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Note

Thermodynamics of binary mixtures

Excess volumes of mixing of some binary dioxane mixtures

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It is the purpose of this paper to examine statistical mechanical theory of Flory of mixtures of non-electrolytes for some binary dioxane mixtures varying from nearly ideal to far from ideal.

EXPERIMENTAL

Benzene, toluene, *p*-xylene, carbon tetrachloride, carbon disulphide and dioxane were purified and their purity was checked as reported earlier[1,2]. The excess volumes were measured dilatometrically as reported earlier[1].

RESULTS

The results at 30°C are given in Table 1. The results at 20°C can be calculated from the parameters given in Table 2. The data were fitted to the expression:

$$V^E/x_1x_2 = A+B(x_1-x_2)+C(x_1-x_2)^2 \qquad (1)$$

where A, B and C are constants and x_1 and x_2 are the mole fractions of components 1 and 2 in the mixture. These parameters were evaluated by fitting the experimental values of V^E/x_1x_2 to eqn (1) by the method of least squares. The values obtained along with the standard deviations $\sigma(V^E)$ of the observed and calculated V^E values are recorded in Table 2.

DISCUSSION

V^E for dioxane+benzene has been determined by Ramakrishna and Chand[3] but their values are considerably higher than ours. However, our V^E values for this system at 30°C are comparable to the V^E values determined by Naidu and Krishnan[4]. We are unaware of any data at 30°C with which to compare our results for the other mixtures.

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TABLE 1

EXCESS VOLUMES V^E AT MOLE FRACTIONS x_1 OF COMPONENT 1 AT 303.15 K, AND COMPARISON OF EXPERIMENTAL AND THEORETICAL V^E VALUES AT ($x_1 = 0.2, 0.5, 0.8$)

x_1	V^E (cm^3 mol^{-1})	Flory (cm^3 mol^{-1})	x_1	V^E (cm^3 mol^{-1})	Flory (cm^3 mol^{-1})
Dioxane (1) + benzene (2)					
0.0702	−0.0430		0.6804	−0.0842	
0.1400	−0.0700		0.7665	−0.0637	
(0.2000)	(−0.0900)	(−0.0350)	(0.8000)	(−0.0540)	(−0.0349)
0.2031	−0.0910		0.8092	−0.0518	
0.3021	−0.1078		0.8710	−0.0361	
(0.5000)	(−0.0108)	(−0.0343)			
0.5031	−0.1071		0.9005	−0.0275	
0.5771	−0.1010				
Dioxane (1) + toluene (2)					
			(0.5000)	(−0.0170)	(0.1227)
0.0986	−0.0045		0.5848	−0.0151	
0.1900	−0.0091		0.6229	−0.0140	
(0.2000)	(−0.0090)	(0.0011)			
0.2599	−0.0118		0.7170	−0.0100	
0.3338	−0.0139		0.7700	−0.0080	
			(0.8000)	(−0.0070)	(0.0343)
0.3692	−0.0152		0.8100	−0.0068	
0.3912	−0.0151		0.8901	−0.0039	
0.4200	−0.0164				
Dioxane (1) + carbon tetrachloride (2)					
0.0721	−0.1248		0.6935	−0.2511	
0.1870	−0.2368		0.7058	−0.2510	
(0.2000)	(−0.2400)	(−0.0618)	(0.8000)	(−0.1700)	(−0.0547)
0.3499	−0.3118		0.8050	−0.1685	
0.3676	−0.3211		0.8880	−0.0954	
0.4894	−0.3395		0.9160	−0.0768	
(0.5000)	(−0.3401)	(−0.1021)			
0.6090	−0.3178				
Dioxane (1) + *p*-xylene (2)					
0.1100	0.0349		0.6327	0.1368	
0.1805	0.0585		0.7453	0.1189	
(0.2000)	(0.0640)	(0.0491)			
0.2500	0.0802		0.7578	0.1180	
0.3168	0.1000		0.7743	0.1132	
			(0.8000)	(0.1040)	(0.0667)
0.4078	0.1201		0.8440	0.0900	
(0.5000)	(0.1350)	(0.0460)			
0.5189	0.1364		0.9303	0.0475	
Dioxane (1) + carbon disulphide (2)					
			(0.5000)	(0.8880)	(−0.0690)
0.0805	0.2078		0.5756	0.8908	
0.1602	0.4397		0.6701	0.8500	
(0.2000)	(0.5200)	(−0.0454)			
0.2445	0.6021		0.7788	0.6910	

(Continued on p. 320)

TABLE 1 (*continued*)

x_1	V^E (cm^3 mol^{-1})	Flory (cm^3 mol^{-1})	x_1	V^E (cm^3 mol^{-1})	Flory (cm^3 mol^{-1})
Dioxane (1) + Carbon disulphide (2) (*continued*)					
			(0.8000)	(0.6450)	(−0.0339)
0.3198	0.7198		0.8787	0.4516	
0.3800	0.7964		0.9400	0.2425	
0.4599	0.8681				
Carbon disulphide (1) + toluene (2)					
0.1001	0.1198		0.6221	0.3565	
(0.2000)	(0.2200)	(−0.0361)			
0.2076	0.2274		0.7100	0.3165	
0.3110	0.3047		0.7710	0.2736	
			(0.8000)	(0.2400)	(−0.0694)
0.4303	0.3583		0.8550	0.1940	
0.4811	0.3688		0.8990	0.1420	
(0.5000)	(0.3700)	(−0.0863)			
0.5841	0.3659				
Carbon disulphide (1) + *p*-xylene (2)					
			(0.5000)	(0.3600)	(−0.0791)
0.0801	0.0850		0.5786	0.3573	
0.1300	0.1395		0.6960	0.2982	
0.1820	0.1901		0.7916	0.2489	
(0.2000)	(0.2050)	(−0.0435)	(0.8000)	(0.2400)	(−0.0676)
0.2502	0.2432		0.8136	0.2292	
0.3200	0.2938		0.8401	0.2032	
0.4112	0.3387		0.9282	0.0992	
0.4809	0.3572				

