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SOLUBILITY AND EXCESS VOLUMES OF THE MIXTURE Di-*n*-OCTYL ETHER + BENZENE

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ABSTRACT

Differential scanning calorimetry has been used to investigate the solid–liquid equilibria for the mixture di-*n*-octyl ether + benzene. Solubilities and activities of benzene in di-*n*-octyl ether are reported. In addition, the excess molar volumes of the liquid mixture di-*n*-octyl ether + benzene were obtained from density measurements at 298.15 K over the whole mole-fraction range.

INTRODUCTION

Di-*n*-octyl ether (DOE) is of particular interest with regard to extraction of rare earth elements [1]. Mixtures of DOE with octadecane and *N*,*N*-dioctylamine and their solubilities have been discussed previously by Djordjevic and Laub [2]. The present work was undertaken to provide information about the solubility of solid benzene in DOE, and the volumetric behaviour of the liquid mixture DOE + benzene. We are unaware of any previous studies of this mixture.

For this purpose, we report finite concentration activities calculated from the solubility equation and excess molar volumes derived from precise density measurements at 298.15 K. In order to detect any contribution from properties other than differences in molar volumes, the results are compared with those for the mixture *n*-hexadecane + benzene [3].

EXPERIMENTAL

Di-*n*-octyl ether (Aldrich Chemical Co.) was vacuum-distilled prior to use. Benzene (J.T. Baker Chemical Co.), HPLC grade, was used without further purification. Good agreement was found between the reported melting points and those observed experimentally, for both benzene ($T_{obs} = 278.9$ K; 278.6 K [4]) and DOE ($T_{obs} = 265.4$ K; 265.0 K [2]). The differential scanning calorimeter, Perkin–Elmer model DSC II, was equipped with an

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Intracooler II, permitting subambient operation of the calorimeter. Calibration of the calorimeter and sample preparation have been described elsewhere [2].

Measurements of the densities of the pure liquids and mixtures were carried out by means of an Anton Paar densimeter model DMA 60 equipped with a remote cell, model DMA 512. The temperature of the cell was controlled using a constant-temperature water bath, to better than ± 0.01 K. The temperature was monitored using a calibrated quartz thermometer, Hewlett–Packard model 2804A. The overall precision of the density measurements is estimated to be better than $\pm 4 \times 10^{-5}$ g cm^{-3}.

RESULTS AND DISCUSSION

Solubility studies

The solubility of solid in liquid [2] is expressed by eqn. (1)

$$\ln(x\gamma) = -(\Delta H_m/R)(1/T - 1/T_m) - (\Delta C_p/R)[\ln(T/T_m) + (T_m/T) - 1] \quad (1)$$

where x, γ, ΔH_m, ΔC_p, T_m and T stand for mole fraction, activity coefficient, enthalpy of fusion, difference in solute heat capacity between solid and liquid state, melting temperature of the solute and equilibrium temperature, respectively. If the melting point of the solute is not more than 100 K above the solution temperature, the terms involving ΔC_p can be neglected and eqn. (1) simplifies to

$$\ln(x\gamma) = -(\Delta H_m/R)(1/T - 1/T_m) \quad (2)$$

or

$$\ln(x\gamma) = -(\Delta S_m/R)[(T_m/T) - 1] \quad (3)$$

When $\gamma = 1$ ("ideal" solubility), plots of $\ln x$ vs. $1/T$ or T_m/T are linear, with the slopes corresponding to $\Delta H_m/R$ or $\Delta S_m/R$, respectively.

Table 1 lists the observed melting points T of the solution DOE + benzene. Figure 1 presents the plot of $\ln x$ vs. reciprocal temperature $1/T$, the full line representing ideal slope. Least-squares fitting was used to derive coefficients for the equation

$$\ln x = (A/T) + B \quad (4)$$

in the temperature range corresponding to the linear region of the plot (278.9–264.4 K) and mole fractions of benzene from $x = 1$ to $x = 0.8074$. The enthalpy of fusion derived from the slope of eqn. (4), $\Delta H_m = 9.219$ kJ mol^{-1}, is smaller than the literature value $\Delta H_m = 9.824$ kJ mol^{-1} K^{-1} [4], indicating that the system deviates from ideality.

