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Note

Mixed solvents in gas-liquid chromatography

Activity coefficients for hexane in squalane and dinonyl phthalate mixtures at 303 °K

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With the aim of providing a simple basis for predicting the behaviour of a mixture of solvents in gas-liquid chromatography (GLC) Purnell and Vargas de Andrade¹ have proposed the equation

$$K_R = \varphi'_B K_{R(B)}^\bullet + \varphi'_C K_{R(C)}^\bullet \quad (1)$$

relating the infinite dilution solute partition coefficient in a stationary phase composed of a binary (B + C) mixture, K_R , to the corresponding partition coefficients in pure B and pure C, $K_{R(B)}^\bullet$ and $K_{R(C)}^\bullet$, respectively. In the equation φ'_B and φ'_C are the solvent volume fractions in the mixed binary solvent, *i.e.* $\varphi'_B + \varphi'_C = 1$. The equation is valid if there is no specific interaction between B and C and they form an ideal solution. Purnell and Vargas de Andrade indicate that it can also be derived for a non-ideal solution of B and C, if it is assumed that the activity coefficient of the solute A at infinite dilution in the solvent mixture can be simply related to the infinite dilution activity coefficients of A in pure B and pure C in terms of the composition of the solvent mixture. Finding the equation applicable to many systems Purnell *et al.*^{1,2} conclude that there is no random mixing in these (B + C) mixtures but there are local concentrations of B or C corresponding to those existing in the pure state. That is, they propose that the liquids B and C exist in their macroscopic solution as microscopically immiscible groups of like molecules.

Recently we have determined activity coefficients for several C₆ and related hydrocarbons in squalane-dinonyl phthalate mixtures over a considerable part of the solute concentration range³. These measurements were made using a vacuum microbalance to determine the absorption of the volatile solute in a known mixture of the two involatile solvents. The involatile liquids were spread on an inert particulate support to give a thin liquid film as in GLC, enabling a more rapid approach to equilibrium to be achieved than if the bulk involatile liquids had been used. The results were expressed in terms of the Flory-Huggins expression for ternary solutions⁴ which is incompatible with eqn. 1 except in the limiting case where B and C form an ideal solution. However, eqn. 1 is only proposed for infinite dilution, the situation normally pertaining in GLC when used as an analytical method. It was therefore decided to

extend the measurements made for hexane in squalane-dinonyl phthalate mixtures to the lower solute concentration region, so that activity coefficients at infinite dilution could be determined and the relation expressed in eqn. 1 examined for a relatively simple system. The solvent mixture squalane-di(*n*-nonyl)phthalate and the solute hexane being one of the systems considered by Laub and Purnell^{2,5}.

EXPERIMENTAL

Apparatus

Absorption isotherms were determined using a Sartorius Model 4102 electronic vacuum microbalance in conjunction with a Texas Instr. quartz Bourdon gauge with a 100-cm Hg range gauge head. The balance was operated at ten times the basic range allowing a weight change of 200 mg and a resolution of 0.01 mg on a total load of 1.8 g. Weight change and pressure measurements were believed to have been accurate to ± 0.01 mg and ± 0.01 mmHg, respectively. The apparatus and experimental technique have been described previously^{6,7}. The temperature of the system measured by a mercury-in-glass thermometer calibrated against a platinum resistance thermometer was controlled at 303.12 ± 0.01 °K. A nominal temperature of 303 °K is used throughout.

Materials

The di(3,5,5-trimethylhexyl)1,2-benzene dicarboxylate (DNP) was a BDH (Poole, Great Britain) sample for chromatographic analysis. The 2,6,10,15,19,23-hexamethyl tetracosane (squalane) was a Hopkins and Williams sample material for chromatography. The solid particulate support was J.J.'s (Chromatography) grade M diatomaceous earth chromatography support of sieve sizes B.S.S. 100-120. Samples of DNP and squalane coated on the support by evaporation from a 40-60 °C petroleum ether solution were prepared in the mole ratios 3:1, 1:1 and 1:3, respectively to an accuracy of better than 0.1% and to an approximate liquid-support weight ratio of 20:80. The hexane was a high purity sample from the National Physical Laboratory and was handled throughout under vacuum.

