

CHROM. 15,828

MIXED SOLVENTS IN GAS-LIQUID CHROMATOGRAPHY

ACTIVITY COEFFICIENTS FOR DIETHYL ETHER IN SQUALANE AND DINONYL PHTHALATE MIXTURES AT 303°K

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(Received February 7th, 1983)

SUMMARY

Activity and partition coefficients for the polar solute diethyl ether at infinite dilution in squalane and dinonyl phthalate solvent mixtures have been determined at 303°K by the extrapolation of measurements made using a vacuum microbalance technique. The results are compared to predictions using the Purnell-Andrade and the Tiley-Perry relationships.

The effect on the activity coefficients resulting from various solvent-solid support ratios has also been investigated.

INTRODUCTION

The activity and partition coefficients for the non-polar solutes tetrachloromethane¹, benzene², cyclohexane², pentane², hexane³ and heptane² at infinite dilution in squalane and dinonyl phthalate solvent mixtures have been reported, and used to demonstrate the deviations of these systems from the Purnell-Andrade relation⁴ which predicts the behaviour of mixed solvents in gas-liquid chromatography (GLC). In this work we extend the range of solutes to include the polar solute diethyl ether.

We have also investigated the effect on the activity coefficient of different solvent-solid support ratios, and found a small but significant deviation at low solvent loadings.

EXPERIMENTAL

Isotherms for the absorption of the diethyl ether by the solvents were determined at $302.99 \pm 0.01^\circ\text{K}$ using a Sartorius Model 4102 electronic vacuum microbalance together with a Texas Instruments quartz Bourdon gauge. The apparatus and experi-

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mental technique have been described previously³. In this work, the solvents, SQ and DNP, were added directly to the solid support contained in the balance sample bucket and dispersed using light petroleum of boiling range 310–320°K.

The solvents, di(3,5,5-trimethylhexyl)1,2-benzene dicarboxylate (dinonyl phthalate, DNP) obtained from BDH, and 2,6,10,15,19,23-hexamethyl tetracosane (squalane, SQ) obtained from Hopkins and Williams, were used without further purification. The diethyl ether, obtained from BDH, of AristaR grade with a purity > 99.7%, was distilled before use and its purity confirmed by GLC. Two types of diatomaceous earth solid support were used. All isotherms but one were determined using Celite 545 AW of sieve size B.S.S. 100–120 obtained from Phase Separations. One isotherm was determined using hexamethyldisilazane (HMDS) coated diatomaceous earth support, grade M, of sieve size B.S.S. 100–120 obtained from J.J.'s (Chromatography).

SQ–DNP mixtures were prepared at mole ratios of 2.845:1; 1:1.029 and 1:2.916.

RESULTS AND DISCUSSION

It is known that with polar solutes in non-polar solvents adsorption effects can contribute errors to the determination by GLC of accurate retention results and activity coefficients⁵. This has been demonstrated recently in the work of Nitta *et al.*⁶. In order to investigate the possible adsorption of diethyl ether (A) by the involatile solvents SQ (B) and DNP (C), absorption isotherms were determined using pure solvents at various solvent–solid support ratios. The activity coefficients γ_A at 302.99°K were calculated from the mole fraction x_A of the solute absorbed by the involatile solvent at a solute vapour pressure P_A using a second virial coefficient⁷ B_{AA} of $-1160 \text{ cm}^3 \text{ mol}^{-1}$, a molar volume⁸ V_A^0 of $105.6 \text{ cm}^3 \text{ mol}^{-1}$, and a vapour pressure⁹ P_A^0 of 643.96 mmHg for the diethyl ether, and the equations

$$\ln \gamma_{P,A} = \ln [P_A / (P_A^0 x_A)] \quad (1)$$

$$\ln \gamma_A = \ln \gamma_{P,A} + [(V_A^0 - B_{AA})(P_A^0 - P_A) / RT] + [B_{AA}^2 (P_A^{02} - P_A^2) / 2(RT)^2] \quad (2)$$

where $\gamma_{P,A}$ is the activity coefficient uncorrected for gas phase non-ideality and liquid phase compressibility. The effect on the activity coefficient of the solvent loading is clearly shown in Figs. 1 and 2. In Fig. 1, with SQ as the solvent, the 28% and 41% (w/w) solvent loaded samples produced similar activity coefficients. These results are slightly higher than the results from the 20% (w/w) loaded sample and significantly higher than the results from the 10% (w/w) loaded sample. We have regarded these results as an indication that at the higher solvent loadings the adsorption is negligible compared to the bulk solubility. A similar effect was noticed with DNP as the solvent, as can be seen in Fig. 2. As a result all measurements on mixtures of SQ and DNP were made on approximately 40% (w/w) solvent loaded samples.

