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MIXED SOLVENTS IN GAS–LIQUID CHROMATOGRAPHY

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

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SUMMARY

    Activity and partition coefficients for tetrachloromethane at infinite dilution in squalane–dinonyl phthalate solvent mixtures have been determined at 303°K by the extrapolation of measurements made using a vacuum microbalance technique. The deviation from solution ideality shown in the mixed solvents is greater than that shown in the separate solvents. This results in the activity and partition coefficients in the mixed solvents lying outside the range delineated by the coefficients for the separate solvents for a large part of the mixed solvent composition. The partition coefficients can be accounted for to within 0.2% by conventional solution theory but values predicted by the Purnell–Andrade relation differ by as much as 7%.

INTRODUCTION

    The activity coefficients at infinite dilution for several C_6 and related hydrocarbons in squalane (SQ) and dinonyl phthalate (DNP) solvent mixtures have been reported previously[1,2] and used to demonstrate the deviation of the systems from the simple relation proposed by Purnell and Vargas de Andrade[3] to predict the solute partition coefficient for mixed solvents in gas–liquid chromatography (GLC). It was further demonstrated that the experimentally determined partition coefficients for the mixed solvent systems could be accounted for, to within 1%, by a relation derived from basic solution theory.
    It was decided to investigate further the ability of these relations to express mixed solvent behaviour by examining the solubility of tetrachloromethane in the same solvent mixture. It was thought that the simple symmetrical and therefore nonpolar nature of the tetrachloromethane molecule would make it a very suitable solute for this purpose. Moreover, by extrapolation of their static vapour absorption results Freeguard and Stock[4] estimated the activity coefficient at infinite dilution at 30°C for tetrachloromethane to be 0.522 in squalane and 0.600 in dinonyl phthalate, showing the negative deviation from ideal solution behaviour to be very similar in the separate solvents.

TABLE I

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

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

$n_B:n_C = 1:0$			$n_B:n_C = 3:1$			$n_B:n_C = 1:1$			$n_B:n_C = 1:3$			$n_B:n_C = 0:1$		
x_A	P_A (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
0.0641	5.095	0.5659	0.0495	3.795	0.5495	0.0578	4.430	0.5496	0.0593	4.670	0.5642	0.0543	4.590	0.6058
0.1114	9.150	0.5883	0.0971	7.590	0.5599	0.1020	7.985	0.5611	0.1084	8.765	0.5791	0.1078	9.450	0.6278
0.1689	14.370	0.6091	0.1414	11.430	0.5787	0.1511	12.270	0.5814	0.1564	13.040	0.5984	0.1573	14.210	0.6468
0.2163	18.935	0.6266	0.1925	15.990	0.5948	0.2064	17.265	0.5988	0.2080	17.915	0.6163	0.2067	19.180	0.6640
0.2534	22.725	0.6418	0.2490	21.510	0.6181	0.2515	21.730	0.6182	0.2693	24.180	0.6423	0.2555	24.430	0.6840
0.2997	27.650	0.6599	0.2996	26.705	0.6376	0.3041	27.180	0.6394	0.3212	29.875	0.6649	0.3057	30.140	0.7050
0.3420	32.510	0.6796	0.3523	32.575	0.6610	0.3550	32.920	0.6629	0.3680	35.270	0.6852	0.3502	35.450	0.7236
0.3899	38.190	0.7000	0.3930	33.320	0.6787	0.3921	37.270	0.6794	0.4157	41.230	0.7086	0.3969	41.410	0.7454

EXPERIMENTAL

Absorption isotherms were determined at 303.04 ± 0.01 °K using a Sartorius Model 4102 electronic vacuum microbalance in conjunction with a Texas Instruments quartz Bourdon gauge. (A nominal temperature of 303°K is used throughout this report.) The apparatus, the techniques and the materials were as described previously[1], except for the tetrachloromethane which was supplied by BDH (Poole, Great Britain) as "specially pure for spectroscopy".

Squalane–dinonyl phthalate mixtures were prepared for nominal mole ratios of 3:1, 1:1 and 1:3. The actual ratios were 3.011:1, 1:0.999 and 1:2.989.