RESULTS AND DISCUSSION

The absorption isotherms determined are presented in Table I in the form of mole fraction of solute absorbed x_A , in the involatile solvent mixture at a solute vapour pressure p_A . The activity coefficient γ_A of the solute in the involatile solvent mixture was then calculated from these measurements using the equations

$$\ln \gamma_{p,A} = \ln [p_A / (p_A^\bullet x_A)] \quad (2)$$

and

$$\ln \gamma_A = \ln \gamma_{p,A} + [(V_A^\bullet - B_{AA}) (p_A^\bullet - p_A) / RT] + [B_{AA}^2 (p_A^{\bullet 2} - p_A^2) / 2 (RT)^2] \quad (3)$$

where p_A^\bullet and V_A^\bullet are the vapour pressure and the molar volume, respectively, of the pure liquid hexane, and B_{AA} is the second virial coefficient of the pure gaseous hexane.

TABLE I

ABSORPTION OF HEXANE (A) IN SQUALANE (B)-DNP (C) MIXTURES AT 303 °K

 $n_B : n_C =$ Solvent mole ratio.

Other symbols: see text.

$n_B:n_C$	x_A	p_A (mmHg)	$\gamma_{p,A}$	γ_A
3:1	0.08418	11.21	0.71266	0.72399
	0.15872	21.74	0.73299	0.74392
	0.22468	31.66	0.75405	0.76464
	0.28471	41.22	0.77476	0.78496
	0.34815	51.88	0.79744	0.80718
	0.39858	60.82	0.81656	0.82587
	0.45299	70.88	0.83733	0.84612
	0.50360	80.66	0.85710	0.86533
1:1	0.07829	11.63	0.79498	0.80759
	0.14488	22.04	0.81407	0.82621
	0.20118	31.25	0.83124	0.84295
	0.25834	40.99	0.84908	0.86028
	0.31647	51.28	0.86710	0.87773
	0.36894	60.90	0.88333	0.89339
	0.42279	71.08	0.89968	0.90910
	0.47041	80.43	0.91495	0.92376
1:3	0.06963	12.14	0.93297	0.94772
	0.12351	21.87	0.94753	0.96168
	0.17620	31.63	0.96064	0.97411
	0.22975	41.76	0.97267	0.98544
	0.28035	51.53	0.98361	0.99563
	0.33150	61.60	0.99440	1.00566
	0.38022	71.31	1.00364	1.01412
	0.42969	81.38	1.01349	1.02315

TABLE II

VALUES OF γ_A^∞ FOR HEXANE (A) IN SQUALANE (B)-DNP (C) MIXTURES AT 303 °K $n_B:n_C =$ Solvent mole ratio.

$n_B:n_C$	γ_A^∞
1:0	0.640*
3:0	0.697
1:1	0.785
1:3	0.933
0:1	1.201*

* Values from ref. 8.

The B_{AA} , V_A^\bullet and p_A^\bullet values employed were as previously reported^{3,8}. The values of γ_A and the activity coefficient uncorrected for gas non-ideality $\gamma_{p,A}$ are included in Table I.

The activity coefficients at infinite dilution for these systems can be determined quite simply, as shown in Fig. 1, by a linear extrapolation of $\ln \gamma_A$ for the most dilute solutions when plotted against x_A . A more rigorous extrapolation giving the γ_A^∞ values reported in Table II can be achieved by fitting the results to the Flory-Huggins expression for a ternary system⁴ rearranged for a pseudo-binary system³ using the equations (see eqns. 2, 4 and 9-13 of ref. 3).