In order to investigate the possible effect of the adsorption of diethyl ether on the solid support, an isotherm was determined using squalane on a silanized diatomaceous earth support. The results are shown in Fig. 1. The activity coefficients calculated from this isotherm are well within the experimental error of the activity coefficients determined from squalane on the non-silanized Celite support at a similar % solvent loading. Thus we assumed that the adsorption of diethyl ether on the solid Celite surface when coated with involatile solvents was negligible and that the adsorp-

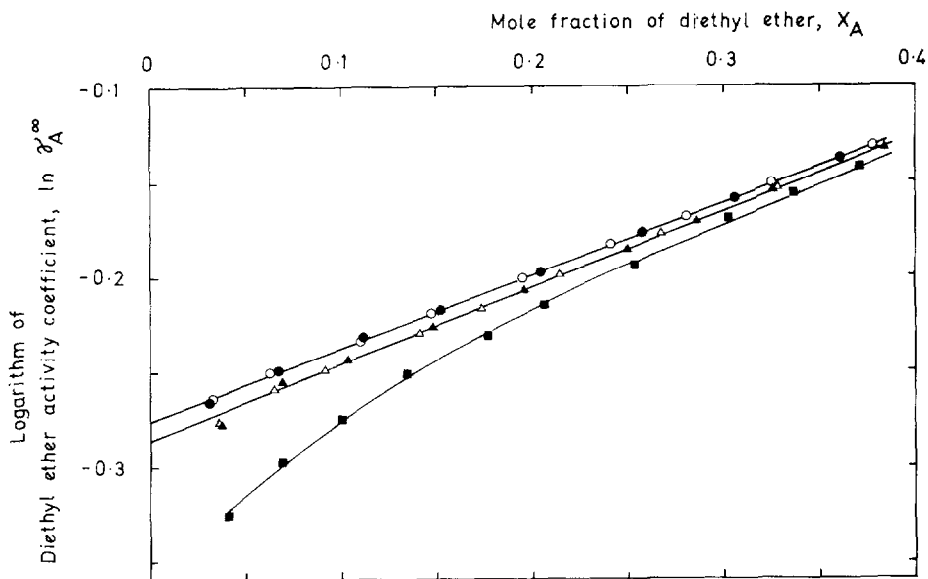


Fig. 1. The natural logarithm of the activity coefficient for diethyl ether in squalane $\ln \gamma_A^\infty$ plotted against the diethyl ether mole fraction x_A . The squalane loadings on Celite are 10.48% (■), 20.30% (▲), 28.41% (○), 40.85% (●) and on HMDS-coated support; 18.32% (△).

