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MIXED SOLVENTS IN GAS–LIQUID CHROMATOGRAPHY

ACTIVITY COEFFICIENTS FOR ACETONE IN SQUALANE–DINONYL PHTHALATE MIXTURES AT 303 K

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SUMMARY

Activity and partition coefficients for the polar solute acetone at infinite dilution in squalane–dinonyl phthalate mixtures have been determined at 303 K by the extrapolation of measurements made using a magnetic suspension vacuum microbalance. The results are used to examine the ability of the Purnell–Andrade and Tiley–Perry relations to describe the behaviour of mixed solvents in gas–liquid chromatography.

The effect of solvent–solid support ratios on the determined activity coefficients was also examined. Adsorption was found to occur even at a 40% liquid loading. As a result the activity and partition coefficients reported were determined using bulk solvents and not solvents spread on solid supports.

INTRODUCTION

The infinite dilution activity and partition coefficients have been reported for a number of non-polar solutes[1–3] and polar solutes[4,5] in mixtures of squalane and dinonyl phthalate. These results have been used to examine two relations proposed to account for the behaviour of mixed solvents in gas–liquid chromatography (GLC). One of these relations proposed by Purnell and Vargas de Andrade[6] is empirical and the other has been derived from conventional solution theory by Perry and Tiley[7]. In this work the range of solutes is extended to include acetone which is significantly more polar than the solutes studied previously. Also, an investigation has been made of the effect on the measured activity coefficient of different solvent–solid support ratios, with Celite and silanized Chromosorb W AW DMCS as the solid support.

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EXPERIMENTAL

The isotherms for the absorption of acetone by the solvents were determined at 302.96 ± 0.01 K with a Sartorius Model 4201 magnetic suspension vacuum microbalance and a MKS Instruments Type 270/370 Baratron pressure gauge. This allowed the weight changes to be monitored to ±0.1 mg on an absorbent sample of *ca.* 2 g of bulk solvent or *ca.* 20 g of solvent and solid support, and the pressure to be measured to ±0.1 Torr. The apparatus and the techniques have been described previously[1,8].

The solvents, squalane (2,6,10,15,19,25-hexamethyl tetracosane, Hopkins and Williams) and dinonyl phthalate [di-(3,5,5-trimethylhexyl)-1,2-benzene dicarboxylate, BDH] were used without further purification. The acetone, obtained from BDH of Aristar grade with a purity >99.8%, was also used without further purification. The diatomaceous earth solid support (Celite 545 AW, 100–120 mesh or Chromosorb W AW DMCS, 100–200 mesh) was supplied by Phase Separations. The solvents were coated onto the solid support by using 40–60°C boiling range petroleum ether. Squalane–dinonyl phthalate (DNP) bulk liquid mixtures were prepared at mole ratios of 2.999:1; 1:1.012 and 1:3.053.

RESULTS AND DISCUSSION

Activity coefficients γ_A were calculated from the mole fraction of solute absorbed x_A at a vapour pressure P_A using eqns. 1 and 2

$$\gamma_{P,A} = P_A/(P_A^0 \, x_A) \tag{1}$$

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

where $\gamma_{P,A}$ is the activity coefficient uncorrected for gas phase non-ideality and liquid phase compressibility. The values used for the saturated vapour pressure P_A^0 (ref. 9), the molar volume V_A^0 (ref. 10) and the second virial coefficient B_{AA} (ref. 11) of the acetone at 302.96 K were 281.45 Torr, 74.56 cm^3 mol^{-1} and -1.905 dm^3 mol^{-1} respectively.