TABLE 2

VALUES OF PARAMETERS OF EQN 1

Mixture	*Temp.* (*K*)	*A* (cm^3 mol^{-1})	*B* (cm^3 mol^{-1})	*C* (cm^3 mol^{-1})	V^E (cm^3 mol^{-1})
Dioxane (1) + benzene (2)	293.15	−0.352	0.1012	0.1500	0.001
	303.15	−0.4288	0.1852	−0.0584	0.007
Dioxane (1) + toluene (2)	293.15	−0.0671	0.010	0.0381	0.0008
	303.15	−0.0650	0.0097	0.0341	0.001
Dioxane (1) + carbon tetrachloride (2)	293.15	−0.9400	0.2500	−0.048	0.002
	303.15	−1.3600	0.7054	0.5491	0.002
Dioxane (1) + *p*-xylene (2)	293.15	0.380	−0.0531	0.083	0.001
	303.15	0.5333	0.2114	0.0005	0.001
Dioxane (1) + carbon disulphide (2)	293.15	2.680	−0.0407	1.026	0.003
	303.15	3.3605	0.7472	0.1455	0.002
Carbon disulphide (1) + toluene (2)	293.15	1.200	0.0001	0.1450	0.001
	303.15	1.4832	0.1463	−0.0423	0.001
Carbon disulphide (1) + *p*-xylene (2)	293.15	0.940	0.2010	0.3283	0.002
	303.15	1.4388	0.1988	−0.1318	0.001

The results were examined for Flory's theory[5]. Flory considered a molecule in a liquid to be composed of segments each having a 'hard-core' volume v^* but occupying an effective volume v in the liquid. Excess volumes V^E, according to this theory, were calculated from the formula[5]:

$$V^E = \frac{(x_1 V_1/\tilde{v}_1 + x_2 V_2/\tilde{v}_2(\phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2)^{7/3}(\tilde{T} - \tilde{T}^{\circ})}{4/3 - (\phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2)^{1/3}} \tag{2}$$

where x_i, V_i and ϕ_i denote the mole fraction of i, the molar volume of i and the site fraction $x_1 V_1/\tilde{v}_1/(x_1 V_1/\tilde{v}_1 + x_2 V_2/\tilde{v}_2)$ of i (i = 1, 2), respectively, and $\tilde{T}$ and $\tilde{T}^{c}$ are reduced temperatures defined by the formulae:

$$\tilde{T} = (\phi_1 P_1^* \tilde{T}_1^{\circ} + \phi_2 P_2^* \tilde{T}_2)/(\phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \theta_2 \chi_{12}) \tag{3}$$

$$\tilde{T}^{\circ} = \{(\phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2)^{1/3} - 1)\}(\phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2)^{-4/3} \tag{4}$$

where P_i^* is the characteristic pressure defined by

$$P_1^* = \alpha_1 T \tilde{v}_1^2 / K_i \,. \tag{5}$$

Where K_i denotes the isothermal compressibility, and $\theta_2 \chi_{12}$ is a pair–interaction parameter. The reduced volume $\tilde{v}_i = v_1/v^*$ for the pure substance i was calculated from the expansivity α_i using the relation

$$\tilde{v}_i = \{1 + \alpha_i T/3(1 + \alpha_i T)\}^3. \tag{6}$$

There is, however, an inherent difficulty in Flory's original method of computing V^E. The difficulty stems from the fact that the reduced temperature $\tilde{T}$ of the mixture is dependent on the parameter $\theta_2 \chi_{12}$ which could be evaluated from a knowledge of some other excess functions for the system. However, in the absence of values of $\theta_2 \chi_{12}$ for example from the measured values of H^E, we have made the approximation that $\theta_2 \chi_{12} \approx 0$. The reduced temperature $\tilde{T}$ of the mixture was then calculated from the relation

$$\tilde{T} = P_1^* \phi_1 \tilde{T}_1 + \phi_2 P_2^* \tilde{T}_2/(\phi_1 P_1^* + \phi_2 P_2^*) \,. \tag{7}$$

The V^E values calculated in this manner at 30 °C are given in Table 1.

Examination of Table 1 shows that the theory correctly predicts the sign of V^E for dioxane + benzene, dioxane + *p*-xylene and dioxane + carbon tetrachloride systems only, although the quantitative agreement is not very impressive. For all other systems the theory fails to predict the sign as well as the magnitude of V^E. The agreement might have been better or worse if we had been able to use the original expression for $\tilde{T}$.

Nevertheless there is a possible acid–base interaction between dioxane and benzene as a factor leading to negative volume change. Further if dioxane forms charge-transfer complexes of increasing stability as the electron donating power of the hydrocarbon increases, it is to be expected that V^E at a constant mole-fraction should increase in a reasonably regular manner[6]. The present results indicate that

V^E for an equimolar mixture of dioxane varies as

Benzene > toluene > *p*-xylene.

This is suggestive of the fact that dioxane forms charge-transfer complexes of decreasing stability with toluene and *p*-xylene.

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