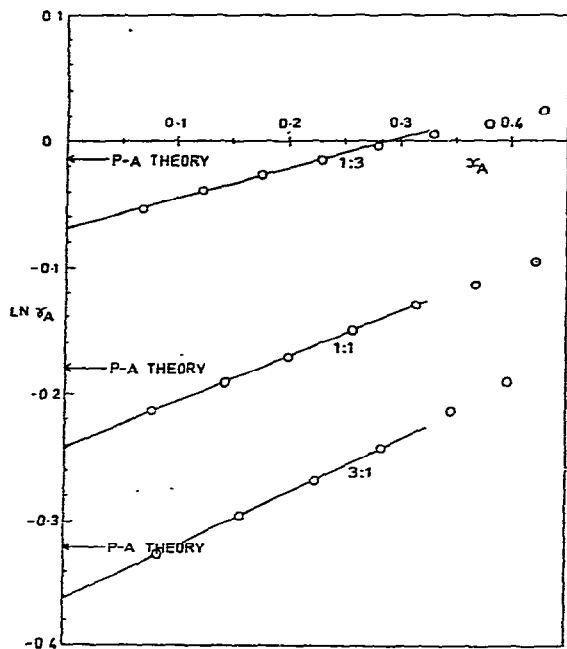


Fig. 1. Plots of the natural logarithm of the hexane activity coefficient $\ln \gamma_A$ vs. hexane mole fraction x_A in squalane-DNP mixtures of mole ratios 1:3, 1:1 and 3:1 at 303 °K extrapolated to infinite dilution. Also shows values of $\ln \gamma_A^\infty$ for the three solvent mole ratios calculated from the Purnell-Vargas de Andrade theory.

$$\ln \gamma_A = \ln (\varphi_A/x_A) + 1 - \varphi_A/x_A + (1 - \varphi_A)^2 \chi \quad (4)$$

$$\varphi_A = x_A/[x_A + r(1 - x_A)] \quad (5)$$

$$r = (r_B n_B + r_C n_C)/(n_B + n_C) \quad (6)$$

$$r_B = V_B^\bullet/V_A^\bullet \quad \text{and} \quad r_C = V_C^\bullet/V_A^\bullet \quad (7)$$

$$\chi = \varphi_B \chi_{AB}/(\varphi_B + \varphi_C) + \varphi_C \chi_{AC}/(\varphi_B + \varphi_C) - \varphi_B \varphi_C \chi_{BC}/(\varphi_B + \varphi_C)^2 \quad (8)$$

$$\varphi_B = r_B n_B/(n_A + r_B n_B + r_C n_C) \quad (9)$$

with φ_C similarly defined. The pseudo-binary interaction parameter χ is allowed to vary linearly with φ_A so that

$$\chi = \chi^0 + \chi' \varphi_A \quad (10)$$

Using the relation

$$K_R = RT/(p_A^\bullet \gamma_{p,A}^\infty \bar{V}_L) \quad (11)$$

where \bar{V}_L = molar volume of the solvent, and the basic eqn. 1, Purnell and Vargas de Andrade¹ derive the equation

$$\frac{1}{\gamma_{p,A}^\infty} = \frac{x'_B}{\gamma_{p,A(B)}^\infty} + \frac{x'_C}{\gamma_{p,A(C)}^\infty} \quad (12)$$

where $\gamma_{D,A(B)}^{\infty}$ and $\gamma_{D,A(C)}^{\infty}$ are the uncorrected solute activity coefficients at infinite dilution in the pure solvents B and C, respectively; x'_B and x'_C are the mole fractions of the involatile solvent in the binary solvent mixture, *i.e.* $x'_B + x'_C = 1$. The same relation holds for the activity coefficients corrected for gas non-ideality γ_A^{∞} , since from eqn. 3 γ_A^{∞} is the product of $\gamma_{D,A}^{\infty}$ and a correction factor which is a constant for a given solute at infinite dilution. Thus eqn. 12 may be rewritten in the form

$$1/\gamma_A^{\infty} = x'_B [(1/\gamma_{A(B)}^{\infty}) - (1/\gamma_{A(C)}^{\infty})] + I(1/\gamma_{A(C)}^{\infty}) \quad (13)$$

enabling γ_A^{∞} to be calculated on the basis of the Purnell-Vargas de Andrade (P-A) theory from the γ_A^{∞} values for pure squalane and pure DNP previously determined⁸ and given in Table II.

The values of γ_A^{∞} calculated using the P-A theory are compared with those determined by extrapolation of the experimentally measured γ_A values in Fig. 1. It might be claimed that the extrapolation used in our method could lead to error. Fig. 1 shows that the γ_A^{∞} values calculated from P-A theory lie far outside any possible extrapolation error. It might also be claimed that our static method involves some systematic error leading to low values of γ_A . As shown previously by one of us, the values extrapolated from this microbalance technique show excellent agreement with reliable GLC work⁸, *e.g.* with the measurements of Conder and Purnell for hexane-squalane and heptane-DNP⁹.

CONCLUSION

For the ternary system hexane-squalane-DNP the activity coefficient for hexane in the solvent mixture differs from the value predicted by the P-A theory by as much as 7%. This theory may be a useful approximation for predicting the behaviour of mixed solvents in GLC but our measurements indicate that the ternary system we have studied conforms more to conventional theory of liquid mixtures rather than to a "micro-partitioning" theory.

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