It is well known that adsorption effects can contribute to the retention properties of liquid solvents coated on solid supports[12]. In the absorption of the polar solutes, diethyl ether[4] and ethyl acetate[5], by squalane and DNP, these effects resulted in a variation of the activity coefficient determined with liquid loadings below 27% and 40% respectively. (As before[1–5], the liquid loadings are quoted as a percentage by mass.) To test the effect with acetone, absorption isotherms were measured at liquid loadings of 30% and 40% for squalane and DNP using the Celite 545 AW solid support. These results were compared with the absorption isotherms determined for acetone in bulk squalane and in bulk DNP. Furthermore the absorption isotherm for acetone in squalane was measured at a liquid loading of 30% using the silanized solid support, Chromosorb W AW DMCS. The results expressed as the logarithm of the activity coefficient plotted against mole fraction of acetone are presented in

Figs. 1 and 2, and show that adsorption effects are important even at loadings of 40% on the Celite support. The results for the 30% loaded sample on the dimethylchlorosilane treated support show slightly less adsorption than those for the 30% loaded sample on the untreated support, and are similar to those for the 40% loaded sample on the untreated support. In the investigation of the absorption of diethyl ether by these solvents[4] no detectable difference was found between activity coefficients determined with a hexamethyldisilazane treated support and those determined with an untreated support at liquid loadings of *ca.* 20%. It was concluded that adsorption of the diethyl ether on the solid Celite surface when coated with the involatile solvents was negligible and that adsorption of diethyl ether at solvent loadings of $<27\%$ arose from adsorption at the gas–liquid interface. In the study of the absorption of ethyl acetate[5] it was also concluded that adsorption was taking place at the gas–liquid interface at loadings of $<40\%$. Clearly the same phenomenon is occurring here with acetone, as indeed was suggested by Pecsok and Gump[13] when examining the acetone–squalane system. As a result of these findings, the absorption isotherms required for the determination of the activity coefficients were measured using bulk solvent and not solvent supported on Celite. The results are given in Table I together with the activity coefficients γ_A.

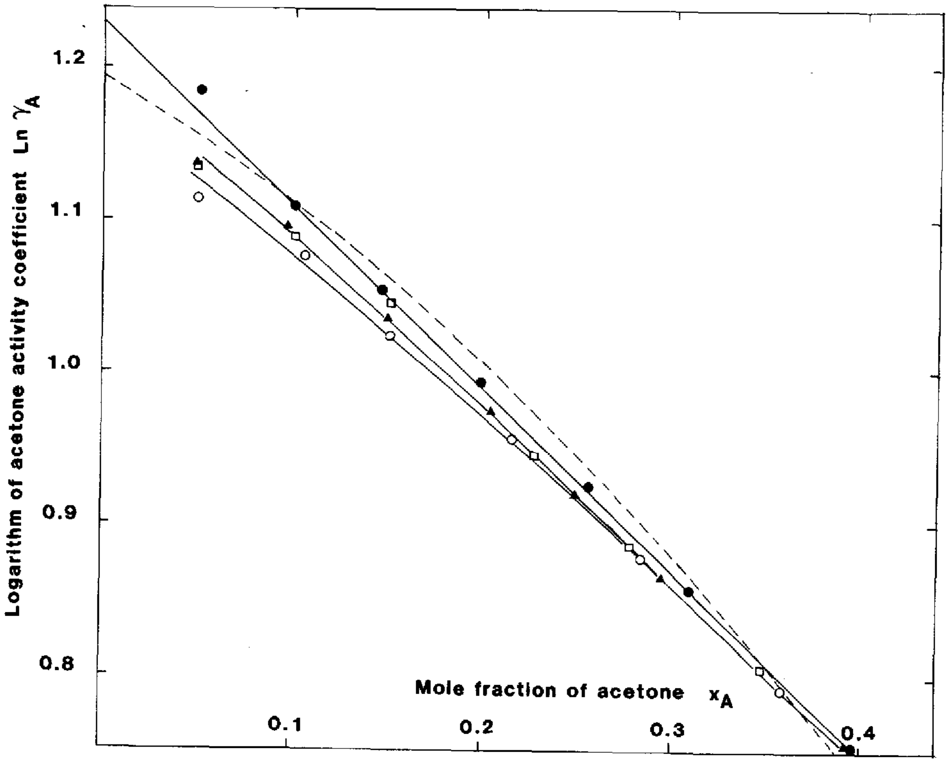

Fig. 1. The natural logarithm of the activity coefficient ln γ_A at 303 K for acetone in squalane plotted against the acetone mole fraction x_A. The squalane loadings on Celite are 30% (○) and 40% (□), and on Chromosorb W AW DMCS 30% (▲). Bulk squalane is denoted by (●). Full curves show the experimental isotherms and the dotted line shows the best fit of eqn. 3 to the bulk squalane results.

