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EXCESS VOLUMES OF MIXING AND EXCESS ENTHALPIES OF MIXING OF 1,2-DIBROMOETHANE WITH AROMATIC HYDROCARBONS AT 298.15 K

D.C. SPAH, P.K. VERMA, K.C. SINGH and K.C. KALRA *

Chemistry Department, Maharshi Dayanand University, Rohtak - 124001 (India)

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ABSTRACT

The excess volumes and enthalpies of mixing of binary mixtures of 1,2-dibromoethane with benzene, toluene, *o*-xylene, *m*-xylene and *p*-xylene have been measured experimentally over the whole composition range at 298.15 K. Qualitatively, the data have been explained on the basis of electron donor/acceptor interactions between 1,2-dibromoethane and the aromatic hydrocarbons and also on the basis of the loss of favourable orientational order of the pure components.

The Flory theory is not able to correctly predict the V^E and H^E values of the studied systems. However, the Sanchez and Lacombe theory correctly predicts the change of sign of the H^E values with change of mole fraction. H^E calculated by this theory is of the same order as the experimental H^E. The calculated values for V^E are in poor agreement with the corresponding experimental values for V^E.

INTRODUCTION

The trans and gauche conformational isomers of 1,2-dibromoethane are in equilibrium with each other at room temperature. It has been shown by Neckel and Volk [1,2] and later by Kohler and Liebermann [3,4] that the gauche molecules are stabilized in a medium of high dielectric constant or by a polarizable surrounding. In solutions with non-polar solvents, gauche molecules are destabilized and favourable orientation between the molecules decreases. This loss of orientational energy yields the high values of H^E.

However, aromatic hydrocarbons are potential electron donors and their mixtures with such simple compounds as carbon tetrachloride have been interpreted in terms of charge-transfer interactions between the π electrons of the aromatic ring and the empty 3d levels of the halogens in carbon tetrachloride [5].

The present work was carried out in order to predict the interactions between aromatic hydrocarbons and 1,2-dibromoethane. The applicability of the statistical mechanical theories of Flory and Abe [6,7] and of Sanchez and Lacombe [8,9] to our data has been critically examined.

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TABLE 1

Experimentally measured excess volumes of mixing, V^E, for 1,2-dibromoethane (1) and aromatic hydrocarbon (2) mixtures at 298.15 K

Mole fraction of (1)	V^E (cm^3 mol^{-1})
1,2-Dibromoethane (1) + benzene (2)	
0.0388	0.0485
0.1603	0.1563
0.2258	0.1958
0.3382	0.2382
0.4139	0.2520
0.5515	0.2438
0.6574	0.2083
0.7613	0.1568
0.8948	0.0757
1,2-Dibromoethane (1) + toluene (2)	
0.0813	0.0321
0.1594	0.0591
0.2406	0.0813
0.3098	0.0986
0.4095	0.1220
0.5032	0.1364
0.5760	0.1373
0.6898	0.1259
0.7638	0.1087
0.8381	0.0888
0.8916	0.0602
0.9532	0.0340
1,2-Dibromoethane (1) + *o*-xylene (2)	
0.1185	0.0843
0.2612	0.1650
0.3242	0.1882
0.4662	0.2412
0.5168	0.2538
0.5393	0.2675
0.7021	0.2441
0.7989	0.1889
0.8586	0.1474
0.8586	0.1474
0.9304	0.0712
1,2-Dibromoethane (1) + *m*-xylene (2)	
0.1145	0.0721
0.1985	0.1129
0.3395	0.1966
0.4950	0.2504
0.6396	0.2598
0.6952	0.2486
0.7956	0.1951
0.8930	0.1277
0.9646	0.0555

TABLE 1 (continued)

Mole fraction of (1)	V^E (cm^3 mol^{-1})
1,2-Dibromoethane (1) + *p*-xylene (2)	
0.0855	0.0302
0.1798	0.0581
0.3159	0.1082
0.4493	0.1477
0.5249	0.1707
0.6526	0.1671
0.6847	0.1583
0.7750	0.1305
0.8573	0.0981
0.9413	0.0476

EXPERIMENTAL

1,2-Dibromoethane, benzene, toluene, *o*-xylene, *m*-xylene and *p*-xylene (all BDH AnalaR grade) were purified by standard procedures [10]. The purity of the final samples was checked by density determinations at 298.15 ± 0.01 K. (293.15 K in the case of *m*-xylene and 1,2-dibromoethane) which agreed to within ±0.00005 g cm^{-3} with the corresponding literature values [11–13].

