MIXED SOLVENTS IN GAS–LIQUID CHROMATOGRAPHY

ACTIVITY COEFFICIENTS FOR CHLOROFORM, DICHLOROMETHANE AND ETHYL ACETATE IN SQUALANE–DINONYL PHTHALATE MIXTURES AT 303°K

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SUMMARY

Activity and partition coefficients for the polar solutes chloroform, dichloromethane and ethyl acetate at infinite dilution in squalane–dinonyl phthalate mixtures have been determined at 303°K by the extrapolation of measurements made using a vacuum microbalance technique. The results are compared with predictions using the Purnell–Andrade and Tiley–Perry relationships.

The effect of solvent–solid support ratios on the determined activity coefficients and the adsorption phenomena involved have been examined. Whereas 20% by weight of solvent yields true bulk liquid activity coefficients for chloroform and dichloromethane, a 40% loading is necessary for ethyl acetate.

INTRODUCTION

The infinite dilution activity and partition coefficients for a number of non-polar solutes[1-3] and one moderately polar solute[4] (diethyl ether) in mixtures of squalane and dinonyl phthalate have been reported and used to illustrate the deviation of these systems from the simple relation proposed by Purnell and Vargas de Andrade[5] to predict the retention behaviour of mixed solvents in gas–liquid chromatography (GLC). It has also been shown that these systems are better represented by conventional solution theory. The study has been extended in the present work by the use of the more polar solutes chloroform, dichloromethane and ethyl acetate. In addition, the effect on the measured activity coefficients of different solvent to solid support ratios has been determined and the resulting adsorption phenomena examined.

EXPERIMENTAL

Absorption isotherms for chloroform and dichloromethane at $302.99 \pm 0.01°K$ were determined using a Sartorius Model 4102 electronic vacuum microbal-

ance in conjunction with a Texas Instruments quartz Bourdon pressure gauge. The apparatus and the techniques have been described previously[1]. The isotherms for the absorption of ethyl acetate at the same temperature were determined using a Sartorius Model 4201 magnetic suspension vacuum microbalance with a MKS Instruments Type 270/370 Baratron pressure gauge having a maximum reading of 100 Torr. This allowed the weight changes to be monitored to ± 0.1 mg on an absorbent sample of *ca.* 20 g, and the pressure to be measured to ± 0.01 Torr. The vacuum microbalance and the experimental techniques have again been described previously[6]. Measurements of the absorption of ethyl acetate by the bulk solvents were made by filling a series of trays suspended from the microbalance with solvent to a depth of *ca.* 1 mm. The magnetic suspension balance was used to determine the ethyl acetate isotherms as this solute was found to interact strongly with the VITON vacuum sealing rings employed in the other balance.

The solvents, squalane (2,6,10,15,19,23-hexamethyl tetracosane, Hopkins and Williams) and dinonyl phthalate [di-(3,5,5-trimethylhexyl)-1,2-benzene dicarboxylate, BDH] were used without further purification. The solutes were BDH Aristar grade. The ethyl acetate had a certified purity $> 99.5\%$. The chloromethanes were treated by passage down a column of active basic alumina to remove the ethanol stabilizer, and a minimum purity of 99.9% was determined by GLC. The solvents squalane and dinonyl phthalate (DNP) and their mixtures were coated onto Celite 545 AW of sieve size B.S.S. 100–120, obtained from Phase Separations, using 40–60°C boiling range petroleum ether. The squalane–DNP mixtures were prepared at mole ratios of *ca.* 3:1, 1:1 and 1:3. The actual mole ratios are given in Table I.

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.

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

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

where $\gamma_{P,A}$ is the activity coefficient uncorrected for gas phase non-ideality and liquid phase compressibility. Values used for the saturated vapour pressure P_A^0 and the

TABLE I

ACTUAL MOLE RATIOS $n_B:n_C$ FOR THE SQUALANE (B)–DNP (C) MIXTURES

Solute	$n_B:n_C$		
	3:1	1:1	1:3
Chloroform	2.987:1	1:1.038	1:2.854
Dichloromethane	3.029:1	1:1.081	1:3.144
Ethyl acetate	3.165:1	1:1.010	1:2.999

TABLE II

SATURATED VAPOUR PRESSURES P_A^0, SECOND VIRIAL COEFFICIENTS B_{AA} AND MOLAR VOLUMES V_A^0 OF THE SOLUTES AT 303°K

Solute	P_A^0 (Torr)[7]	B_{AA} (dm^3 mol^{-1})[8]	V_A^0 (cm^3 mol^{-1})[9]
Chloroform	240.80	−1.16	81.18
Dichloromethane	525.88	−0.81	64.98
Ethyl acetate	119.17	−2.04	99.24

molar volume V_A^0 of the pure liquid solutes, and the second virial coefficient B_{AA} of the pure gaseous solutes, are given in Table II.

