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MEASUREMENT OF ACTIVITY COEFFICIENTS BY REVERSED-FLOW GAS CHROMATOGRAPHY

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SUMMARY

The determination of activity coefficients for various two-component liquid–vapour systems was accomplished by reversed-flow gas chromatography. By means of derived mathematical equations, the gaseous equilibrium concentration of each component under study, in the pure state and in the binary mixture, was determined. From these equilibrium concentrations, activity coefficients for the alcohol component in the binary mixtures methanol–water, ethanol–water and 1-propanol–water were calculated. The coefficients found depend on the nature of the alcohol component, its molar fraction and temperature.

From the activity coefficients measured and their variation with temperature, excess partial molar thermodynamic functions of mixing were calculated. The activity coefficients found are compared with those at infinite dilution, calculated by an empirical equation.

INTRODUCTION

Distillation is the most important method for separating mixtures of volatile components in the chemical process industries. The key to its successful design and operation is a knowledge of vapour–liquid equilibria. The most fundamental variable in calculating vapour–liquid equilibria is the activity coefficient, which is a measure of non-ideality in the liquid mixture. For an ideal liquid mixture, all activity coefficients are equal to unity at all compositions. For a non-ideal system, however, these coefficients are either greater or smaller than unity. Several methods for calculating activity coefficients are in fairly common use. Gas chromatography (GC) is a rapid method of reasonable precision, whereas the conventional methods are time consuming, but sometimes of higher precision. GC can be employed for vapour pressure measurements and because of its high speed it can be profitably used to select the systems which are sufficiently interesting to justify further study by different basic methods, such as calorimetry, dilatometry and compressibility measurements.

Methods in which chromatography is used are of four types: (a) chromatographic analysis of the vapour phase in the presence of an inert gas and a liquid mixture; (b) measurement of the retention time in the elution of a substance by an inert carrier gas flowing in a column with the solvent as the stationary phase; (c) the

dilution technique, where the bubbling of an inert gas through a liquid mixture strips a volatile and dilute solute from it, the variation with time of the solute concentration in the gas phase, measured by GLC, providing a measure of infinite dilution activity coefficients; (d) a new method, proposed in this paper, in which reversed-flow GC (RFGC), which is based on perturbations imposed on the carrier gas flow, is used.

The first technique is used only in vapour-liquid equilibrium measurements for finding the composition of the vapour phase over the solution, kept at a constant temperature¹⁻⁴. The second has been used exclusively for determining thermodynamic properties, such as activity coefficients, second virial coefficients, relative volatilities and Henry's constants⁵⁻⁸. The third technique, developed by Leroi *et al.*⁹, is based on the variation of the vapour phase composition when the highly diluted components of the liquid mixture are stripped from the solution by a constant carrier gas flow, and simply leads to the infinite dilution activity coefficient of a solute, dissolved in a solvent.

The RFGC method, which has been reviewed recently¹⁰, is really a sampling technique and consists in reversing the direction of flow of the carrier gas from time to time. If the carrier gas contains other gases and their concentration depends on a rate process taking place within the chromatographic column, each flow reversal creates perturbations in the chromatographic elution curve, having the form of extra peaks ("sample peaks"). The mathematical dependence of the heights of the sample peaks on the time when the last reversal was made is considered under Theoretical.

RFGC has been used successfully to determine rate constants and activation parameters, and also catalytic conversions of the reactants to products, for various important surface-catalysed reactions¹¹⁻¹⁸, rates of drying of catalysts¹⁹, diffusion coefficients in binary and ternary gas mixtures²⁰⁻²², adsorption equilibrium constants²³, critical parameters²⁴, Lennard-Jones parameters²⁵ and rate coefficients for the evaporation of liquids²⁶. The experimental set-up for the last application of the RFGC method was used in this work for the determination of activity coefficients in liquid-vapour systems with two components: water and an alcohol (methanol, ethanol or 1-propanol).

THEORETICAL

The principle on which the RFGC method is based is illustrated in Fig. 1. A long diffusion column, of length L (longer than 1 m), containing the liquid is connected perpendicularly to the mid-point of a so-called sampling column, of length $l' + l$, and the whole cell is thermostated inside the oven of the chromatograph. The two ends, D_2 and D_1 , of the sampling column are connected to the carrier gas inlet and the flame-ionization detector through a six-port valve as shown. By switching this valve from one position (solid lines) to the other (broken lines), the direction of the carrier gas flow through the column of length $l' + l$ is reversed, producing "sample peaks" in the recorder line.