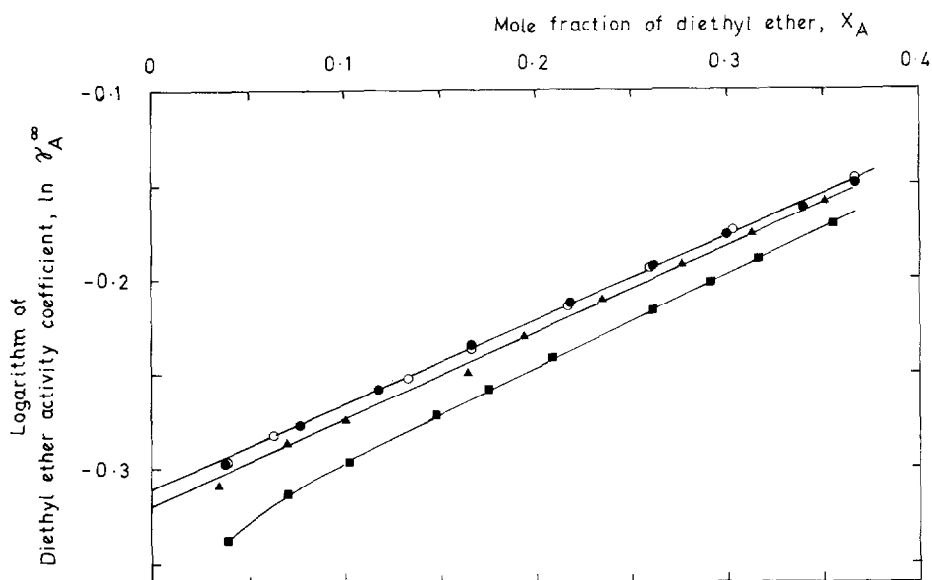


Fig. 2. The natural logarithm of the activity coefficient for diethyl ether in dinonyl phthalate $\ln \gamma_A^\infty$ plotted against the diethyl ether mole fraction x_A . The dinonyl phthalate loadings on Celite are 10.37% (■), 19.48% (▲), 27.09% (○) and 39.91% (●).

TABLE I
 ABSORPTION OF DIETHYL ETHER (A) IN SQUALANE (B) AND DINONYL PHTHALATE (C) MIXTURES AT 303°K
 $n_B:n_C$ = solvent mole ratio; for other symbols see text.

x_A	$n_B:n_C = 1:0^*$			$n_B:n_C = 2.845:1^{**}$			$n_B:n_C = 1:1029^{***}$			$n_B:n_C = 1:2.916^{\S}$			$n_B:n_C = 0:188^{\parallel}$			
	P_A (mmHg)	γ_A	x_A	P_A (mmHg)	γ_A	x_A	P_A (mmHg)	γ_A	x_A	P_A (mmHg)	γ_A	x_A	P_A (mmHg)	γ_A	x_A	P_A (mmHg)
0.0316	14.93	0.7663	0.0410	18.17	0.7188	0.0380	16.70	0.7122	0.0403	17.90	0.7199	0.0385	17.61	0.7421		
0.0675	32.49	0.7795	0.0761	34.36	0.7314	0.0675	30.02	0.7201	0.0665	29.92	0.7286	0.0770	36.01	0.7569		
0.1107	52.24	0.7920	0.1044	47.86	0.7413	0.1341	61.63	0.7427	0.1086	49.98	0.7444	0.1176	56.14	0.7717		
0.1509	75.06	0.8032	0.1512	70.70	0.7550	0.1566	72.92	0.7517	0.1461	68.35	0.7558	0.1657	81.06	0.7895		
0.2035	103.59	0.8201	0.1854	88.07	0.7662	0.2079	98.99	0.7674	0.1833	87.25	0.7678	0.2171	108.69	0.8066		
0.2573	133.93	0.8369	0.2355	114.67	0.7839	0.2489	120.60	0.7799	0.2176	105.34	0.7799	0.2603	133.16	0.8226		
0.3048	161.86	0.8524	0.2774	137.63	0.7977	0.2934	144.92	0.7938	0.2757	137.33	0.8008	0.3002	156.50	0.8370		
0.3601	195.73	0.8705	0.3373	172.24	0.8189	0.3331	167.98	0.8091	0.3236	165.02	0.8184	0.3401	180.22	0.8494		

* Solvent loading: 40.85% (w/w).

** Solvent loading: 38.74% (w/w).

*** Solvent loading: 37.45% (w/w).

§ Solvent loading: 37.27% (w/w).

|| Solvent loading: 39.91% (w/w).

tion found at solvent loadings of < 27–28% (w/w) arose from adsorption at the gas-liquid interface.

The absorption isotherms for the pure solvents and their mixtures at approximately 40% (w/w) solvent loadings are given in Table I in terms of the mole fraction x_A of the solute absorbed by the involatile solvent at a solute vapour pressure P_A . The finite activity coefficients γ_A calculated from these results using eqns. 1 and 2 are also reported in this table. By regarding the SQ–DNP solvent mixture as a single component, the finite concentration activity coefficients for individual isotherms were fitted to the Flory–Huggins expression for a binary system:

$$\ln \gamma_A = \ln (\phi_A/x_A) + 1 - \phi_A/x_A + (1 - \phi_A)^2 \chi \quad (3)$$

From the interaction parameter χ which was allowed to vary linearly with the solute volume fraction ϕ_A , a value of γ_A^∞ was determined. A similar value at infinite dilution can be determined by linear extrapolation of the logarithm of the activity coefficient plotted against the solute mole fraction, as can be seen from Figs. 1 and 2.