The excess volumes of mixing as a function of composition were measured dilatometrically as described earlier [14]. The temperature of the water bath was controlled to 0.01 K. Molar excess enthalpies, H^E, at 298.15 K were measured by an LKB flow microcalorimeter (LKB-2107, M/S LKB, Broma, Sweden) as described by Monk and Wadso [15]. According to the specifications of the instrument, the temperature can be set with a precision of 0.1 K and its stability is ±0.02 K over 24 h. Two identical Braun perfusor pumps (B-Braun Melsungen AG, W. Germany) and gas-tight Hamilton syringes were employed to pump liquids through the calorimeter. Using 10, 20 and 50 cm^3 syringes and 10-speed gear boxes on the perfusor pumps, different mixing ratios were achieved. The flow rates were determined by pumping distilled water through the calorimeter and weighing the amounts collected in a specific time interval. For each typical H^E measurement, different calibration constants were determined according to the flow rate, the amplification needed and the composition of the mixture.

RESULTS

The V^E and H^E data for the binary mixtures of 1,2-dibromoethane + benzene, + toluene, + *o*-xylene, + *m*-xylene and + *p*-xylene as a function of

TABLE 2

Experimentally measured excess heats of mixing, H^E, for 1,2-dibromoethane (1) and aromatic hydrocarbons (2) at 298.15 K

Mole fraction of (1)	H^E (J mol^{-1})
1,2-Dibromoethane (1) + benzene (2)	
0.0915	79.06
0.1710	122.20
0.2881	187.17
0.3438	216.96
0.4954	248.70
0.5068	247.84
0.7239	208.05
0.8309	140.50
0.9082	96.03
1,2-Dibromoethane (1) + toluene (2)	
0.1074	−6.58
0.1977	−3.23
0.3259	21.73
0.3850	41.21
0.5398	97.13
0.5512	108.16
0.7581	111.40
0.8545	89.32
0.9220	47.87
1,2-Dibromoethane (1) + *o*-xylene (2)	
0.1216	−43.32
0.2167	−45.00
0.3518	−14.38
0.4091	21.61
0.5759	77.18
0.5815	78.38
0.7360	114.75
0.7761	114.07
0.8743	99.93
0.9334	61.35
1,2-Dibromoethane (1) + *m*-xylene (2)	
0.1236	−59.76
0.2198	−61.32
0.3560	−22.21
0.4135	−2.43
0.5804	100.23
0.7395	132.99
0.7792	132.81
0.8763	103.04
0.9345	71.01
1,2-Dibromoethane (1) + *p*-xylene (2)	
0.1377	−87.77
0.2358	−121.07
0.3627	−128.17
0.4285	−90.56

TABLE 2 (continued)

Mole fraction of (1)	H^E (J mol^{-1})
0.5803	−16.81
0.6126	22.91
0.7377	60.79
0.7729	63.69
0.8777	67.90
0.9351	45.14

composition at 298.15 K are recorded in Tables 1 and 2 and shown graphically in Figs. 1 and 2 respectively.

The data have been fitted to the equation

$$\frac{M^E}{X_1(1-X_1)} = A_M + B_M(2X_1 - 1) + C_M(2X_1 - 1)^2 \tag{1}$$

where X_1 is the mole fraction of 1,2-dibromoethane, M^E is the excess property, e.g. V^E or H^E, and A_M, B_M and C_M are disposable parameters. These parameters were evaluated by the method of least-squares and are given, together with the standard deviations of M^E, in Tables 3 and 4 for V^E and H^E respectively.

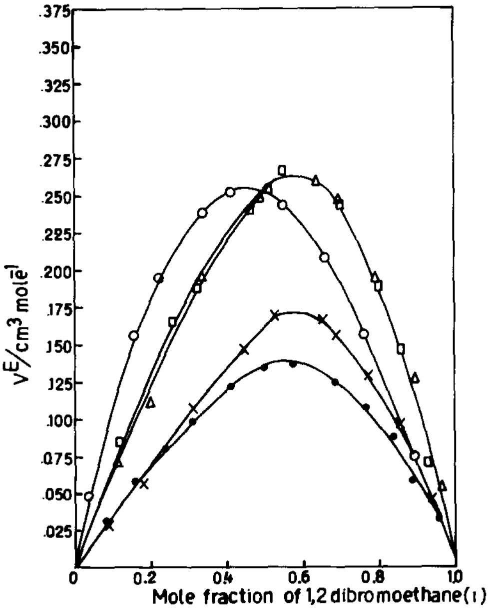

Fig. 1. Molar excess volume of mixing V_m^E of 1,2-dibromoethane (1) + benzene (2) ○; + toluene (2) ●; + *o*-xylene (2) □; + *m*-xylene (2) △; + *p*-xylene (2) ×. At 298.15 K.