TABLE 1

Observed melting points T with their standard deviations δ for various mole fractions x and activities of benzene in DOE a

x	a	T (K)	δ (K)
1.0000	1.000	278.9	0.1
0.9842	0.986	277.4	0.3
0.9746	0.971	277.0	0.1
0.9070	0.898	272.0	0.3
0.8469	0.835	267.5	0.2
0.8074	0.795	264.6	0.3
0.7042		253.4	0.2
0.4840		258.1	0.3
0.3823		259.5	0.3
0.2837		261.4	0.3
0.1855		263.6	0.4
0.1139		264.7	0.4
0.0000		265.5	0.1

Solute activities, reported in Table 1, were determined by substituting values of $\Delta H_m = 9.824$ kJ mol^{-1}, $T_m = 278.9$ K and the solution melting temperatures T from Table 1 into eqn. (2). Examination of Table 1 and Fig. 1 reveals a small negative deviation from ideality. Specific chemical forces lead to activity coefficients that are less than unity, and to solubilities that are greater than those expected on the basis of the enthalpy of fusion of the solute (ideal behaviour). Further proof of specific interaction is obtained from volumetric measurements of this system.

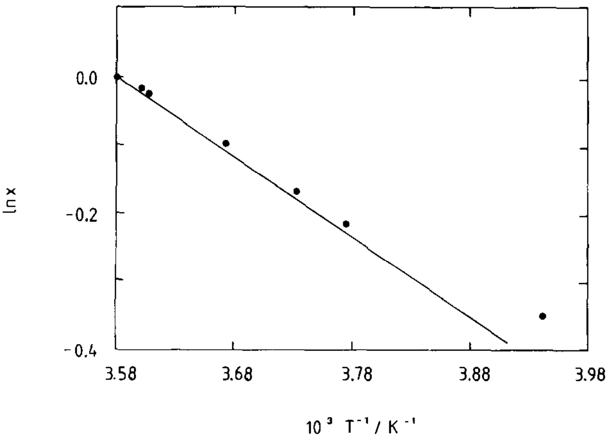

Fig. 1. Solubility curve plot of ln x vs. $1/T$ (K^{-1}) for DOE + benzene mixture: ●, observed values; ———, ideal ($\gamma = 1$) solubility calculated using eqn. (2) and $\Delta H_m = 9.824$ kJ mol^{-1}.

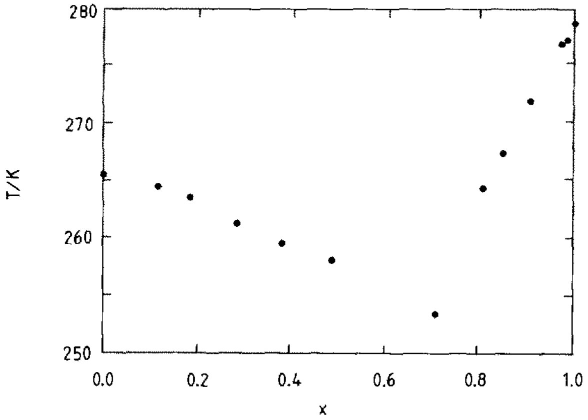

Fig. 2. Plot of temperature dependence of solubility of benzene in DOE, showing eutectic point at 253 K.

A freezing point diagram, derived from the data listed in Table 1, is presented in Fig. 2. It shows a single eutectic point at 253 K.

Volumetric properties

The excess molar volumes V_m^E, and corresponding mole fractions of DOE x, for the mixture $\{x\text{DOE} + (1 - x)\text{benzene}\}$ at 298.15 K are listed in Table

