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Note

SOLUBILITIES OF *TRANS*-1,2-DIPHENYLETHENE AND *CIS*-2,3-DIPHENYLPROPENOIC ACID IN BENZENE, TETRACHLOROMETHANE AND 1,4-DIOXANE

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The solubility data of a variety of solutes in different organic solvents have been analysed on the basis of Hildebrand's regular solution theory to compare the solvent properties and to predict the solute—solvent interactions [1—8]. Although the solutes investigated include both inorganic (including inner complex salts) and organic compounds, almost no attempt has been made to study the solubility behaviour of compounds exhibiting a liquid crystalline phase or compounds having a molecular structure similar to them. A vast majority of such compounds are known to have aromatic rings as flexible end-groups attached to a rigid central group [9,10]. As part of our investigations on the thermodynamic properties of solutions containing such compounds as one of the components, we have determined the solubilities of *trans*-1,2-diphenylethene (DPE) and *cis*-2,3-diphenylpropenoic acid (DPPA) in three non-polar organic solvents, benzene, tetrachloromethane and 1,4-dioxane. The data have been used to calculate the entropy of solutions of these compounds and the results are discussed.

EXPERIMENTAL

Reagent grade (B.D.H.) benzene, tetrachloromethane and 1,4-dioxane were purified according to standard procedures [11]. Their densities and refractive indexes showed good agreement with the accepted literature values [11,12].

The sample of DPPA (m.p. 172°C) was prepared and purified following the procedure described by Vogel [13]. Chemically pure DPE (m.p. 124°C) supplied by "Fluka AG" was used without further purification. The saturated solutions were prepared by continuous stirring of the solute with solvent under thermostated conditions for periods of 6—8 h, sometimes starting with unsaturated solvent and at other times with solutions which had been

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saturated at higher temperatures. Replicate experiments showed practically no difference in the final solute concentration.

The technique and saturator used in the present investigations are similar to those of Glew and Hildebrand [14]. In place of a teflon bearing for the stirring shaft, we have used a conventional mercury seal. The saturator was thermally insulated by glass wool. The temperature of the circulating water was controlled to ±0.01°C and the difference between inlet and outlet temperature was not greater than 0.03°C at the highest temperature of determination. After the attainment of saturation, the stirrer was temporarily stopped and samples were taken for analysis from the inner vessel through the bottom stopcock.

The concentrations of the solutes in their saturated solutions were estimated by tapping a known weight (~15—25 ml) of the saturated solution from the saturator in a tarred dish, which was then carefully evaporated under slightly reduced pressure. Constancy of weight over three successive weighings was taken as indicative of the final value. The maximum error in the solubility values reported is estimated to be less than ±0.3%.

TABLE 1

Solubilities of *trans*-1,2-diphenylethene (DPE) and *cis*-2,3-diphenylpropenoic acid (DPPA) in benzene, tetrachloromethane and 1,4-dioxane at various temperatures

Solvent	Solute	Temp. (K)	$x_{2(\mathrm{satd.})}$
Benzene	DPE	303.15	7.501×10^{-2}
		308.15	8.683×10^{-2}
		313.15	9.831×10^{-2}
		318.15	11.65×10^{-2}
Tetrachloromethane	DPE	303.15	4.811×10^{-2}
		308.15	6.242×10^{-2}
		313.15	7.895×10^{-2}
		318.15	9.840×10^{-2}
1,4-Dioxane	DPE	308.15	8.064×10^{-2}
		313.15	10.05×10^{-2}
		318.15	11.79×10^{-2}
		323.15	14.79×10^{-2}
Benzene	DPPA	313.15	2.561×10^{-2}
		318.15	2.703×10^{-2}
		323.15	2.946×10^{-2}
		328.15	3.123×10^{-2}
Tetrachloromethane	DPPA	293.15	2.064×10^{-3}
		303.15	2.926×10^{-3}
		308.15	3.800×10^{-3}
		318.15	5.328×10^{-3}
1,4-Dioxane	DPPA	308.15	9.856×10^{-2}
		313.15	10.64×10^{-2}
		318.15	11.97×10^{-2}
		328.15	14.58×10^{-2}
		333.15	16.04×10^{-2}