RESULTS

The absorption isotherms are presented in Table I in the form of the 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 solvent mixture was then calculated from these measurements using a second virial coefficient B_{AA} and a molar volume V_A^* for the tetrachloromethane of −1423 and 97.667 cm^3 mol^{-1}, respectively (see eqns. 2 and 3 of ref. 1). The second virial coefficient was obtained by extrapolation of experimentally determined values[5] to 303.04°K by plotting ln B_{AA} against ln T. The molar volume was determined from the specific volume measurements of Wood and Gray[6].

TABLE II

ACTIVITY COEFFICIENTS γ_A^x AND PARTITION COEFFICIENTS K_R FOR TETRACHLORO-METHANE IN SQUALANE (B)–DNP (C) MIXTURES AT 303°K

$n_B:n_C$ = solvent mole ratio.

| | $n_B:n_C$ | | | | |
	1:0	3:1	1:1	1:3	0:1
γ_A^x	0.5447	0.5262	0.5241	0.5384	0.5838
K_R	466.2	504.8	531.1	543.2	527.8

The activity coefficients at infinite dilution shown in Table II were determined by regarding the SQ–DNP solvent mixture as a single component and fitting the absorption results for an individual isotherm to the conventional Flory–Huggins expression for the solute activity coefficient in a binary system (see eqn 1 of ref. 2). Effectively, the same values at infinite dilution can be found by a simple linear extrapolation of the logarithm of the activity coefficients plotted against solute mole fraction as shown in ref. 1. The partition coefficients for the solute between the solvent and the vapour phase at infinite dilution given in Table II were calculated using the standard relation

$$K_R = RT/(p_A^* \gamma_{x,A}^x V_L)$$
$$= [RT/(p_A^* \gamma_A^x V_L)] \exp \{[V_A^* - B_{AA} + (B_{AA}^2 p_A^*/2RT)]p_A^*/RT\} \quad (1)$$
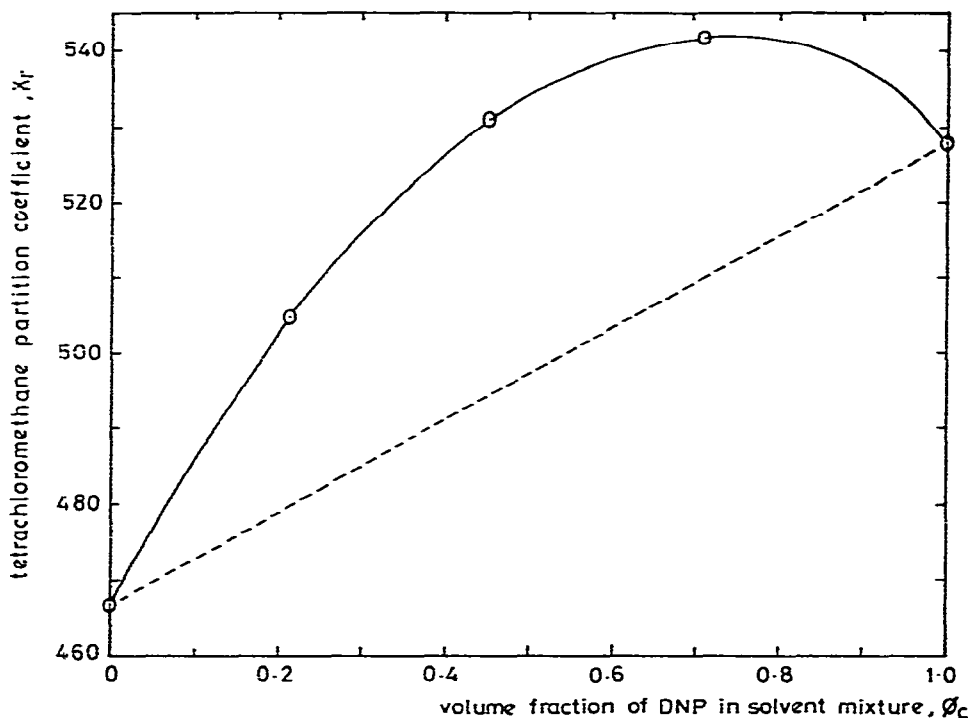
Fig. 1. Plot of the tetrachloromethane partition coefficient at infinite dilution, K_R, at 303 K $vs.$ the volume fraction of DNP in the SQ–DNP solvent mixture. The full curve is given by eqn. 3 with $\chi_{BC} = 0.306$. The dashed line is given by the Purnell–Andrade relation, eqn. 2.