TABLE I

ABSORPTION OF ACETONE (A) IN SQUALANE (B)–DINONYL PHTHALATE (C) MIXTURES AT 303 K

n_B:n_C = Solvent mole ratio; other symbols see text.

n_B:n_C = *1:0*			n_B:n_C = *2.999:1*			n_B:n_C = *1:1.012*			n_B:n_C = *1:3.053*			n_B:n_C = *0:1*		
x_A	P_A (*Torr*)	γ_A	x_A	P_A (*Torr*)	γ_A	x_A	P_A (*Torr*)	γ_A	x_A	P_A (*Torr*)	γ_A	x_A	P_A (*Torr*)	γ_A
0.0510	45.7	3.262	0.0483	27.0	2.037	0.0545	22.4	1.498	0.0532	17.2	1.182	0.0459	12.1	0.964
0.1021	85.2	3.027	0.0985	54.1	1.999	0.1112	45.2	1.480	0.1086	35.4	1.188	0.1013	27.2	0.980
0.1480	117.3	2.865	0.1487	79.1	1.932	0.1620	65.2	1.464	0.1536	50.0	1.186	0.1507	40.9	0.990
0.1997	149.3	2.695	0.2018	104.3	1.871	0.2034	81.3	1.451	0.1951	63.6	1.184	0.1948	53.5	0.999
0.2563	179.7	2.519	0.2584	129.0	1.803	0.2562	101.3	1.432	0.2465	80.3	1.182	0.2364	65.5	1.007
0.3099	203.7	2.355	0.3129	151.5	1.744	0.3069	119.8	1.411	0.2927	95.8	1.186	0.3031	84.9	1.016
0.3536	220.8	2.233	0.3731	174.2	1.678	0.3722	142.9	1.385	0.3391	111.1	1.185	0.3502	99.0	1.024
0.3956	235.4	2.125	0.4617	203.6	1.580	0.4099	155.8	1.369	0.4033	132.1	1.183	0.4040	114.9	1.029