It is known that adsorption effects can contribute to the retention properties of liquid solvents coated on solid supports[10]. In the absorption of diethyl ether into SQ and DNP[4] these effects resulted in a variation of the activity coefficient determined with liquid loadings below 27%. (Throughout this work, the liquid loading is quoted as the percentage by weight of the absorbent sample that is solvent.) Freeguard and Stock[11] studied the absorption of chloromethanes by squalane and DNP as separate solvents using a McBain–Bakr balance and found no such adsorption effects when liquid loadings of ca. 30% were employed. To confirm these findings, as this type of apparatus becomes increasingly inaccurate at low solute concentrations[12], absorption isotherms for chloroform and dichloromethane were measured at liquid loadings of 20% and 30% for each solvent. The results for the absorption into the separate solvents are shown in Figs. 1 and 2 as plots of the logarithm of activity coefficient versus mole fraction of solute. The figures show that for both solvents the results at the two liquid loadings were negligibly different, so confirming the absence of adsorption effects and that true bulk solubility was being measured.
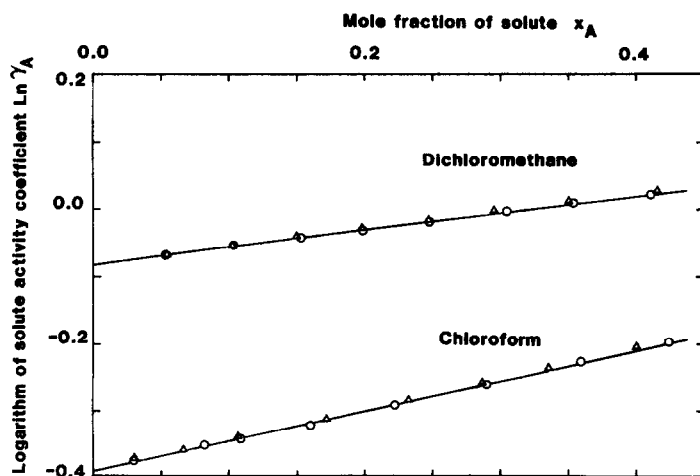

Fig. 1. The natural logarithm of the activity coefficient ln γ_A at 303°K for the solutes, chloroform and dichloromethane, in squalane plotted against the solute mole fraction x_A. The squalane loadings on Celite are 19.8% (△) and 31.5% (○). The full curves show the best fit of eqn. 3 to the results.

TABLE III

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

$n_B:n_C$ = approximate mole ratio (see Table I); for other symbols see text.