In equation 1 p_A^* is the vapour pressure of the pure solute and $\gamma_{x,A}^\infty$ is the uncorrected activity coefficient at infinite dilution (*i.e.* $\lim_{x_A \cdot p_A \to 0} [p_A/(p_A^* x_A)]$). The molar volume V_L of the SQ–DNP mixture is taken as a linear function of the mole fraction composition using the molar volumes of the separate solvents[7]. It has been established by density measurements that there is effectively a zero volume of mixing between these solvents[8]. The vapour pressure of the tetrachloromethane at 303.04 °K, $p_A^* = 141.1$ mmHg, was calculated from the constants for the Antoine equation determined by Boublik and Aim[9].

DISCUSSION

The activity coefficients at infinite dilution determined for tetrachloromethane in squalane and dinonyl phthalate as separate solvents shown in Table II are 1.3% and 2.7% smaller, respectively, than those reported by Freeguard and Stock[4]. The difference is probably a result of the greater experimental error present in the Freeguard and Stock results where measurements of vapour absorption using a quartz spring balance and a mercury manometer were extrapolated to infinite dilution. Measurements by this technique are subject to increasing errors as the concentration of the solute in the solvent decreases, giving small spring extensions and small differences in manometer heights[10,11].

Fig. 1 shows the deviation of the partition coefficients in the SQ–DNP solvent mixtures from those predicted using the linear relation of Purnell and Andrade,

$$K_R = \varphi_B K_{R(B)} + \varphi_C K_{R(C)} \tag{2}$$

The partition coefficient at infinite dilution in the (B + C) solvent mixture, K_R, is related linearly to the partition coefficients at infinite dilution in the separate solvents $K_{R(B)} + K_{R(C)}$ through the volume fractions in the mixed solvent, φ_B and φ_C. The full curve in Fig. 1 is that given by the relation derived from conventional Flory–Huggins theory[2],

$$\ln K_R = \varphi_B \ln K_{R(B)} + \varphi_C \ln K_{R(C)} + \varphi_B \varphi_C \chi_{BC} \tag{3}$$

The parameter $\chi_{BC} = 0.306$ accounting for the interaction between the solvent molecules was obtained by analysis of all five isotherms in Table I in terms of the Flory–Huggins expression for a ternary system as explained in ref. 2. The Flory–Huggins based relation can account to within 0.2% for the experimentally derived mixed solvent partition coefficients, whereas the values derived from the Purnell–Andrade relation, described by the dashed line in Fig. 1, show a deviation as great as 7%. It is interesting to note that for over more than half of the composition range the partition coefficients for the mixed solvents lie outside the range delineated by the partition coefficients for the two separate solvents.

It has been realised for some time that the dinonyl phthalate supplied commercially for chromatographic analysis and purported to be the *bis*(3,5,5-trimethylhexyl) isomer is impure[8,10,12]. In spite of this, excellent agreement has been found between static[11] and GLC[8] determinations of the activity and partition coefficients at infinite dilution of several C_6 and related hydrocarbons in DNP supplied commercially. Moreover, a comparison of static[1,2] and GLC[8] derived infinite dilution activity and partition coefficients for hexane in three mixtures of SQ–DNP agree on average within 0.5%. Laub and Purnell[13] proposed that systems which are described by eqn. 2 be termed "diachoric" and point out that the presence of isomers of DNP in no way affects the validity of the diachoric relation. The same may be said for the use of eqn. 3, as it has been shown that each SQ + DNP solvent mixture can be treated as a single solvent[1,2], and that the solubility of each of the solutes studied can be accounted for in terms of the Flory–Huggins equation for a binary system.

