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MIXED SOLVENTS IN GAS-LIQUID CHROMATOGRAPHY

ACTIVITY COEFFICIENTS FOR BENZENE, CYCLOHEXANE, PENTANE AND HEPTANE IN SQUALANE-DINONYLPHTHALATE MIXTURES AT 303 °K

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SUMMARY

Activity coefficients at infinite dilution for benzene, cyclohexane, pentane and heptane in mixtures of squalane and dinonyl phthalate at 303 °K have been determined by the extrapolation of measurements made using a vacuum microbalance technique. Partition coefficients for the solutes at infinite dilution in the solvent mixtures have been derived and found to differ by as much as 6% from those calculated from the partition coefficients for the pure single solvents using the Purnell-Andrade equation, whereas those calculated on the basis of the Flory-Huggins solution theory differ from the experimentally derived values by no more than 1%.

INTRODUCTION

In a previous note¹ the activity coefficients at infinite dilution for hexane in squalane-dinonylphthalate (DNP) solvent mixtures were reported and used to demonstrate the deviation of the system from the relationship proposed by Purnell and Vargas de Andrade² to predict the behaviour of mixed solvents in gas-liquid chromatography (GLC). We have now determined activity coefficients for benzene, cyclohexane, pentane and heptane in the lower solute concentration region so that activity coefficients at infinite dilution can be derived and the deviation from the Purnell-Andrade relation examined further.

EXPERIMENTAL

Absorption isotherms were determined as before¹, using a Sartorius Model 4102 electronic vacuum microbalance in conjunction with a Texas Instruments quartz Bourdon gauge. The apparatus, the techniques and the materials have been described previously^{1,3,4}. The temperature of the absorption isotherms was controlled at 303.04 ± 0.01 °K. A nominal temperature of 303 °K is used throughout.

TABLE I

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

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

$n_B:n_C$	Benzene			Cyclohexane			
	x_A	P_A (mmHg)	$\ln \gamma_A$	x_A	P_A (mmHg)	$\ln \gamma_A$	
3:1	0.0901	6.91	-0.4290	0.0986	6.95	-0.5318	
	0.1631	13.05	-0.3869	0.1639	12.06	-0.4890	
	0.2258	18.77	-0.3490	0.2378	18.27	-0.4464	
	0.2818	24.18	-0.3177	0.2986	23.85	-0.4081	
	0.3368	29.86	-0.2856	0.3598	29.90	-0.3690	
	0.3900	35.64	-0.2557	0.4143	35.66	-0.3345	
	0.4419	41.72	-0.2237	0.4720	42.27	-0.2954	
1:1	0.4859	47.10	-0.1976	0.5149	47.51	-0.2658	
	0.0899	6.43	-0.4987	0.0876	6.86	-0.4260	
	0.1626	12.21	-0.4506	0.1524	12.43	-0.3866	
	0.2345	18.35	-0.4094	0.2162	18.20	-0.3551	
	0.2972	24.17	-0.3715	0.2744	23.85	-0.3237	
	0.3555	29.99	-0.3353	0.3322	29.83	-0.2916	
	0.4101	35.81	-0.3013	0.3878	35.86	-0.2629	
1:3	0.4660	42.28	-0.2633	0.4366	41.53	-0.2348	
	0.5115	47.76	-0.2351	0.4842	47.30	-0.2089	
	0.1152	8.02	-0.5261	0.0663	6.09	-0.2666	
	0.1737	12.55	-0.4888	0.1273	11.98	-0.2430	
	0.2408	18.13	-0.4483	0.1848	17.78	-0.2214	
	0.3057	24.02	-0.4061	0.2389	23.52	-0.1992	
	0.3687	30.19	-0.3652	0.2924	29.43	-0.1773	
Pentane	0.4229	35.87	-0.3304	0.3464	35.63	-0.1562	
	0.4718	41.44	-0.2957	0.3931	41.24	-0.1369	
	0.5229	47.58	-0.2609	0.4421	47.29	-0.1180	
	Pentane			Heptane			
	x_A	P_A (mmHg)	$\ln \gamma_A$	x_A	P_A (mmHg)	$\ln \gamma_A$	
	3:1	0.0733	29.96	-0.3668	0.0750	3.22	-0.2956
		0.1411	59.50	-0.3371	0.1401	6.18	-0.2690
0.2052		89.35	-0.3068	0.1979	8.97	-0.2418	
0.2638		118.43	-0.2783	0.2567	11.94	-0.2166	
0.3212		148.59	-0.2502	0.3164	15.06	-0.1938	
0.3740		117.93	-0.2241	0.3673	17.85	-0.1733	
0.4248		207.68	-0.1987	0.4163	20.68	-0.1517	
1:1	0.4730	237.33	-0.1747	0.4669	23.64	-0.1331	
	0.0652	29.75	-0.2577	0.0607	2.96	-0.1689	
	0.1292	60.51	-0.2323	0.1363	6.78	-0.1456	
	0.1870	89.76	-0.2092	0.1783	9.03	-0.1328	
	0.2429	119.46	-0.1869	0.2316	11.92	-0.1167	
	0.2953	148.47	-0.1660	0.2835	14.78	-0.1014	
	0.3474	178.74	-0.1454	0.3353	17.78	-0.0864	
1:3	0.3953	207.76	-0.1267	0.3876	20.87	-0.0719	
	0.4424	237.23	-0.1087	0.4365	23.79	-0.0588	
	0.0581	30.86	-0.1023	0.0506	2.94	0.0063	
	0.1112	60.35	-0.0860	0.1011	5.91	0.0151	
	0.1620	89.35	-0.0708	0.1503	8.89	0.0233	
	0.2126	119.26	-0.0559	0.2009	11.98	0.0311	
	0.2604	148.41	-0.0422	0.2467	14.79	0.0376	
0.3083	178.33	-0.0289	0.2943	17.76	0.0438		
0.3547	208.02	-0.0166	0.3400	20.66	0.0489		
0.3995	237.39	-0.0053	0.3897	23.77	0.0537		