| $n_B:n_C$ = 1:0			$n_B:n_C$ = 3:1			$n_B:n_C$ = 1:1			$n_B:n_C$ = 1:3			$n_B:n_C$ = 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
Chloroform														
0.0292	4.74	0.6848	0.0578	6.54	0.4776	0.0530	4.50	0.3585	0.0691	4.91	0.2996	0.0598	3.93	0.2774
0.0825	13.74	0.7017	0.1088	12.85	0.4978	0.0955	8.40	0.3711	0.1251	9.36	0.3156	0.1124	7.78	0.2919
0.1082	18.20	0.7091	0.1592	19.58	0.5181	0.1587	14.89	0.3954	0.1855	14.83	0.3370	0.1589	11.54	0.3062
0.1601	27.52	0.7241	0.2097	26.96	0.5414	0.2079	20.50	0.4155	0.2407	20.48	0.3585	0.2086	15.99	0.3230
0.2216	39.25	0.7455	0.2597	34.95	0.5664	0.2424	24.85	0.4319	0.2975	27.08	0.3833	0.2520	20.30	0.3394
0.2895	53.07	0.7706	0.3000	41.86	0.5870	0.2848	30.59	0.4523	0.3519	34.32	0.4106	0.2980	25.40	0.3590
0.3598	68.19	0.7961	0.3523	51.69	0.6169	0.3371	38.58	0.4792	0.3963	40.96	0.4349	0.3432	30.94	0.3795
0.4232	82.75	0.8206	0.3933	59.90	0.6401	0.3856	46.57	0.5080	0.4445	49.10	0.4646	0.3995	38.80	0.4087
Dichloromethane														
0.0523	25.10	0.9337	0.0551	18.08	0.6340	0.0530	12.78	0.4693	0.0588	11.40	0.3775	0.0597	10.69	0.3489
0.1019	49.50	0.9447	0.0977	32.76	0.6525	0.0996	24.87	0.4860	0.1192	24.36	0.3978	0.1062	19.85	0.3640
0.1503	74.02	0.9566	0.1755	62.01	0.6865	0.1572	41.15	0.5093	0.1844	40.09	0.4229	0.1562	29.83	0.3803
0.1984	99.23	0.9700	0.2197	79.96	0.7066	0.2155	59.41	0.5358	0.2517	58.59	0.4525	0.1972	40.30	0.3976
0.2475	125.33	0.9812	0.2739	103.57	0.7334	0.2892	85.34	0.5728	0.3150	78.29	0.4827	0.2509	54.32	0.4208
0.3040	156.50	0.9960	0.3170	123.37	0.7543	0.3243	98.75	0.5908	0.3708	98.01	0.5128	0.2994	68.29	0.4430
0.3558	185.99	1.0099	0.3710	149.97	0.7824	0.3778	121.14	0.6214	0.4338	123.35	0.5511	0.3536	85.66	0.4703
0.4104	217.62	1.0229	0.4152	173.29	0.8069	0.4395	149.81	0.6597	0.4950	151.46	0.5922	0.4004	102.51	0.4966
Ethyl acetate														
0.0432	9.19	1.8058	0.0466	7.10	1.2958	0.0761	9.52	1.0631	0.0607	6.74	0.9434	0.0569	5.62	0.8389
0.0917	19.23	1.7791	0.0943	14.42	1.2984	0.1524	19.26	1.0716	0.1216	13.70	0.9571	0.1226	12.35	0.8559
0.1319	27.36	1.7592	0.1438	22.05	1.3008	0.2292	29.31	1.0841	0.1839	21.06	0.9715	0.1608	16.45	0.8683
0.1759	35.99	1.7335	0.1881	28.78	1.2971	0.2988	38.50	1.0912	0.2396	27.80	0.9839	0.2140	22.27	0.8829
0.2256	45.30	1.6993	0.2303	35.16	1.2937	0.3709	48.03	1.0955	0.3012	35.36	0.9947	0.2743	29.11	0.8996
0.2693	53.10	1.6670	0.2687	40.98	1.2914	0.4384	56.85	1.0960	0.3413	40.46	1.0038	0.3160	33.97	0.9109
0.3065	59.45	1.6385	0.3239	49.07	1.2814	0.4718	61.24	1.0965	0.4071	48.71	1.0121	0.3962	43.62	0.9319
0.3639	68.59	1.5907	0.3636	54.84	1.2748	0.5086	66.03	1.0960	0.4736	57.50	1.0260	–	–	–
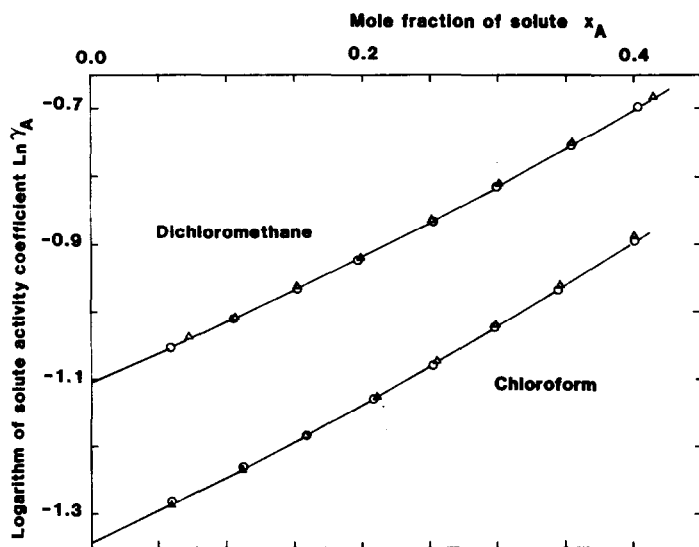
Fig. 2. The natural logarithm of the activity coefficient ln γ_A at 303°K for the solutes, chloroform and dichloromethane, in dinonyl phthalate plotted against the solute mole fraction x_A. The dinonyl phthalate loadings on Celite are 19.6% ($\triangle$) and 28.9% ($\bigcirc$). The full curves show the best fit of eqn. 3 to the results.