The possibility of the coefficients for the mixed solvents having values outside the range delineated by the values for the two separate solvents is more strikingly shown when the activity coefficients are examined. Fig. 2 shows the activity coefficients determined at infinite dilution plotted as a function of solvent composition. The full curve is that given by the Flory–Huggins expression for a ternary system with interaction parameters given in Table III. The interaction parameters were determined from analysis of the five combined isotherms in Table I according to eqn. 5 and 6 of ref. 2. The value of the interaction parameter for the mixed solvents per unit molar volume of the solute χ_{BC}/V_A^* of 3.13 mol dm^{-3} lies between that found with benzene as the solute[2] (3.80 mol dm^{-3}) and that for pentane, hexane, heptane and cyclohexane as solutes[2] (2.70 ± 0.06 mol dm^{-3}). The dashed line gives the activity coefficients in the mixed solvents according to the Purnell–Andrade relation expressed in
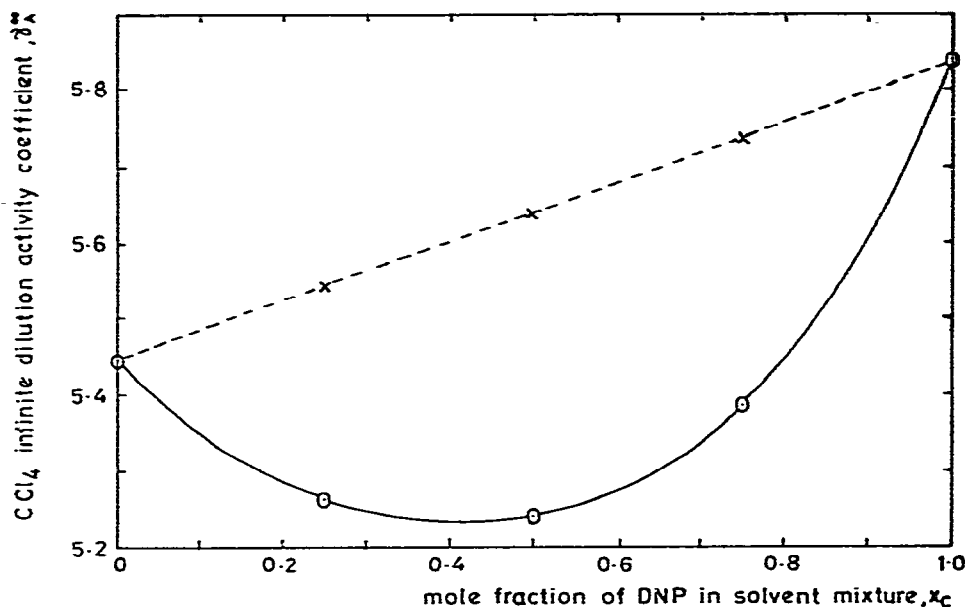
Fig. 2. Plot of the tetrachloromethane activity coefficient at infinite dilution, γ_A^∞, at 303°K vs. the mole fraction of DNP in the SQ–DNP solvent mixture. The full curve is given by the Flory–Huggins expression for a ternary system (eqn. 5 and 6 of ref. 2) using interaction parameters given in Table III. The dashed curve is given by the Purnell–Andrade relation expressed in terms of activity coefficients (eqn. 13 of ref. 1).

terms of activity coefficients (see eqn. 13, ref. 1). Since the relation for the partition coefficients (eqn. 2) is linear with respect to composition and K_R is inversely proportional to the reciprocal of γ_A^∞ (eqn. 1), it is surprising that the relation produces what is almost a linear plot for the solute activity coefficient with solvent mole fraction. This is a result, however, of the small difference between the activity coefficients for the tetrachloromethane in the separate solvents. The activity coefficients for tetrachloromethane in the mixed solvents lie outside the range given by the activity coefficients in the separate solvents for more than 80% of mixed solvent composition when expressed as a mole fraction. There is with this particular system a greater deviation from ideality with the mixed solvents than is shown by the separate solvents. Hence the use of an empirical relation based on the assumption of a linear relation between the partition coefficients for the separate solvents could well lead to a misleading conclusion.

TABLE III

INTERACTION PARAMETERS DETERMINED FROM ANALYSIS OF THE COMBINED ISO-THERMS (THREE TERNARY AND TWO BINARY) IN TABLE I FOR TETRACHLORO-METHANE (A) IN SQUALANE (B)–DNP (C) MIXTURES AT 303°K

$V_A^\bullet$ = solute molar volume.

χ_{AB}^0	χ_{AB}'	χ_{AC}^0	χ_{AC}'	χ_{BC}	$\chi_{BC}/V_A^\bullet$ $(mol\ dm^{-3})$
0.273	−0.028	0.202	0.097	0.306	3.13

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