RESULTS AND DISCUSSION

The absorption isotherms are presented in Table I in terms of the mole fraction x_A , of the solute absorbed in the involatile solvent mixture at a solute vapour pressure P_A . The activity coefficient of the solute γ_A was calculated from these measurements as before^{1,5}. Activity coefficients at infinite dilution for these systems were determined by regarding the squalane–DNP mixture as a single component and fitting the results for an individual isotherm to the Flory–Huggins expression for a binary system⁶:

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

In this expression (eqn. 1) the volume fraction φ_A of the solute is defined in terms of the molar volumes of the components. The pseudo-binary interaction parameter χ , allowed to vary linearly with φ_A , calculated for the solute in a particular solvent mixture enables the activity coefficient at infinite dilution γ_A^∞ to be determined¹. The γ_A^∞ value resulting from each isotherm is reported in Table II, together with those determined earlier⁵ for the solutes with the pure single solvents.

TABLE II

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

$n_B:n_C$ = solvent mole ratio.

$n_B:n_C$	C_6H_6		C_6H_{12}		C_5H_{12}		C_6H_{14}		C_7H_{16}	
	γ_A^∞	K_R	γ_A^∞	K_R	γ_A^∞	K_R	γ_A^∞	K_R	γ_A^∞	K_R
1:0	0.698*	436	0.510*	587	0.620*	98.2	0.640*	306	0.669*	929
3:1	0.622	512	0.557	561	0.669	95.2	0.697**	294	0.723	899
1:1	0.580	576	0.627	522	0.753	88.6	0.785**	273	0.829	822
1:3	0.554	633	0.745	462	0.887	79.1	0.933**	242	0.997	718
0:1	0.549*	673	0.931*	389	1.115*	66.2	1.201*	198	1.313*	574

* Values from ref. 5.

** Values from ref. 1.

A partition coefficient for the solute at infinite dilution between the solvent and the vapour phase, can be calculated using the equation

$$K_R = RT/(P_A^\circ \gamma_{P,A}^\infty V_L) \quad (2)$$

where P_A° is the vapour pressure of the pure solute, $\gamma_{P,A}^\infty$ is the uncorrected activity coefficient and V_L is the molar volume of the solvent. Values of K_R calculated for the four solutes studied here are presented in Table II, together with the values for hexane derived from the previously reported results¹. The vapour pressures, P_A° , were calculated from the constants for the Antoine equation given in ref. 7. The molar volume V_L of the squalane–DNP mixture was taken as a linear function of the mole fraction composition using the molar volumes of the two pure solvents reported

TABLE III

CORRECTION USED IN CALCULATING THE SOLUTE ACTIVITY COEFFICIENT AT INFINITE DILUTION

$\ln \gamma_A^\infty - \ln \gamma_{P,A}^\infty$				
C_6H_6	C_6H_{12}	C_5H_{12}	C_6H_{14}	C_7H_{16}
0.0089	0.0104	0.0398	0.0167	0.0069

previously⁶. The corrections necessary to calculate the activity coefficient at infinite dilution,

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

are tabulated in Table III. The second virial coefficients B_{AA} and the molar volumes V_A^\bullet of the solutes employed were as given previously^{5,6}. The inclusion of V_A^\bullet in eqn. 3 corrects for the effect of pressure on the activity of the liquid, and the terms in B_{AA} allow for the imperfection of the vapour.