In view of these findings, loadings of *ca.* 30% were employed for the solvent mixtures and the results are given in Table III.

If bulk solubility is the only retention process in operation, the same vapour uptake per unit weight of liquid absorbent would be expected at the same relative vapour pressure irrespective of liquid loading. That this is not so with ethyl acetate as the solute is clearly seen in Fig. 3, which shows that the absorption is virtually identical for the bulk liquid and the 30% loaded samples, but that the 10% loaded samples absorbed significantly higher amounts of vapour. A more critical examination of the effects of liquid loading is presented by the plots of the activity coefficient of ethyl acetate absorbed by squalane and DNP shown in Figs. 4 and 5, respectively. In both cases the results for the bulk liquids and the 40% loaded samples agree within experimental error, although the former are slightly higher, but there are significant differences between results obtained at lower loadings and the 30% sample is seen to show greater absorption than the 40% sample. Thus, in these systems adsorption effects are important for loadings less than 40%.

Adsorption can occur onto the solid support, whether bare or coated with solvent, and at the gas–liquid interface. It was originally thought that gas–liquid interfacial adsorption would only occur with polar solvents, but Pecsok and Gump[13] and others[14,15] showed that it was possible when using polar solutes in non-polar solvents, such as hexadecane or squalane. To gain an idea of the amount of adsorption onto the solid support that might be expected, an adsorption isotherm for ethyl acetate was determined on bare Celite. The results are shown in Fig. 6. The adsorption amounted to 0.2 mg g^{-1} Celite at the relative pressure (P_A/P_A^0) of 0.3 and 0.3 mg g^{-1} Celite at a relative pressure of 0.5. The 10% loaded samples contained *ca.* 18 g of Celite, so the maximum weights of ethyl acetate that could have been adsorbed by the bare support were 3.6 and 5.4 mg at relative pressures of 0.3 and 0.5, respec-
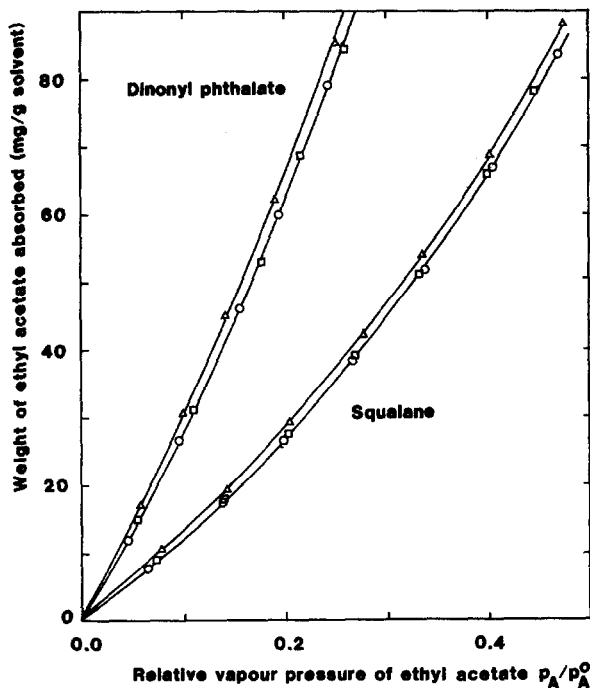
Fig. 3. The weight of ethyl acetate absorbed per gram of the solvents, squalane and dinonyl phthalate, at 303°K plotted against ethyl acetate relative vapour pressure P_A/P_A^0. The solvent loadings on Celite are 10.0% ($\triangle$) and 30.0% ($\square$), bulk liquid is denoted by ($\bigcirc$).
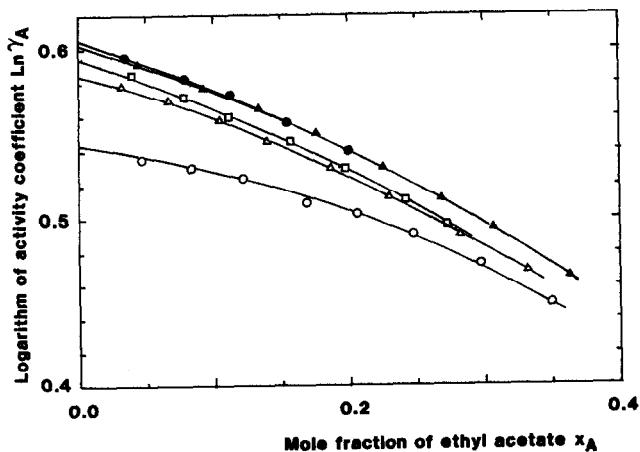