It has been pointed out in previous work^{10,21} that if the gas flow is reversed for a short time, t' , shorter than both gas hold-up times in the column sections l' and l , and is then restored again to the original direction, a symmetrical sample peak is produced, as shown in Fig. 2. The maximum height, h , of the peak, measured from the ending baseline, is given by

$$h \approx 2c(l', t_0) \quad (1)$$

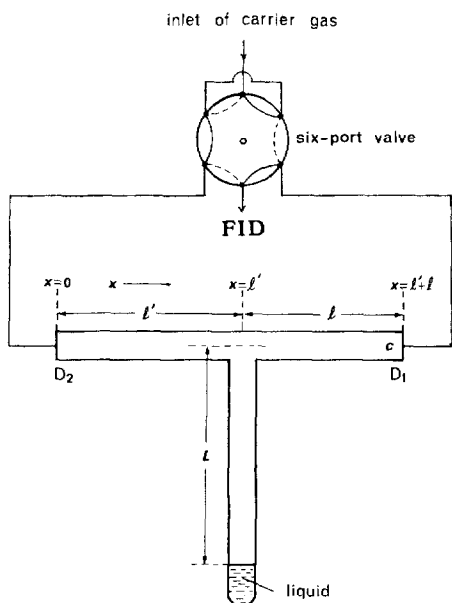


Fig. 1. Experimental set-up for measuring activity coefficients by the reversed-flow GC method.

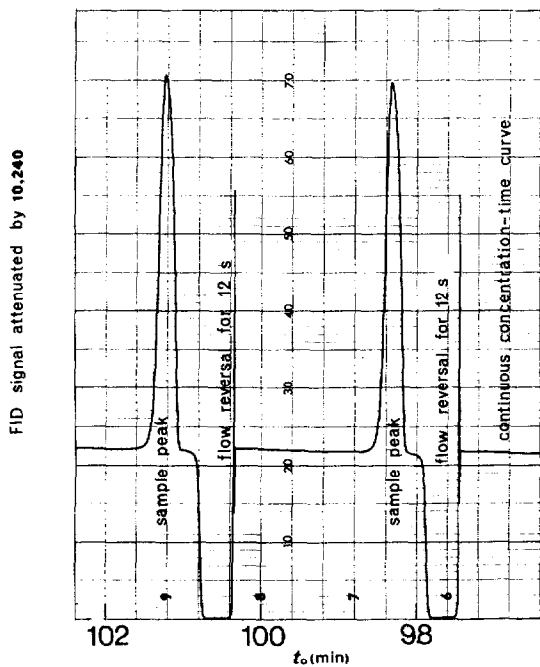


Fig. 2. A reversed-flow chromatogram, showing two sample peaks for the diffusion of 1-propanol vapour at 342.4 K and 1 atm with $\bar{V} = 0.635 \text{ cm}^3 \text{ s}^{-1}$.

where $c(l, t_0)$ is the vapour concentration at $x = l$, and the time t_0 is measured from the moment of placing the liquid at the bottom of column of length L to the last backward reversal of gas flow.

The concentration $c(l, t_0)$ is given by²⁶

$$c(l, t_0) = \frac{k_c D c_0}{v(k_c L + D)} \{1 - \exp[-2(k_c L + D)t_0/L^2]\} \quad (2)$$

where k_c is the rate coefficient for solute evaporation, D the diffusion coefficient of the solute vapour into the carrier gas, c_0 the concentration of the solute vapour in equilibrium with the bulk liquid phase and v the linear velocity of the carrier gas.

Substituting $h/2$ for $c(l, t_0)$ from eqn. 1 into eqn. 2, one obtains h as an analytical function of the time t_0 , and the infinite value h_∞ for the peak height becomes

$$h_\infty = \frac{2k_c D c_0}{v(k_c L + D)} \quad (3)$$

Rearrangement of this equation gives the equilibrium concentration, c_0 , of the solute (alcohol vapour):

$$c_0 = \frac{v h_\infty}{2} (L/D + 1/k_c) \quad (4)$$

As the values of D and k_c can be determined as described in detail elsewhere²⁶, all quantities on the right-hand side of eqn. 4 are measurable, thus yielding the value of the concentration c_0 in equilibrium with the liquid bulk phase.