Table IV shows the partition coefficients calculated for the mixed solvents from those for the pure single solvents $K_{R(B)}$ and $K_{R(C)}$, given in Table II, using the Purnell-Andrade equation²:

$$K_R = \varphi_B K_{R(B)} + \varphi_C K_{R(C)} \quad (4)$$

The solvent volume fractions φ_B and φ_C , like φ_A , are defined in terms of the molar volumes of the components. The percentage deviation of the partition coefficient

TABLE IV

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

$n_B:n_C$ = solvent mole ratio; $K_R(PA)$ = partition coefficient calculated from the Purnell-Andrade equation (eqn. 4); $K_R(FH)$ = partition coefficient calculated from the Flory-Huggins theory (eqn. 7); %Δ = percentage deviation of calculated K_R from experimentally derived value in Table II.

Solute	$n_B:n_C$	$K_R(PA)$	%Δ	$K_R(FH)$	%Δ
Benzene	3:1	487	4.9	507	1.0
	1:1	543	5.7	577	0.3
	1:3	605	4.4	637	0.6
Cyclohexane	3:1	544	3.0	564	0.5
	1:1	498	4.6	524	0.4
	1:3	446	3.5	465	0.6
Pentane	3:1	91.3	4.1	95.0	0.2
	1:1	83.7	5.5	88.7	0.1
	1:3	75.4	4.7	79.0	0.1
Hexane	3:1	233	3.7	296	0.7
	1:1	257	5.9	275	0.7
	1:3	229	5.4	242	0.0
Heptane	3:1	852	5.2	898	0.1
	1:1	769	6.4	828	0.7
	1:3	676	5.8	717	0.1

$K_R(\text{PA})$, thus calculated, from the value given in Table II based on the extrapolated experimental measurements is given in the adjacent column in Table IV.

The three isotherms reported here in Table I for a particular solute in the mixed solvents may be combined with the two isotherms for that solute with the pure solvents reported previously⁵, and the combined results for the five isotherms fitted to the Flory-Huggins expression for a ternary system⁶,

$$\ln \gamma_A = \ln (\varphi_A/x_A) + 1 - \varphi_A/x_A + (1 - \varphi_A) (\varphi_B \chi_{AB} + \varphi_C \chi_{AC}) - \varphi_B \varphi_C \chi_{BC} \quad (5)$$

In the curve-fitting procedure the interaction parameters χ_{AB} and χ_{AC} are allowed to vary linearly with φ_A , thus

$$\chi_{AB} = \chi_{AB}^{\circ} + \varphi_A \chi'_{AB} \quad (6)$$

and similarly χ_{AC} , while the parameter χ_{BC} for the two solvents is assumed to be constant. The isothermal results for a particular solute in the three solvent mixtures and the two pure solvents are thus represented by these parameters, which are reported in Table V. The interaction parameter for the two solvents χ_{BC} can be used to calculate the partition coefficients in the mixed solvent phase from those in the pure solvent phase by using the relation pointed out by Perry and Tiley⁸, namely that

$$\ln K_R = \varphi_B \ln K_{R(B)} + \varphi_C \ln K_{R(C)} + \varphi_B \varphi_C \chi_{BC} \quad (7)$$

Note that our χ_{BC} is equivalent to the product of the solute molar volume and the interaction parameter used by Perry and Tiley. The partition coefficients $K_R(\text{FH})$ derived on this basis are shown in Table IV. The percentage deviation of the partition coefficients calculated using the Flory-Huggins theory from those based on the experimental measurements is given in the adjacent column. The deviation of the partition coefficients calculated from the Purnell-Andrade equation, which basically assumes that the two solvents are immiscible, can be seen to be much greater than that using eqn. 7 based on conventional Flory-Huggins solution theory. The success of the Flory-Huggins theory in representing these systems can be seen by examination

TABLE V

FLORY-HUGGINS INTERACTION PARAMETERS DETERMINED FROM ANALYSIS OF THE COMBINED ISOTHERMS (THREE TERNARY—TABLE I AND REF. 1 AND TWO BINARY—REF. 5) FOR EACH SOLUTE (A) IN SQUALANE (B)-DNP (C) MIXTURES AT 303 °K

V_A^* = solute molar volume.