These results were used to determine the partition coefficient for the solute at infinite dilution between the solvent and the vapour phase using the relation

$$K_R = RT/(P_A^0 \gamma_{P,A}^\infty V_L) \quad (4)$$

where V_L is the molar volume of solvent calculated by assuming it to be a linear function of the mole fraction composition. The molar volumes of the pure solvents have been reported previously¹⁰ and were calculated from measured densities for SQ and DNP, of 0.8017 g cm⁻³ and 0.9630 g cm⁻³, respectively, at the temperature used throughout this work. The values of γ_A^∞ and K_R for the pure and mixed solvents are given in Table II.

These values of K_R have been compared to the values predicted by the Purnell–Andrade equation:

$$K_R(\text{PA}) = \phi_B K_{R(B)} + \phi_C K_{R(C)} \quad (5)$$

and the percentage deviation of the calculated K_R from the experimentally derived values is given in Table II.

Our experimental values of K_R have also been compared to the values calculated from the relation of Perry and Tiley¹¹:

$$\ln K_R(\text{TP}) = \phi_B \ln K_{R(B)} + \phi_C \ln K_{R(C)} + \phi_B \phi_C \chi_{BC} \quad (6)$$

In equation 6, χ_{BC} was determined by fitting the results of the three isotherms for the mixed solvents together with the results of the two isotherms for the pure solvents, to the Flory–Huggins expression¹⁰ for a ternary system:

$$\ln \gamma_A = \ln (\phi_A/x_A) + 1 - \phi_A/x_A + (1 - \phi_A)(\phi_B \chi_{AB} + \phi_C \chi_{AC}) - \phi_B \phi_C \chi_{BC} \quad (7)$$

TABLE II

ACTIVITY COEFFICIENTS γ_A^λ AND PARTITION COEFFICIENTS K_R FOR DIETHYL ETHER IN SQUALANE (B) + DINONYL PHTHALATE (C) MIXTURES AT 303°K

$n_B:n_C$ = solvent mole ratio; $K_R(PA)$ = partition coefficient calculated from the Purnell-Andrade equation (eqn. 5); $K_R(TP)$ = partition coefficient calculated from the Tiley-Perry equation (eqn. 6); $\Delta\%$ = percentage deviation of calculated K_R from experimental value.

$n_B:n_C$	γ_A^λ	K_R	$K_R(PA)$	$\Delta\%$	$K_R(TP)$	$\Delta\%$
1:0	0.7585	76.64				
1:0.3515	0.7079	86.05	81.06	5.8	84.55	1.7
1:1.029	0.7015	90.97	85.68	5.8	90.99	0.1
1:2.916	0.7076	94.52	90.54	4.2	95.21	0.7
0:1	0.7321	96.33				

In the fitting procedure, χ_{AB} and χ_{AC} are allowed to vary linearly with ϕ_A according to

$$\chi_{AB} = \chi_{AB}^0 + \phi_A \chi_{AB} \quad (8)$$

and similarly for χ_{AC} , while the parameter χ_{BC} is assumed constant. The results obtained are $\chi_{AB}^0 = 0.514$, $\chi_{AB} = -0.015$, $\chi_{AC}^0 = 0.365$, $\chi_{AC} = -0.102$ and $\chi_{BC} = 0.267$.

The percentage deviation between the experimental partition coefficients and those predicted by eqn. 6 are also given in Table II.

The Tiley-Perry equation (eqn. 6) is shown here to give a better fit to the partition coefficients for diethyl ether in the mixed solvents than does the Purnell-Andrade equation (eqn. 5). In this respect our results support the conclusion from the earlier work but extend it to include a polar solute. The Tiley-Perry equation, based as it is on Flory-Huggins solution theory, would not be expected to give as good a fit with a polar solute as was found with the non-polar solutes previously studied. However, it is interesting to note that the interaction parameter for the mixed solvents per unit molar volume of the solute χ_{BC}/V_A^0 of 2.53 mol dm^{-3} determined with diethyl ether is very similar to that found for pentane, hexane, heptane and cyclohexane³ of $2.70 \pm 0.06 \text{ mol dm}^{-3}$.

ACKNOWLEDGEMENTS

T.M.L. gratefully acknowledges the financial support of Rhodes University and the CSIR (South Africa). G.J.P. wishes to thank the Science and Engineering Research Council (Great Britain) for the award of a research studentship.

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