TABLE 2

Densities ρ and excess molar volumes V_m^E for the mixture $\{x\ \text{DOE}+(1-x)\ \text{benzene}\}$, and the deviations from smoothing eqn. (5)

x	ρ (g cm^{-3})	V_m^E (cm^3 mol^{-1})	$10^4\ \delta V_m^E$ (cm^3 mol^{-1})
0.0512	0.86047	0.2521	−1
0.0570	0.85924	0.2725	−1
0.0814	0.85448	0.3465	−6
0.1398	0.84513	0.4279	16
0.2173	0.83586	0.5623	−8
0.3126	0.82751	0.6053	−5
0.4240	0.82043	0.5903	−1
0.4752	0.81784	0.5658	1
0.5114	0.81620	0.5428	0
0.5349	0.81522	0.5261	3
0.5986	0.81279	0.4723	2
0.6649	0.81060	0.4065	1
0.7440	0.80835	0.3181	−1
0.8130	0.80664	0.2349	−3
0.9465	0.80384	0.0670	−2

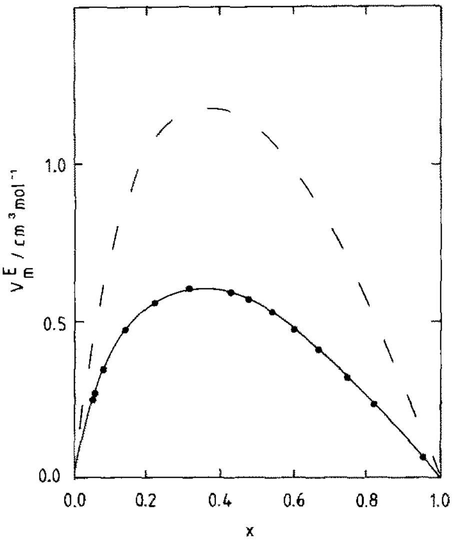

Fig. 3. Excess molar volume of $\{x[CH_3(CH_2)_7]_2O+(1-x)C_6H_6\}$: ●, experimental data; ———, eqn. (1); - - - - -, excess molar volume of $\{xC_{16}H_{34}+(1-x)C_6H_6\}$ data from ref. 3.

2 and plotted in Fig. 3. The solid curve in Fig. 3 was calculated using eqn. (5)

$$V_m^E/(\text{cm}^3\ \text{mol}^{-1}) = x(1-x)\{2.2018 - 0.4563(1-2x) - 0.4190(1-2x)^2 + 0.8017(1-2x)^3\} \quad (5)$$

where the coefficients were determined by the method of least squares with all points weighted equally. Also given in Table 2 are the standard deviations δV_m^E from this equation.

TABLE 3

Densities ρ, molar volumes V_m and internal pressures $T(\partial P/\partial T)_V$ of the pure liquids at 298.15 K

Liquid	ρ (g cm^{-3})	V_m (cm^3 mol^{-1})	$T(\partial P/\partial T)_V$ (atm.)
Benzene	0.87354 0.87360 [a] 0.87315 [b]	89.41	3646 [c]
DOE	0.80286	302.09	2993 [d]
n-Hexadecane	0.77003 [b]	294.04	2996 [e]

[a] From ref. 5. [b] From ref. 3. [c] From ref. 6.

[d] The second order polynomial fit of data from ref. 7 into the equation $P_i = a + a_1 n + a_2 n^2$ (where n is the number of carbon atoms, $a = 7.081$, $a_1 = 0.349$, $a_2 = -0.011$) with standard deviation $s = 0.019$.

[e] From ref. 8.

Figure 3 reveals that V_m^E is positive over the whole mole-fraction range. A broken curve representing literature results [3] for *n*-hexadecane + benzene is also shown, for comparison. The magnitude of V_m^E observed for the mixture DOE + benzene may be explained qualitatively in terms of several opposing contributions: the possibility of electron donor–acceptor type interactions in which the aromatic ring behaves as an electron donor; self-association of the ether molecules; and geometrical effects due to differences in molar volumes. Table 3 lists properties of the pure liquids: molar volumes V_m ($cm^3\ mol^{-1}$), densities ($g\ cm^{-3}$) and internal pressures $P_i = T(\partial P/\partial T)_V$ (atm). If the difference in molar volumes governs the volumetric behaviour of the DOE + benzene mixture, the values for V_m^E should be close to those obtained for the system *n*-hexadecane + benzene, since the molar volumes of DOE and *n*-hexadecane differ by only 2%, they have the same internal pressure, and both molecules are chain-like. A lower value of V_m^E for the mixture DOE + benzene can be attributed to electron donor–acceptor interaction.

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