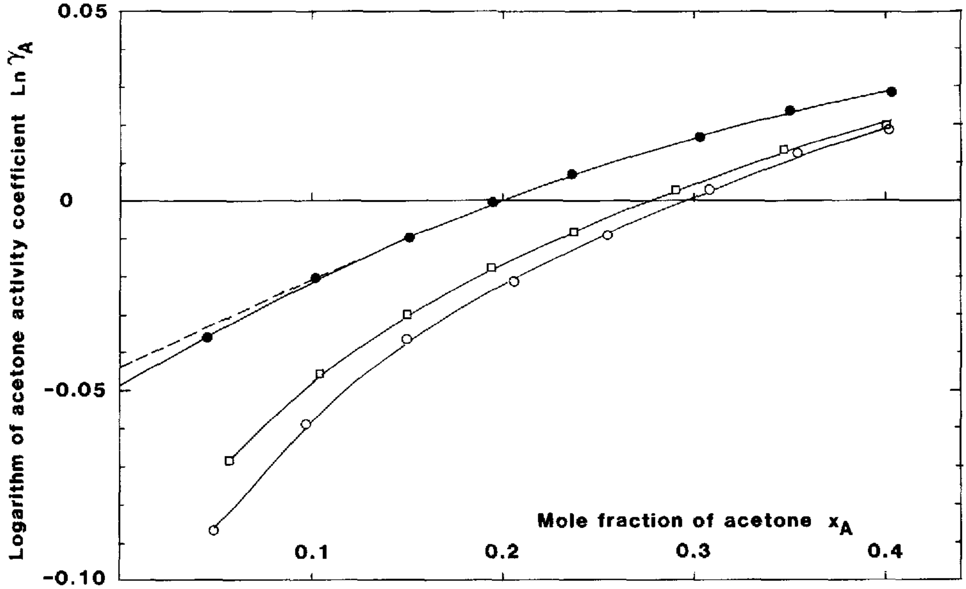

Fig. 2. The natural logarithm of the activity coefficient ln γ_A at 303 K for acetone in dinonyl phthalate plotted against the acetone mole fraction x_A. The dinonyl phthalate loadings on Celite are 30% (○) and 40% (□). Bulk dinonyl phthalate is denoted by (●). Full curves show the experimental isotherms and the dotted line shows the best fit of eqn. 3 to the bulk dinonyl phthalate results.

In the previous studies$^{1-5}$ the results for each isotherm for a particular solute were fitted to the Flory–Huggins expression for a binary system (eqn. 3), regarding each squalane–DNP mixture as a single component, and allowing the interaction parameter χ to vary linearly with the solute volume fraction φ_A

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

Activity coefficients at infinite dilution γ_A^∞ were then obtained from this analysis of the results using eqn. 4

$$\ln \gamma_A = \ln (1/r) + (1 - 1/r) + \chi^\infty \quad (4)$$

where r is the ratio of the molar volumes and χ^∞ is the interaction parameter at infinite dilution of the solute. However, as can be seen from the dotted curves in Figs. 1 and 2, the Flory–Huggins expression does not give a good fit to the results for acetone. The fit is poorest for acetone absorbed by squalane and improves as the DNP content is increased. As a consequence, values of the activity coefficients at infinite dilution γ_A^∞ were obtained by linear extrapolation of ln γ_A for the more dilute solutions when plotted against acetone mole fraction.

The partition coefficient for the solute at infinite dilution between the solvent and the vapour phase, K_R was calculated using

$$K_R = RT/(P_A^0\gamma_{P,A}^\infty V_L) \quad (5)$$

where V_L is the molar volume of the liquid absorbent taken as the molar average of that for the pure solvents. The values of the infinite dilution activity coefficients and the calculated partition coefficients are given in Table II. The value of γ_A^∞ for acetone in squalane at 303 K of 2.85 determined by Pecsok and Gump[13] using a microbalance is significantly lower than the value of 3.42 determined here. However Nitta *et al.*[14] have also determined γ_A^∞ for this system using GLC with a silanized support and found it to be 3.70 at 298.15 K and 2.85 at 323.15 K. Interpolation of their results on the basis of $\ln \gamma_A^\infty \propto 1/T$ gives a value of 3.51 at 303 K, supporting the higher value determined in this work.

In the previous studies of this mixed solvent system all the isotherms determined for a particular solvent were fitted to the Flory–Huggins expression for a ternary solution to find the best fit interaction parameters for the interaction between the solute and solvents, χ_{AB} and χ_{AC}, and between the solvents, χ_{BC}. The intersolvent interaction parameter χ_{BC} was then used in the Tiley–Perry equation[7], (eqn. 6) derived on the basis of conventional solution theory, to predict the partition coefficient of the solute in the mixed solvents, K_R, from those for the pure solvents, $K_{R(B)}$ and $K_{R(C)}$

$$\ln K_R = \varphi_B \ln K_{R(B)} + \varphi_C \ln K_{R(C)} + \varphi_B\varphi_C\chi_{BC} \tag{6}$$

With the non-polar solutes, pentane, hexane, heptane, cyclohexane, benzene and carbon tetrachloride, the equation predicted K_R for the mixed solvents to within 1%, whereas the simple empirical relation proposed by Purnell and Vargas de Andrade[6] (eqn. 7) gave deviations of up to 7%.