Fig. 4. The natural logarithm of the activity coefficient of ethyl acetate in squalane at 303°K plotted against ethyl acetate mole fraction x_A. The squalane loadings on Celite are 10.0% ($\bigcirc$), 20.0% ($\triangle$), 30.0% ($\square$) and 40.0% ($\blacktriangle$). Bulk squalane is denoted by ($\bullet$). The full curves show the best fit of eqn. 3 to the results.
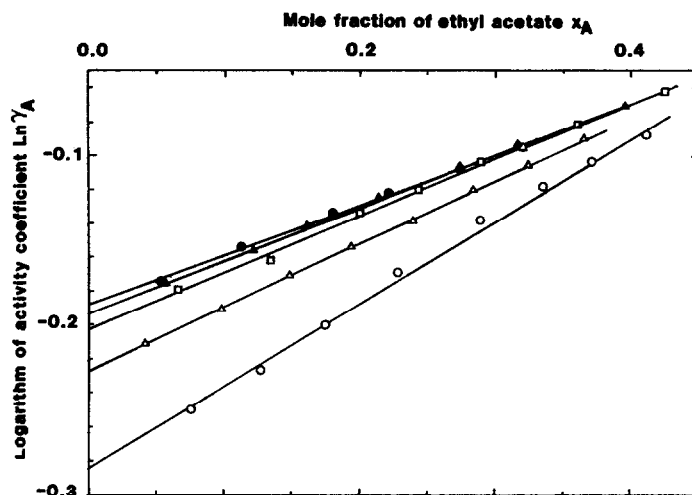
Fig. 5. The natural logarithm of the activity coefficient of ethyl acetate in dinonyl phthalate at 303°K plotted against ethyl acetate mole fraction x_A. The dinonyl phthalate loadings on Celite are 10.0% (O), 20.0% (△), 30.0% (□) and 40.0% (▲). Bulk dinonyl phthalate is denoted by (●). The full curves show the best fit of eqn. 3 to the results.

tively. Freeguard and Stock[16] found Celite to be virtually inert, but firebrick (a pink diatomaceous earth) quite active. Significantly they found that a 5% loaded sample on this latter support showed a lower vapour uptake than the bare support, suggesting that the absorbent liquid had a deactivating effect on the solid. The same effect may be expected with Celite, particularly with the slightly polar DNP which would cover some of the active sites on the solid. Thus, the values given above for adsorption onto the bare Celite undoubtedly overestimate the ethyl acetate adsorbed at the solid–liquid interface when the solid is coated by the solvent.

With bulk squalane as absorbent there was an approximate uptake of 93 mg (g squalane)$^{-1}$ at a relative pressure of 0.5, while the value for the 10% loaded sample was 97 mg g^{-1}. Thus, the 1.96 g of squalane in the 10% sample showed an "excess absorption" of ca. 7.8 mg. The DNP samples showed absorptions of ca. 103 mg g^{-1} for the bulk liquid and ca. 107 mg g^{-1} for the 10% sample at a relative pressure of
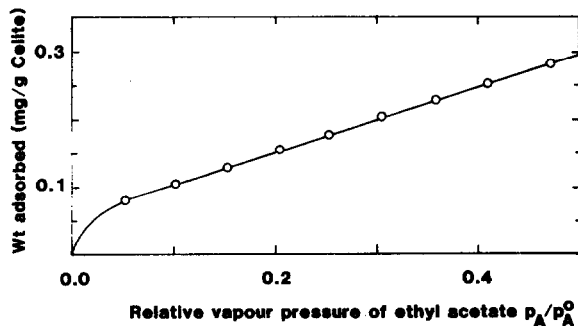

Fig. 6. The adsorption of ethyl acetate on Celite at 303°K plotted against relative vapour pressure P_A/P_A^0.