If experiments are performed with liquid mixtures (in this instance alcohol + water), giving c_0 , and with pure solutes (here alcohols), leading to c_0^* , both by using eqn. 4, then the ratio c_0/c_0^* is equal to P/P^* , and this gives the activity, a_A , of the alcohol in the liquid mixture, assuming that the deviation of the solute vapour from ideal behaviour is small. We can then write

$$c_0/c_0^* = a_A = \gamma_A x_A \quad (5)$$

and can calculate the activity coefficient, γ_A , of the alcohol in the liquid mixture from the known values of c_0 , c_0^* and the molar fraction x_A .

From the measured activity coefficients, the excess chemical potential, μ_A^E , for the solute alcohol is calculated by the well known equation

$$\mu_A^E = RT \ln \gamma_A \quad (6)$$

and from the variation of γ_A with temperature, the excess partial molar heat of mixing, H_A^E , and the excess partial molar entropy of mixing, S_A^E , for the solute alcohol can be found by means of the equation

$$\ln \gamma_A = \frac{H_A^E}{RT} - \frac{S_A^E}{R} \quad (7)$$

which is derived from the classical equation $\mu_A^E = H_A^E - TS_A^E$ and eqn. 6. If a narrow temperature range is used, the above excess partial molar quantities can be assumed to remain constant, and thus, plotting $\ln\gamma_A$ versus $1/T$, H_A^E can be found from the slope and S_A^E from the intercept of the resulting linear plot.

EXPERIMENTAL

The solutes used were methanol (Uvasol), ethanol (pro analysi), and 1-propanol (pro analysi) from Merck. The carrier gas was helium of 99.99% purity from Linde.

The apparatus used and the experimental procedure followed have been described elsewhere²⁶. Lengths of $L = 112.8$ cm for the diffusion column and $l' + l = 100 + 100$ cm for the sampling column were used. All of the columns were 1/4-in. empty stainless-steel chromatographic tubes of 4 mm I.D. At the end of column of length L , a 2-cm tube containing 0.5 cm^3 of the liquid mixture or the pure alcohol was connected by means of a simple 1/4-in. union. Packing of the column of length $l' + l$ with chromatographic material would be necessary if a separation problem in the vapour phase occurred. This was not the case here, and any other packing, such as non-sorbing glass beads, would simply reduce the gas hold-up time in sections $l' + l$, which is undesirable.

About 20 min after placing the liquid in position, an asymmetric concentration-time curve for the vapour of the pure liquid or the liquid mixture was recorded, rising continuously and approaching a limiting plateau. During the rise period, and also when the plateau was reached, flow reversals for 12 s were effected by means of the six-port valve. This time period is shorter than the gas hold-up time in column sections l' and l . When the gas flow was restored to its original direction, sample peaks were recorded, corresponding to various times, t_0 , from the beginning (*cf.*, Fig. 2).

The pressure drop along column of length $l' + l$ was negligible. The working temperature was in the range 302.6–350.9 K and the volumetric carrier gas flow-rate, \dot{V} (corrected at the column temperature) was in the range $0.569\text{--}0.681 \text{ cm}^3\text{s}^{-1}$.

RESULTS AND DISCUSSION

The activity coefficients for the alcohol component in the binary mixtures methanol-water, ethanol-water and 1-propanol-water were determined from eqns. 4 and 5, as described under Theoretical. Table I gives these activity coefficients for various alcohol molar fractions.

In the systems ethanol-water and 1-propanol-water the activity coefficient of the alcohol increases with decreasing molar fraction. The positive deviation from Raoult's law in these systems has also been observed by other workers^{27–29}. In the methanol-water system the activity coefficient of the alcohol at various x_A values shows an irregular dispersion above unity, indicating that, under these experimental conditions, the system approaches ideal behaviour.

The activity coefficients at infinite dilution, γ_A^∞ ($x_A \rightarrow 0$), can be estimated by various empirical or semi-empirical equations. The most useful of these for primary alcohol-water systems is³⁰

$$\log \gamma_A^\infty = a + \varepsilon N + \frac{y}{N} \quad (8)$$

where N is the number of carbon atoms in the solute molecule and a , ε and y are constants depending on the solute-solvent system and temperature. Values for these constants are given in ref. 30.

