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Note

PARTIAL MOLAR VOLUMES OF *TRANS*-1,2-DIPHENYLETHENE AND *TRANS*-2,3-DIPHENYLPROPENOIC ACID IN BENZENE, 1,4-DIOXANE AND TETRACHLOROMETHANE

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In earlier studies [1], we reported the solubilities of *trans*-1,2-diphenylethene (DPE) and *trans*-2,3-diphenylpropenoic acid (DPPA) in three non-polar organic solvents, namely benzene, 1,4-dioxane and tetrachloromethane. In the present paper, we have extended our investigations to determine the partial molar volume, $\bar{V}_2$, of DPE and DPPA in these solvents at 298.15, 308.15 and 318.15 K in an attempt to determine its relationship with the solubility and to locate the source of deviation of these solutions from ideality on the basis of volume effects.

EXPERIMENTAL

The samples of DPE, DPPA and the three solvents used in the present investigations were essentially the same as used previously [1].

The partial molar volumes at various temperatures (controlled to within $\pm 0.01°C$) were computed from the experimental density data, which in turn were measured using a single stem capillary pyknometer of ~ 20 cm^3 capacity [2]. The solutions for the density measurements were prepared by weight and the correction for buoyancy was applied. Details of the experimental technique for the preparation of solutions and the measurement of density has been described earlier [2]. Duplicate densities agreed within 3×10^{-5} g cm^{-3}.

The densities of DPE and DPPA melts at various temperatures above their respective melting temperatures were determined with an uncertainty of $\pm 5 \times 10^{-4}$ g cm^{-3} using a pipette type pyknometer described elsewhere [3].

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RESULTS

The experimental density data for the binary solutions and for the melts are recorded in Tables 1 and 2, respectively. Since DPPA is only weakly soluble in tetrachloromethane [1], no density data for solutions of DPPA in tetrachloromethane have been reported.

The partial molar volumes of the solutes, $\bar{V}_2$, in different solvents at low concentration were taken to be equal to the apparent molar volume and were calculated from the data given in Table 1 using the relationship

$$\bar{V}_2 = \frac{M_2}{W_2}\left[\frac{1}{\rho} + \frac{W_2 - 1}{\rho_0}\right] \tag{1}$$

TABLE 1

Densities (g cm^{-3}) of dilute solutions of DPE and DPPA in organic solvents at 298.15, 308.15 and 318.15 K

Solute	Solvent	Wt.% solute	Density at		
			298.15 K	308.15 K	318.15 K
DPE	C_6H_6	0	0.87374	0.86274	0.85230
		2.776	0.87849	0.86761	0.85723
		3.892	0.88018	0.86964	0.85950
		5.101	0.88214	0.87145	0.86149
		6.262	0.88424	0.87312	0.86355
		7.037	0.88540	0.87475	0.86474
	1,4-$C_4H_8O_2$	0	1.02813	1.01746	1.00526
		1.016		1.01737	1.00552
		2.062	1.02794		1.00562
		3.354	1.02792	1.01734	1.00573
		4.310	1.02787	1.01734	
		5.126	1.02780	1.01732	1.00582
		5.623	1.02780	1.01745	1.00588
	CCl_4	0	1.58453	1.56507	1.54619
		0.936	1.57674	1.55748	1.53886
		1.184	1.57453	1.55556	1.53677
		1.565	1.57151	1.55282	1.53293
		1.950	1.56877	1.54968	1.53133
		2.412	1.56487	1.54624	1.52794
		2.865	1.56111	1.54260	1.52433
DPPA	C_6H_6	0.884	0.87630	0.86537	
		1.320	0.87742	0.86642	0.85597
		1.490	0 37793	0.86698	0.85648
		2.380	0.88052	0.86934	0.85895
		2.920	0.88223		0.86069
	1,4-$C_4H_8O_2$	1.002	1.02976	1.01919	1.00707
		1.540	1.03069	1.02008	1.00798
		2.258	1.03184	1.02127	1.00920
		2.983	1.03298	1.02250	1.01058
		3.720	1.03421	1.02387	1.01182
		4.514	1.03550	1.02514	1.01328

TABLE 2

Densities of DPE and DPPA melts at various temperatures above the melting temperatures

Compound	Temp. (K)	Density (g cm^{-3})
DPE	396.15	0.9593
	397.15	0.9586
	398.15	0.9579
	400.15	0.9563
	403.15	0.9542
	406.15	0.9517
	408.15	0.9503
	410.15	0.9487
	413.15	0.9465
	416.15	0.9443
	418.15	0.9428
	423.15	0.9391
DPPA	449.15	1.0705
	454.15	1.0610
	459.15	1.0511
	464.15	1.0430
	469.15	1.0328
	474.15	1.0236

where ρ_0 is the density of the solvent, M_2 is the molecular weight of the solute, and W_2 is the weight fraction of the solute in the solution of density ρ.