0.3, giving the 2.0 g of DNP in the 10% sample an "excess absorption" of *ca.* 8.0 mg. Thus with both of these solvents, the presumed maximum adsorption onto the solid support is insufficient to account for the total adsorption, which confirms the previous suggestions of gas–liquid interfacial adsorption in polar solute and non-polar solvent systems. As a result of these findings, liquid loadings of 40–45% were employed to determine absorption isotherms for ethyl acetate for the solvent mixtures. The results are shown in Table III.

The results for each isotherm presented in Table III were fitted to the Flory–Huggins expression for a binary system (eqn. 3) by regarding each squalane–DNP mixture as a single component:

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

The interaction parameter χ was allowed to vary linearly with the solute volume fraction φ_A and from this fit an activity coefficient at infinite dilution γ_A^∞ was calculated. The partition coefficient for the solute at infinite dilution between the solvent and vapour phase, K_R, was calculated using the standard relation,

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

where V_L is the molar volume of the liquid absorbent taken as the molar average of that for the pure solvents. The calculated values of the infinite dilution activity coefficients and partition coefficients are given in Table IV. Freeguard and Stock[11] obtained γ_A^∞ values for chloroform and dichloromethane of 0.653 and 1.076 in squalane and 0.251 and 0.379 in DNP, respectively. These are in reasonable agreement with the results shown here, especially when the experimental errors at low solute vapour pressures of the McBain–Bakr apparatus used by Freeguard and Stock are considered. Nitta *et al.*[17] used GLC to measure a value of γ_A^∞ for ethyl acetate in squalane of 1.96, which is higher than the value of 1.822 found in the present work.

Purnell and Vargas de Andrade[5] proposed a linear relation between the partition coefficient of a solvent mixture and its volume fraction composition at infinite solute dilution,

$$K_R(PA) = \varphi_B K_{R(B)} + \varphi_C K_{R(C)} \qquad (5)$$

TABLE IV

ACTIVITY COEFFICIENTS γ_A^∞ AND PARTITION COEFFICIENTS K_R FOR THE SOLUTES AT INFINITE DILUTION IN SQUALANE (B)–DNP (C) MIXTURES AT 303°K

$n_B:n_C$ = approximate solvent mole ratio.

$n_B:n_C$	Chloroform		Dichloromethane		Ethyl acetate	
	γ_A^∞	K_R	γ_A^∞	K_R	γ_A^∞	K_R
1:0	0.6752	223.9	0.9153	76.3	1.8218	167.3
3:1	0.4573	346.2	0.6166	118.4	1.2953	245.6
1:1	0.3409	487.1	0.4508	170.4	1.0488	318.7
1:3	0.2795	621.7	0.3596	224.1	0.9290	377.8
0:1	0.2615	701.3	0.3313	255.7	0.8238	448.9

An alternative expression based on Flory–Huggins solution theory was derived by Perry and Tiley[18], namely

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

In these equations $K_{R(B)}$ and $K_{R(C)}$ are the partition coefficients for the pure solvents, while χ_{BC} is the Flory–Huggins interaction parameter between the two solvents. The intersolvent interaction parameter was calculated for the systems studied here by fitting the results from all five absorption isotherms for a single solute to the Flory–Huggins expression for a ternary system (eqn. 7) in the manner described previously[2].

$$\ln \gamma_A = \ln(\varphi_A/x_A) + 1 - \varphi_A/x_A + (1 - \varphi_A)(\varphi_B \chi_{AB} + \varphi_C \chi_{AC}) - \varphi_B \varphi_C \chi_{BC} \tag{7}$$

The interaction parameters for a solute with each solvent were allowed to vary linearly with φ_A according to

$$\chi_{AB} = \chi_{AB}^0 + [\varphi_A/(\varphi_A + \varphi_B)] \chi'_{AB} \tag{8}$$

and similarly for χ_{AC}, while χ_{BC} was assumed to be independent of concentration. The values of the interaction parameters determined are shown in Table V.