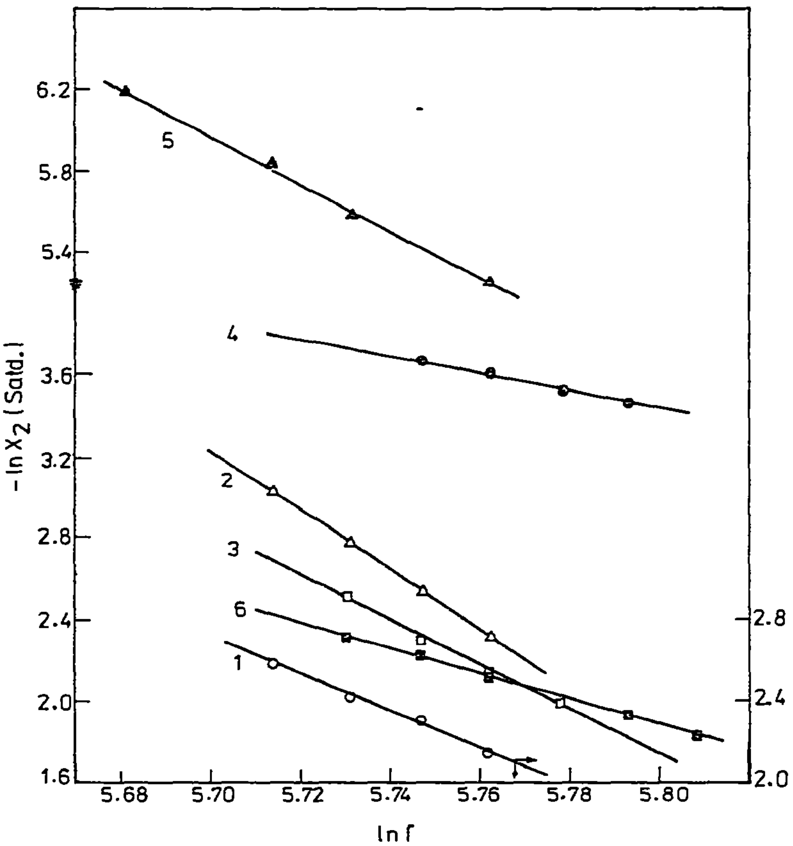

Fig. 1. Solubility of DPE and DPPA in three non-polar solvents. 1, DPE in benzene; 2, DPE in tetrachloromethane; 3, DPE in 1,4-dioxane; 4, DPPA in benzene; 5, DPPA in tetrachloromethane; 6, DPPA in 1,4-dioxane.

RESULTS AND DISCUSSION

The solubilities of DPE and DPPA in benzene, tetrachloromethane and 1,4-dioxane at different temperatures in the range 293.15—333.15 K are recorded in Table 1 as $X_{2(\text{satd.})}$, the mole fraction of the solute in the saturated solution. The results are also shown as plots of ln $X_{2(\text{satd.})}$ vs. ln T in Fig. 1.

It is observed that the solubility of DPPA follows the order: tetrachloromethane < benzene < 1,4-dioxane. The same order has been reported earlier for the solubility of various inorganic and organic compounds [3,5,6] in these solvents. The solubility of DPE in benzene and 1,4-dioxane has been found to be almost of the same order of magnitude, but greater than that in tetrachloromethane. No solubility values for the solute—solvent systems under investigation have been reported in the literature to the best of our knowledge.

Plots of ln X_2(satd.) vs. ln T for all the systems yield straight lines in the studied temperature range. The linearity provides a check on the precision of measurements. It is also an indication that no significant changes have occurred in the structure and composition of the solid phase in equilibrium with solution in the studied temperature range.

The entropy of dissolution of the solid is given by the expression [2]

$$\Delta S = \bar{S}_2 - S_2^s = -R\left(\frac{\partial \ln X_2}{\partial \ln T}\right)_{\text{satd.},P} \left(\frac{\partial \ln a_2}{\partial \ln X_2}\right)_{P,T} \tag{1}$$

The factor $(\partial \ln a_2 | \partial \ln X_2)_{P,T}$, which is "Henry's law factor", is unity for an ideal solution and approaches unity with increasing dilution for regular solutions [2,3]. Hence, the quantity $-R(\partial \ln X_2/\partial \ln T)_{\text{satd.},P}$ can be taken to represent $(\bar{S}_2 - S_2^s)$, the entropy of solution of the solute in the solvent. From the slopes of the straight lines in Fig. 1, the term, $R(\partial \ln X_2/\partial \ln T)_{\text{satd.},P}$ has been calculated and recorded in Table 2 together with the corresponding $-R \ln X_{2(\text{satd.})}$ values at 298.15 K.

According to the regular solution theory [2], the entropy of dissolution of a solid in a liquid obeys the relationship

$$(\bar{S}_2 - S_2^s) = -R \ln X_2 + \Delta S_f \tag{2}$$

The entropy of fusion, ΔS_f, of DPE is reported as 18.0 cal deg^{-1} mole^{-1} [15]. For DPPA, the heats of melting are not known in literature. We have therefore estimated ΔS_f for this compound [16] from the ΔS_f values of propenoic acid (= 9.3 cal deg^{-1} mole^{-1} [17]) and *trans*-3-phenylpropenoic acid (= 13.3 cal deg^{-1} mole^{-1} [17]) as 17.3 cal deg^{-1} mole^{-1}.

In the above estimation of ΔS_f it is assumed that: (i) the increase in ΔS_f is the same for the first and second substitution of phenyl groups in propenoic acid (at β and α positions, respectively); and (ii) the effect of *cis*- and *trans*-configuration of the molecule on ΔS_f is negligible. Although the above assumptions are crude [16], the maximum uncertainty in the estimation of ΔS_f of DPAA is not expected to be more than 10%.

The slopes of the plots of $(\bar{S}_2 - S_2^s)$ vs. $-R \ln X_{2(\text{satd.})}$ are recorded in the last column of Table 2. The data clearly indicate [2,3] the existence of specific interactions resulting in either complexation or intramolecular

TABLE 2

Entropy of solution and solubility of *trans*-1,2-diphenylethene (DPE) and *cis*-2,3-diphenylpropenoic acid (DPPA) at 298.15 K

Solute	Solvent	$(\bar{S}_2 - S_2^s)$ (cal mole^{-1})	$-R \ln X_{2(\text{satd.})}$ (cal mole^{-1})	$-\frac{1}{R}\left[\frac{\partial(\Delta\bar{S}_2 - \Delta S_f)}{\partial \ln X_{2(\text{satd.})}}\right]_{P,T}$
DPE	Benzene	18.4	5.5	0.1
	Tetrachloromethane	29.6	6.5	1.7
	1,4-Dioxane	25.3	5.7	1.2
DPPA	Benzene	8.8	7.7	−1.1
	Tetrachloromethane	23.5	11.9	0.4
	1,4-Dioxane	12.4	5.1	−0.9

bonding of the two solutes with benzene. The extent of such interactions appears to be relatively small with 1,4-dioxane, it being almost negligible with DPE. Further, it is observed that only DPPA exhibits specific intramolecular interactions in tetrachloromethane solutions.

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