The calculated $\bar{V}_2$ values and their standard deviations, σ, are tabulated in Table 3, along with the extrapolated liquid molar volumes of the two solutes, V_2^0, at 298.15 K obtained by fitting the liquid density data of DPE and DPPA into a linear equation of the type

$$\rho_t = a + bt \qquad (2)$$

by the method of least squares.

To the best of our knowledge, no work has been reported in the literature with which to compare our results.

DISCUSSION

It is observed that the two solutes in *p*-dioxane and DPPA in benzene exhibit expansion, whereas DPE in benzene shows a contraction due to strong solute—solvent interactions, in support of our solubility results reported earlier [1].

A comparison of $\bar{V}_2$ at the three temperatures shows that it is not very sensitive to temperature at high dilutions. The small standard deviations (Table 3) indicate that the determination of $\bar{V}_2$ is quite precise and there are no unanticipated concentration dependent interactions in these solutions. Thus the behaviour of the volume change when the concentrations of the

TABLE 3

Partial molar volumes (cm^3 mole^{-1}) of DPE and DPPA in organic solvents

Solute (2)	Solvent (1)	$\overline{V}_2(\sigma)$ at			$\overline{V}_2$ at 298.15 K [eqn. (3)]	V_2^0 at 298.15 K *
		298.15 K	308.15 K	318.15 K		
DPE	C_6H_6	167.25 (0.48)	167.69 (0.93)	167.33 (0.57)	173.82	173.11
	1,4-$C_4H_8O_2$	176.48 (0.17)	177.79 (0.18)	176.49 (0.82)	173.17	
	CCl_4	173.54 (0.64)	173.98 (0.60)	175.46 (0.85)	176.06	
DPPA	C_6H_6	173.42 (1.17)	174.63 (1.03)	176.85 (0.78)	182.60	165.76
	1,4-$C_4H_8O_2$	183.53 (0.24)	183.64 (0.30)	183.91 (0.34)	173.42	

* Extrapolated value; obtained from liquid densities above the melting temperatures.

solutions are varied is consistent with the behaviour of solutions known to be regular [4].

Dymond and Hildebrand [5] showed that the excess partial molar volume $(\bar{V}_2 - V_2^0)$, and solubility parameter, δ_1, of the components of regular solutions are related by the expression

$$\bar{V}_2 - V_2^0 = \frac{(\delta_1 - \delta_2)^2}{(\partial E/\partial V)_T} V_2^0 \tag{3}$$

The experimental $\bar{V}_2$ values have been compared with those calculated from eqn. (3). The numerical values of various parameters used for the purpose of our calculations are given in Tables 4 and 5. The solubility parameters for the solvents recorded in Table 4 were calculated from their heats of vaporization data at 298.15 K [6]. Since, as far as we know, no $C_p(\mathrm{l})$ and $C_p(\mathrm{g})$ values for DPE and DPPA and no heat of vaporization value for DPPA are reported in the literature, we have estimated the solubility parameters of these solutes at 298.15 K from their solubilities (in mole fraction units) X_{2a}(satd.) and X_{2b}(satd.) at this temperature in two different solvents 1a and 1b, respectively, using the following equation [7]

$$(\phi_{1a}^2 - \phi_{1b}^2)\,\delta_2^2 - 2(\phi_{1a}^2\delta_{1a} - \phi_{1b}^2\delta_{1b})\,\delta_2 + \left[(\phi_{1a}\delta_{1a})^2 - (\phi_{1b}\delta_{1b})^2 - \frac{RT}{V_2^0}\ln\frac{X_{2b(\mathrm{satd.})}}{X_{2a(\mathrm{satd.})}}\right] = 0 \tag{4}$$

where ϕ_1 is the volume fraction of the solvent. Equation (4) is based upon the assumption that a_2, the activity of the pure supercooled solute, is a constant at a given temperature. Very satisfactory constant δ_2 values were obtained for the two solutes (Table 5). For DPE, the δ_2 obtained showed good agreement with that obtained from heats of vaporization data.

It is observed that for all systems, except those of DPPA in benzene, the experimental $\bar{V}_2$ values are within ±3% of that predicted by eqn. (3), revealing that these solutions approximate very closely to the regular behaviour defined by Hildebrand and Scott [4]. For solutions of DPPA in benzene, the deviation between the two sets of values is in accordance with our solubility results [1].

TABLE 4

Internal pressures $(\partial E/\partial V)_T$; isochores $(\partial P/\partial T)_V$ and solubility parameters (δ) of solvents at 298.15 K

Solvent	$(\partial E/\partial V)_T$ (cal cm^{-3})	$(\partial P/\partial T)_V$ (atm deg^{-1})	δ (cal$^{1/2}$ cm$^{-3/2}$)
C_6H_6	88.4 *	12.23 *	9.16
1,4-$C_4H_8O_2$	104.0 **	14.31 ***	9.96
CCl_4	81.0 *	11.22 *	8.58

* Ref. 8, p.216.