    The partition coefficients predicted by eqns. 5 and 6 are presented in Table VI together with the percentage deviations ($\Delta\%$) of the predicted values from the experimentally determined values. The predictions by the Purnell–Andrade equation can be seen to differ from the experimental values by up to 10% and are not as good as those based on the Tiley–Perry relation, which predicts the chloroform and dichloromethane partition coefficients to within 3–4%. With ethyl acetate the Tiley–Perry relation gives an average deviation of 4.6%, compared with 6% for the Purnell–Andrade equation. The predictions of the Tiley–Perry equation for these polar solutes are not as good as for the non-polar solutes studied previously[1–3]. This is a consequence of the specific intermolecular interactions possible with polar solutes, which invalidate the model on which Flory–Huggins solution theory is based, assuming as it does random mixing. This is illustrated by the Flory–Huggins intersolvent interaction parameters per unit volume of solute, χ_{BC}/V_A^0, shown in Table V, of 10.95, 12.37 and 5.85 mol dm^{-3} for chloroform, dichloromethane and ethyl acetate respectively, which are considerably larger than the 2.7 $\pm$ 0.1 found for pentane, hexane, heptane and cyclohexane[2], 3.13 for tetrachloromethane[3] and 3.80 mol dm^{-3}

TABLE V

INTERACTION PARAMETERS FOR SOLUTES (A) IN SQUALANE (B)–DNP (C) MIXTURES AT 303°K

V_A^0 = solute molar volume.

Solute	χ_{AB}^0	χ'_{AB}	χ_{AC}^0	χ'_{AC}	χ_{BC}	χ_{BC}/V_A^0 (mol dm^{-3})
Chloroform	0.613	−0.185	−0.503	0.883	0.889	10.95
Dichloromethane	1.085	−0.676	−0.069	1.054	0.804	12.37
Ethyl acetate	1.366	−0.418	0.534	−0.251	0.580	5.85

TABLE VI

PARTITION COEFFICIENTS FOR THE SOLUTES AT INFINITE DILUTION IN SQUALANE (B)–DNP (C) MIXTURES AT 303°K CALCULATED FROM THE PARTITION COEFFICIENTS IN THE PURE SOLVENTS

$n_B:n_C$ = approximate solvent mole ratio; φ_B = volume fraction of squalane in the solvent mixture; $K_R(PA)$ = 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.

Solute	$n_B:n_C$	φ_B	$K_R(PA)$	$\Delta\%$	$K_R(TP)$	$\Delta\%$
Chloroform	3:1	0.7785	329.6	4.8	336.1	2.9
	1:1	0.5389	444.0	8.8	472.7	3.0
	1:3	0.2983	558.9	10.1	600.8	3.4
Dichloromethane	3:1	0.7861	114.7	3.1	113.1	4.4
	1:1	0.5287	160.9	5.6	164.8	3.3
	1:3	0.2784	205.8	8.1	214.6	4.2
Ethyl acetate	3:1	0.7934	225.5	8.2	225.6	8.1
	1:1	0.5457	295.2	7.3	302.5	5.1
	1:3	0.2881	367.8	2.6	380.5	0.7

for benzene[2]. The presence of specific interactions is also indicated by the negative values of the interaction parameter χ^0_{AC} in Table V, for the interaction between the solute and DNP, where hydrogen bonding could occur with the chloromethanes. The much higher values of χ^0_{AB} show the solutes to be much less compatible with squalane than with DNP. An interesting point is that the concentration dependencies as shown by χ'_{AB} and χ'_{AC} are considerably larger than those found with the hydrocarbons[2] or tetrachloromethane[3]. This is presumably due to the greater change of the solution forces on adding polar solutes than would be involved with non-polar solutes. A further consequence of the greater compatibility of polar solutes with DNP than with squalane is that the composition of the mixed solvents might have a greater influence on solution properties than with non-polar solutes. Thus treatment of χ_{BC} as a single concentration-independent parameter may not be justified when using polar solutes and the introduction of an extra parameter to account for concentration dependence might be beneficial to the fit of the Tiley–Perry relation.

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