$$K_{R(PA)} = \varphi_B K_{R(B)} + \varphi_C K_{R(C)} \tag{7}$$

With the polar solutes, diethyl ether, chloroform, dichloromethane and ethyl acetate the prediction of the mixed solvent K_R by the Tiley–Perry equation, although better than that provided by eqn. 7, was not as good as for the non-polar solutes. This is probably to be expected as the specific intermolecular interactions possible with polar solutes invalidate the conventional solution model on which the Tiley–Perry equation is based. This is demonstrated in the present study with acetone where the Flory–Huggins expression for a binary system does not give a good fit to the acetone–

TABLE II

ACTIVITY COEFFICIENTS γ_A^∞ AND PARTITION COEFFICIENTS K_R FOR ACETONE AT INFINITE DILUTION IN SQUALANE (B)–DINONYL PHTHALATE (C) MIXTURES AT 303 K

n_B:n_C = Solvent mole ratio; $K_{R(PA)}$ = partition coefficient calculated from eqn. 7; $\Delta\%$ = percentage deviation of calculated K_R from experimental value.

n_B:n_C	γ_A^∞	K_R	$K_{R(PA)}$	$\Delta\%$
1:0	3.42	38.3		
1:0.334	2.10	65.2	66.0	1.2
1:1.012	1.51	95.3	96.7	1.5
1:3.053	1.18	127.6	130.3	2.1
0:1	0.954	166.8		

squalane results (Fig. 1). Consequently the overall fit to all five isotherms reported in Table I to the Flory–Huggins expression for a ternary system and the prediction of the mixed solvent partition coefficient by eqn. 6 is poor. In contrast the prediction of the mixed solvent K_R by eqn. 7 shown in Table II is much better than that for any of the other solutes studied with these solvents. However, as Perry and Tiley[7] have pointed out, the GLC partition coefficient can never be a strictly linear function of stationary phase composition for mixed solvents as eqn. 7 predicts, except in the extreme case of complete solvent immiscibility. Although there may be systems where linear behaviour is observed within *ca.* 5%, the mixed-solvent linear approximation of eqn. 7 must be used with considerable caution in predicting the behaviour of a mixed-solvent GLC column.

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REFERENCES

1 A. J. Ashworth and D. M. Hooker, *J. Chromatogr.*, 131 (1977) 399.
2 A. J. Ashworth and D. M. Hooker, *J. Chromatogr.*, 174 (1979) 307.
3 A. J. Ashworth and G. J. Price, *J. Chromatogr.*, 238 (1982) 89.
4 A. J. Ashworth, T. M. Letcher and G. J. Price, *J. Chromatogr.*, 262 (1983) 33.
5 A. J. Ashworth and G. J. Price, *J. Chromatogr.*, 324 (1985) 231.
6 J. H. Purnell and J. M. Vargas de Andrade, *J. Am. Chem. Soc.*, 97 (1975) 3585.
7 R. W. Perry and P. F. Tiley, *J. Chem. Soc., Faraday Trans. 1*, 74 (1978) 1655.
8 A. J. Ashworth, *Thermochim. Acta*, 51 (1981) 17.
9 *Selected Values of Properties of Chemical Compounds*, Thermodynamics Research Centre Data Project, Texas A and M University, College Station, TX, 1957, Table 23-2-1 (1.1130)k.
10 M. Hafez and S. Hartland, *J. Chem. Eng. Data*, 21 (1976) 179.
11 J. H. Dymond and E. B. Smith, *The Virial Coefficients of Pure Gases and Mixtures*, Oxford University Press, Oxford, 1980.
12 J. R. Conder and C. L. Young, *Physio-Chemical Measurement by Gas Chromatography*, Wiley, Chichester, 1979.
13 R. L. Pecsok and B. H. Gump, *J. Phys. Chem.*, 71 (1967) 2202.
14 T. Nitta, K. Morinaga and T. Katayama, *Ind. Eng. Chem. Fundam.*, 21 (1982) 396.