** Calculated from the relationship [10] $(\partial E/\partial V)_T = n(\Delta H^{\mathrm{vap}} - RT)/V$.

*** Calculated from the relationship $(\partial P/\partial T)_V = (1/T)[P + (\partial E/\partial V)_T]$.

TABLE 5

Solubility parameters of DPE and DPPA at 298.15 K calculated from eqn. (4)

Solvent pair	δ_2	
	DPE	DPPA
C_6H_6—1,4-$C_4H_8O_2$	8.98	12.15
C_6H_6—CCl_4	10.56	14.06
1,4-$C_4H_8O_2$—CCl_4	9.74	12.93
Average	9.76 *	13.05
Mean deviation	0.53	0.66

* Compared with $\delta_2 = 9.31$ calculated from heat of vaporization [9].

It would be of interest to analyse the entropy of solution ($\bar{S}_2 - S_2^s$) data obtained from solubility determinations [1] in view of the experimentally determined partial molar volumes. The entropy of transfer of a solute from solid to saturated solution was estimated by the pure thermodynamic relation [8]

$$(\bar{S}_2 - S_2^s) = R\left(\frac{\partial \ln a_2}{\partial \ln X_2}\right)_{P,T}\left(\frac{\partial \ln X_2}{\partial \ln T}\right)_{P,\mathrm{satd.}} \tag{5}$$

where

$$\left(\frac{\partial \ln a_2}{\partial \ln X_2}\right)_{P,T} = 1 - \frac{2\phi_1^2(1-\phi_1)\,V_2^0(\delta_1-\delta_2)^2}{(1-X_2)\,RT} \tag{6}$$

where all the terms have their usual meaning [8]. Alternatively, in order to calculate the entropy of solution, the process of transfer of solute from solid to saturated solution at constant temperature may be divided into three steps, namely (i) the fusion of solid solute; (ii) expansion of $[1 - X_2(\mathrm{satd.})]/X_2(\mathrm{satd.})$ mole of solvent by volume equivalents of $(\bar{V}_2 - V_2^0)$; and (iii) mixing the liquid solute and liquid solvent at constant volume, so that

$$\Delta S = \bar{S}_2 - S_2^s = \Delta S_{\mathrm{fusion}} + \Delta S_{\mathrm{expan.}} + (\Delta S_{\mathrm{mix.}})_V \tag{7}$$

The quantities $\Delta S_{\mathrm{expan.}}$ and $(\Delta S_{\mathrm{mix}})_V$ can be calculated from the equations

$$\Delta S_{\mathrm{expan.}} = (\bar{V}_2 - V_2^0)(\partial P/\partial T)_V \tag{8}$$

and

$$(\Delta S_{\mathrm{mix.}})_V = -R\left[\ln(1-\phi_1) + \phi_1\left(1 - \frac{V_2^0}{V_1^0}\right)\right] \tag{9}$$

The numerical values of $(\partial P/\partial T)_V$ used in our calculations are given in Table 4.

A comparison of the values of entropy of solution obtained from eqns. (5) and (7) (Table 6) shows that the two sets of values are in good agreement with each other, except for the systems containing DPPA. The large difference in the two sets of values for DPPA solutions may be attributed to

TABLE 6

Entropy of solution (cal deg^{-1}) of DPE and DPPA in organic solvents at 298.15 K

Solute	Solvent	$\Delta S^{*}_{\text{fusion}}$ + $\Delta S_{\text{expan.}}$ + $(\Delta S_{\text{mx.}})_V = \Delta S$	$R\left(\frac{\partial \ln X_2}{\partial \ln T}\right)^{*}_{P,\text{satd}}$	$\left(\frac{\ln a_2}{\ln X_2}\right)_{P,T}$	$(\overline{S}_2 - S_2^{\text{s}})$
DPE	C_6H_6	18.0 − 1.7 + 5.9 = 22.2	18.4	0.979	18.0
	1,4-$C_4H_8O_2$	18.0 + 1.2 + 6.4 = 25.6	25.3	0.998	25.2
	CCl_4	18.0 + 0.1 + 6.9 = 25.0	29.6	0.953	28.2
DPPA	C_6H_6	17.3 + 2.3 + 8.2 = 27.8	8.8	0.708	6.2
	1,4-$C_4H_8O_2$	17.3 + 6.2 + 5.6 = 29.1	12.4	0.414	5.2

* From ref. 1.

strong solute—solvent interactions resulting in the formation of stable complexes. For other systems, the difference between the two sets of values can, however, be attributed to (i) the uncertainty in the estimation of ΔS_{fusion} being ~0.3—0.5 cal deg^{-1}; (ii) the uncertainty in the estimation of $\Delta S_{\text{expan.}}$ being ~0.3—1.0 cal deg^{-1}; (iii) the uncertainty in the estimation of $(\Delta S_{\text{mix.}})_V$ being ~0.2—0.5 cal deg^{-1}; and (iv) the shortcoming of the simple Flory—Huggins relationship [eqn. (9)] with respect to the individual solute—solvent systems.

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