Solute	χ_{AB}°	χ'_{AB}	χ_{AC}°	χ'_{AC}	χ_{BC}	χ_{BC}/V_A^* (mol dm^{-3})
C_6H_6	0.5698	0.0824	0.1998	-0.0851	0.3416	3.797
C_6H_{12}	0.1135	0.0512	0.5626	-0.0460	0.2900	2.651
C_5H_{12}	0.2454	0.0250	0.6981	-0.0277	0.3076	2.628
C_6H_{14}	0.1908	-0.0093	0.6810	0.0223	0.3658	2.760
C_7H_{16}	0.1524	0.0365	0.6919	0.0154	0.4122	2.778

of the interaction parameter for the mixed solvents per unit molar volume of the solute χ_{BC}/V_A° , shown in the last column of Table V. These values are in good agreement with each other and do not differ greatly from those found earlier for the higher concentration range⁶, except that for benzene. This may be an indication that benzene is involved in molecular complex formation. Should such complexing occur in these systems, then the benzene-dinonyl phthalate system is that in which it is most likely.

CONCLUSION

Partition coefficients for benzene, cyclohexane, pentane, hexane and heptane at infinite dilution in squalane-DNP mixtures differ from the values calculated by the Purnell-Andrade equation by as much as 6%. Values calculated on the basis of the Flory-Huggins solution theory, allowing for interaction between the two solvents, differ from the experimental values by no more than 1%. This supports the previous conclusion¹ that the equation proposed by Purnell and Vargas de Andrade may be a useful approximation for predicting the behaviour of mixed solvents in GLC, but the ternary systems we have studied conform more to conventional theory of liquid mixtures rather than to a "micro-partitioning" theory.

APPENDIX

$$\text{Derivation of } \ln K_R = \varphi_B \ln K_{R(B)} + \varphi_C \ln K_{R(C)} + \varphi_B \varphi_C \chi_{BC} \quad (\text{eqn. 7})$$

$$Q_A = \frac{x_A V_A^\circ}{x_A V_A^\circ + (1 - x_A) V_L}$$

$$\therefore \lim_{x_A \rightarrow 0} \left(\frac{\varphi_A}{x_A} \right) = \frac{V_A^\circ}{V_L}$$

$$\therefore \text{ from eqn. 5 } \ln \gamma_A^\infty = \ln \frac{V_A^\circ}{V_L} + 1 - \frac{V_A^\circ}{V_L} + \varphi_B \chi_{AB} + \varphi_C \chi_{AC} - \varphi_B \varphi_C \chi_{BC}$$

$$\begin{aligned} \therefore \text{ from eqn. 2 } \ln K_R &= \ln \frac{RT}{P_A^\circ} + (\ln \gamma_A^\infty - \ln \gamma_{P,A}^\infty) - \ln V_A^\circ - 1 + \frac{V_A^\circ}{V_L} \\ &\quad - \varphi_B \chi_{AB} - \varphi_C \chi_{AC} + \varphi_B \varphi_C \chi_{BC} \end{aligned}$$

Applying this result to the binary systems:

$$\ln K_{R(B)} = \ln \frac{RT}{P_A^\circ} + (\ln \gamma_A^\infty - \ln \gamma_{P,A}^\infty) - \ln V_A^\circ - 1 + \frac{V_A^\circ}{V_B^\circ} - \chi_{AB}$$

and

$$\ln K_{R(C)} = \ln \frac{RT}{P_A^\circ} + (\ln \gamma_A^\infty - \ln \gamma_{P,A}^\infty) - \ln V_A^\circ - 1 + \frac{V_A^\circ}{V_C^\circ} - \chi_{AC}$$

where V_B° and V_C° are the molar volumes of the pure B and C, and where $(\ln \gamma_A^\infty - \ln \gamma_{P,A}^\infty)$ is, according to eqn. 3, independent of the solvent.

Since $\varphi_B + \varphi_C = 1$ at infinite dilution it follows that

$$\begin{aligned} \varphi_B \ln K_{R(B)} + \varphi_C \ln K_{R(C)} = \ln \frac{RT}{P_A^\circ} + (\ln \gamma_A^\infty - \ln \gamma_{P,A}^\infty) - \ln V_A^\circ - 1 \\ + V_A^\circ \left(\frac{\varphi_B}{V_B^\circ} + \frac{\varphi_C}{V_C^\circ} \right) - \varphi_B \chi_{AB} - \varphi_C \chi_{AC} \end{aligned}$$

But at infinite dilution $\varphi_B = x_B V_B^\circ / V_L$ and $\varphi_C = (1 - x_B) V_C^\circ / V_L$ where x_B is the mole fraction of B.

$$\therefore \frac{\varphi_B}{V_B^\circ} + \frac{\varphi_C}{V_C^\circ} = \frac{1}{V_L}$$

Hence, comparing with the expression for $\ln K_R$ above, eqn. 7 follows.

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