg)		P_{calc} (mmHg)	
a	γ_∞ and $(\partial\gamma/\partial x)_{x=0}$	$A = 2.5295$	61.72		60.87	
		$B = 0.3222$	93.57		97.22	
			$\gamma_{\infty\ exptl}$	$\gamma_{\infty\ calc}$	$[(\partial\gamma/\partial x)_{x=0}]_{exptl}$	$[(\partial\gamma/\partial x)_{x=0}]_{calc}$
c2	Liquid–vapor equilibrium data	$A = 2.3744$	9.09	8.29	−28.4	−26.47
		$B = -0.2593$				

TABLE 6

Data for the System Benzene–NMP

Test	Data utilized	Parameter values	P_{exptl} (mmHg)	P_{calc} (mmHg)
a	γ_∞ and $(\partial\gamma/\partial x)_{x=0}$	$A = -0.2490$	74.54	70.86
		$B = -0.2519$	19.77	16.81

equilibria where the accuracy of the model is not so important. This is partly confirmed by the data obtained for the system *n*-hexane–hexadecane for which fairly complete data are available in the literature up to 1% concentration. The $(\partial\gamma/\partial x)_{x=0}$ value obtained by GLC was -0.24, while that calculated from the data of McGlashan was -0.16. This result appears more satisfactory than those obtained by extrapolating higher concentration data as had been done for the other systems studied.

CONCLUSIONS

The theory of chromatography, with some simplifying assumptions, gives values not only of the limiting activity coefficient but also of its slope $(\partial\gamma/\partial x)_{x=0}$ from the analysis of the retention time vs the size of the sample.

The accuracy in $(\partial\gamma/\partial x)_{x=0}$ should be of the order of 50% because the errors in chromatographic measurement are still too high. In order to improve the test of the validity of the theory, it will be necessary to obtain experimental values of the activity coefficients by equilibrium measurements at high dilution to avoid the use of an expression of g^E in the testing. This work is in progress.

There is potential application of the theory in analytical chemistry for the prediction of the variation of the retention time, taking into account the size of the sample, from thermodynamic data.

APPENDIX

Substitution of $y = mx$ in Eq. (6) gives m as a function of liquid phase concentration. Replacing m in Eq. (3), it follows that

$$[q\eta]_1 = \sum_{K=1}^{\infty} \beta_K \int_0^L \int_0^{+\infty} y^K \, dz \, dt \tag{1A}$$

with

$$\beta_1 = \frac{\varepsilon H}{v_g} + \frac{1}{m_\infty}\frac{\varepsilon(1-H)}{v_s} = \frac{q_0}{L} t_{R\infty}$$

$$\beta_K = \frac{\varepsilon(1-H)\alpha_K}{v_s m_\infty} = (t_{R\infty} - t_m)\frac{q_0}{L}\alpha_K \qquad \text{for } K \geqslant 2 \tag{2A}$$

The concentration in the gas phase being finite, $y \neq \eta$, and Eq. (1A) becomes

$$[q\eta]_1 = \sum_{K=1}^{\infty} \beta_K \int_0^L \int_0^{+\infty} \left(\frac{\eta}{1+\eta}\right)^K dz \, dt \tag{3A}$$

It is possible to replace η by its Gaussian linear approximation value to evaluate the integrals in Eq. (3A):

$$\eta = \frac{\eta_0}{\sigma(2\pi)^{1/2}} \exp\left[-\frac{1}{2}\left(\frac{t - t_R}{\sigma}\right)^2\right] \tag{4A}$$

According to the linear approximation, σ^2 is proportional to z and η_0 is equal to I/q_0, I being the number of moles of solute injected in the column and q_0 the molar flow rate of carrier gas at the entry.

If the input impulse is considered to be instantaneous, the integration can be achieved by means of variables:

$$\theta = \frac{t - t_{R\infty}}{\sigma} \quad \text{and} \quad w = \frac{1}{\sqrt{2\pi}} e^{-\theta^2/2} \tag{5A}$$

Equation (3A) with Eqs. (4A) and (5A) gives

$$[q\eta]_1 = \sum_{K=1}^{\infty} \beta_K \frac{2L}{\sigma_s^2} \int_0^{\infty} d\theta \int_0^{\sigma_s} \left(\frac{w}{w + \theta}\right)^K \sigma^2 \, d\sigma \tag{6A}$$

It is possible to put Eq. (6A) in the form

$$[q\eta]_1 = \sum_{K=1}^{\infty} \beta_K(\lambda_{K-2} - 2\lambda_{K-1} + \lambda_K)L[\eta]_0 \tag{7A}$$

The integrals

$$\lambda_K = \frac{2}{\sigma_s^2} \int_0^{\infty} d\theta \, w^{K+2} \int_w^{w+\sigma_s} v^{-K} \, dv \tag{8A}$$

depend on a single dimensionless parameter

$$\tau_s = \frac{[\eta]_0}{(2\pi)^{1/2}\sigma_s} \tag{9A}$$

and they have the values

$$\begin{aligned}
\lambda_{-1} &= 1 + \sqrt{2}\tau_s \\
\lambda_0 &= \sqrt{2}\tau_s \\
\lambda_1 &= 2\left[\sum_{n=1}^{\infty} (-1)^{n+1} \frac{1}{n(n+3)^{1/2}} \tau_s^{n+2} - \frac{1}{\sqrt{3}}\tau_s^2 \ln \tau_s + \frac{1}{6\sqrt{3}}\tau_s^2\right] \\
\lambda_K &= \frac{2}{1 - K}\left[\sum_{n=0}^{\infty} (-1)^n \left(\frac{n}{n + K - 2}\right) \frac{1}{\sqrt{n + K + 2}} 2\tau_s^{(n+K-1)} - \frac{1}{\sqrt{3}}\tau_s^2\right] \\
&\text{for } K \geqslant 2
\end{aligned} \tag{10A}$$