Using eqn. 8, we calculated the activity coefficients at infinite dilution, given in the last column of Table I. These should be compared with the experimental values corresponding to the smallest molar fraction of each alcohol. The differences between the two values seem rather large, but compared with the differences found in the literature⁹ between various workers and different techniques, they are not large at all.

TABLE I

ACTIVITY COEFFICIENTS FOR THE ALCOHOL COMPONENT IN BINARY LIQUID MIXTURES OF ALCOHOLS AND WATER AT CONSTANT TEMPERATURE AND VARIOUS ALCOHOL MOLAR FRACTIONS

Alcohol	T (K)	\dot{V} ($\text{cm}^3 \text{ s}^{-1}$)	$10^2 x_A$	γ_A	$\gamma_A^{*\star}$
Methanol	323.5	0.607	2.3	1.33	1.814
			4.7	1.37	
			10.0	1.51	
			30.8	1.11	
			64.0	1.16	
Ethanol	335.9	0.611	1.6	6.66	4.436
			3.3	5.17	
			7.2	3.65	
			24.0	2.20	
1-Propanol	342.4	0.681	0.49	23.3	14.412
			0.99	19.3	
			2.6	17.1	
			5.7	13.2	
			7.4	10.1	
			26.5	3.43	
			48.9	1.88	

* The values at infinite dilution, γ_A^∞ , were calculated by means of eqn. 8.

The variation of activity coefficients with temperature was studied for all three alcohol-water systems, and the values found (at fairly dilute solutions) were plotted according to eqn. 7 as $\ln \gamma_A$ versus $1/T$. The values of excess partial molar enthalpy and entropy of mixing, calculated from the slopes and intercepts of these plots, are given in Table II, together with the excess chemical potential of mixing at various temperatures.

The simple relationship

$$T \ln \gamma_A = \text{constant} \quad (9)$$

TABLE II
EXCESS PARTIAL MOLAR THERMODYNAMIC FUNCTIONS OF MIXING FOR ALCOHOLS
IN WATER

Alcohol	x_A	T (K)	μ_A^E (kJ mol ⁻¹)	H_A^E (kJ mol ⁻¹)*	S_A^E (JK ⁻¹ mol ⁻¹)*
Methanol	0.100	303.2	2.09		
		312.9	1.27		
		323.5	1.12		
		324.2	1.48	11 ± 3	30 ± 10
		328.1	1.30		
		333.5	0.94		
Ethanol	0.072	316.3	3.95		
		326.0	3.39		
		330.8	3.27	10 ± 3	20 ± 10
		335.9	3.51		
		344.6	3.30		
1-Propanol	0.057	322.7	5.02		
		330.2	5.66		
		342.4	7.33	-22 ± 8	-83 ± 23
		350.9	7.07		

* The ± values given with H_A^E and S_A^E are standard errors, calculated by regression analysis.

which sometimes holds for mixtures of similar components, is not valid in this instance, as expected for organic compounds-water mixtures with extensive hydrogen bonding. A simple explanation is provided by eqn. 7, which leads to eqn. 9 when S_A^E is zero and H_A^E remains constant with temperature. The results in Table II show that, in this instance, there is a large excess entropy of mixing in all alcohols, which is why eqn. 9 does not hold.

CONCLUSION

An accurate study of the variation of γ_A with temperature is very difficult, if not impossible, with classical chromatographic techniques, and hence these techniques will probably never provide values of excess partial molar enthalpies of mixing as accurate as the direct calorimetric methods. One of the reasons is that careful attention must be paid to the accurate measurement of retention volumes and corrections for gas-phase imperfections³¹. The latter are larger when the carrier gas is helium, and this is contrary to the assumption often made that the choice of helium as a carrier gas generally minimizes all the corrections. No such corrections are necessary with the present method, which is closer to a static than to a GC technique. No real chromatography is performed. Only GC instrumentation is used to sample the space at $x = l'$ (cf., Fig. 1). The method is simple and can be carried out with a conventional gas chromatograph.

The precision of the method cannot be stated with certainty at present, as more experimental data with other liquid mixtures are required.

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