Therefore:

$$[q\eta]_1 = t_{R\infty}q_0[\eta]_0\left[(\lambda_{-1} - 2\lambda_0 + \lambda_1)t_{R\infty}q_0 + \frac{t_{R\infty} - t_m}{t_{R\infty}}\sum_{K=2}^{\infty}\alpha_K(\lambda_{K-2} - 2\lambda_{K-1} + \lambda_K)\beta_K L[\eta]_0\right] \tag{11A}$$

The retention time, corrected for the variation of q along the column, is

$$t_R = t_{R\infty}\left[(\lambda_{-1} - 2\lambda_0 + \lambda_1)q_0 t_{R\infty} + \frac{t_m}{t_{R\infty}}\frac{\tau_s}{\sqrt{2}} + \frac{t_{R\infty} - t_m}{t_{R\infty}}\sum_{K=2}^{\infty}\alpha_K(\lambda_{K-2} - 2\lambda_{K-1} + \lambda_K)\beta_K L[\eta]_0\right] \tag{12A}$$

The relative deviation δ is expressed as:

$$\delta(\tau_s) = (\lambda_{-1} - 2\lambda_0 + \lambda_1)q_0 t_{R\infty}[\eta]_0 + \frac{t_m}{t_{R\infty}}\frac{\tau_s}{\sqrt{2}} - 1 + \frac{t_{R\infty} - t_m}{t_{R\infty}}\sum_{K=2}^{\infty}\alpha_K(\lambda_{K-2} - 2\lambda_{K-1} + \lambda_K)\beta_K L[\eta]_0\Bigg] \tag{13A}$$

In general, a development of m of third order (with α_2 and α_3) is sufficient to express the variation of m with y. Therefore, for the evaluation of λ_K, only the τ_s^2 and τ_s^3 terms are considered. Relation (13A) becomes:

$$\begin{aligned}\delta(\tau_s) = {}& \tau_s\left[\frac{t_m}{t_{R\infty}\sqrt{2}} - \sqrt{2} + \frac{(t_{R\infty} - t_m)^2}{t_{R\infty}^{\;2}}\sqrt{2}\alpha_2^{\;2}\right] \\ & + \tau_s^{\;2}\left[\frac{1}{3\sqrt{3}} + \frac{4}{3\sqrt{3}}\frac{(t_{R\infty} - t_m)^2}{t_{R\infty}^{\;2}}\alpha_2^{\;2} - \frac{8}{3\sqrt{3}}\frac{(t_{R\infty} - t_m)^2}{t_{R\infty}^{\;2}}\alpha_3^{\;2}\right] \\ & + 2\left[-\frac{1}{\sqrt{3}} + \frac{2}{\sqrt{3}}\frac{(t_{R\infty} - t_m)^2}{t_{R\infty}^{\;2}}\alpha_2^{\;2} - \frac{(t_{R\infty} - t_m)^2}{t_{R\infty}^{\;2}}\frac{\alpha_3^{\;2}}{\sqrt{3}}\right]\tau_s^{\;2}\ln\tau_s\end{aligned} \tag{14A}$$

with the boundary condition

$$\lim_{\tau_s \to 0}\delta(\tau_s) = \lim_{t_R \to t_{R\infty}}\delta(\tau_s) = 0 \tag{15A}$$

The first term of development of m, $\alpha_2^{\;2}$, is given in Eq. (9).

SYMBOLS

a	liquid–gas interfacial area per unit volume
y	mole fraction of solute in the gas phase

x	mole fraction of solute in the liquid phase
H	vacuum fraction of the column occupied by the gas phase
I	injected moles of the sample
K	transfer coefficient
L	length of the column
m	equilibrium constant of the solute
m_∞	equilibrium constant of the solute at infinite dilution
Q	flow rate at the inlet to the column
t_R	retention time
$t_{R\infty}$	retention time at infinite dilution
t_m	dead time
q	flow rate per unit section
q_0	flow rate per unit section at the inlet to the column
v_g	molar volume of mobile phase
v_s	molar volume of stationary phase
f_0	fugacity of solute at the column temperature and for a pressure $\bar{p}$
$\bar{p}$	mean pressure of the column

Greek Letters

α_K	coefficients in the development of m
β_K	coefficients in Eq. (1A)
γ	activity coefficient of solute in the liquid phase
δ	relative deviation of the retention time
ε	porosity of the solids
η	mole fraction on a solute-free basis
$\eta_e(t)$	input impulse curve
η_0	time integral of the impulse curve
$[\eta]_n$	moment of n order of quantity $\eta(t)$

$$[\eta]_n = \int_0^\infty t^n \eta(t)\, dt$$

λ_k	integrals
σ	variance of the impulse at z
τ_s	$[\eta]_0/\sqrt{2}\pi\sigma_s$, dimensionless parameter

Subscripts

0	a zero-order moment
1	a first-order moment

e entry of column
s exit of column

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