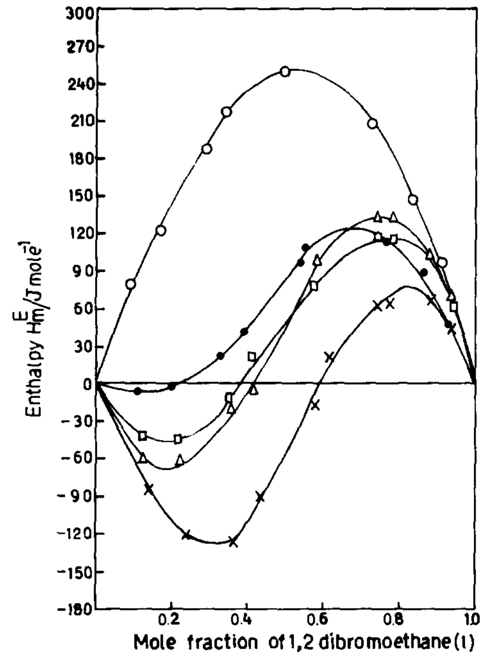

Fig. 2. Molar excess heat of mixing H_m^E of 1,2-dibromoethane (1 + benzene (2) ○; + toluene (2) ●; + *o*-xylene (2) □; + *m*-xylene (2) △; + *p*-xylene (2) ×. At 298.15 K.

TABLE 3

Values of the parameters and standard deviations $\sigma(V^E)$ (cm^3 mol^{-1}) for 1,2-dibromoethane (1) and aromatic hydrocarbons (2) at 298.15 K

System	A_V	B_V	C_V	$\sigma(V^E)$
1,2-Dibromoethane + benzene	0.9501	−0.1442	0.3001	0.0084
1,2-Dibromoethane + toluene	0.5602	0.1267	−0.0525	0.0019
1,2-Dibromoethane + *o*-xylene	1.0306	0.2790	−0.1188	0.0087
1,2-Dibromoethane + *m*-xylene	0.9297	0.4421	0.2257	0.0129
1,2-Dibromoethane + *p*-xylene	0.6029	0.2852	0.0489	0.0084

TABLE 4

Values of the parameters and standard deviations $\sigma(H^E)$ (J mol^{-1}) for 1,2-dibromoethane (1) and aromatic hydrocarbons (2) at 298.15 K

System	A_H	B_H	C_H	$\sigma(H^E)$
1,2-Dibromoethane + benzene	984.86	118.48	−13.42	5.96
1,2-Dibromoethane + toluene	336.01	508.44	−50.24	6.70
1,2-Dibromoethane + *o*-xylene	192.60	823.60	100.88	3.74
1,2-Dibromoethane + *m*-xylene	176.89	1012.01	101.64	3.19
1,2-Dibromoethane + *p*-xylene	−218.78	940.01	260.01	4.09

DISCUSSION

The experimental values of V^E reported in Table 1 for benzene and toluene with 1,2-dibromoethane (DBE) mixtures, over the whole composition range, are in excellent agreement with the values reported by Dhillon and Chugh [16]. However, our values for xylene mixtures are slightly more than theirs [16]. The excess volumes of mixing for 1,2-dibromoethane + aromatic hydrocarbons are positive at all compositions and vary in the order: *m*-xylene ≈ *o*-xylene > benzene > *p*-xylene > toluene.

The heat of mixing values are positive for DBE + benzene mixtures and S-shaped curves are obtained for toluene, *p*-xylene, *o*-xylene and *m*-xylene mixtures with DBE.

At the simplest qualitative level, the V^E and H^E data can be accounted for if it is assumed that electron-donor/acceptor type interactions occur between 1,20-DBE and aromatic hydrocarbons (aromatic hydrocarbons behave as electron donors) and that there is a disruption in the favourable orientational order of 1,2-DBE and aromatic hydrocarbons when they are mixed.

The introduction of one $-CH_3$ group in benzene (as in toluene) would increase the electron density and hence toluene would have a higher electron-donor capacity than benzene. Therefore, it would interact more strongly than benzene. This means that the V^E value for toluene and DBE mixtures should be less than that for benzene and DBE mixtures. The experimental data given in Table 1 support this. However, when two methyl groups are introduced in benzene (as in the xylenes) although there is an increase in the electron donating capacity of these compounds, there is an increased steric repulsion between the methyl groups and the atoms of 1,2-DBE. As a result, the volume of mixing for these mixtures should be more than that of toluene + 1,2-DBE. This is again in agreement with the experimental data as shown in Table 1. Within the xylenes, *p*-xylene is a symmetrical molecule offering little steric hindrance; therefore, its V^E value is less than that of *o*-xylene and *m*-xylene mixtures. It seems that the effect of the placement of the $-CH_3$ groups in *o*-xylene and *m*-xylene is such that the steric repulsion in the mixtures of both is the same order and, therefore, the V^E values are also of the same order.

Excess heat of mixing curves change sign from negative to positive values for all mixtures (except for the mixtures of benzene and DBE) with the increase in the mole fraction of DBE. It seems that loss of the favourable orientational energy of the pure components plays a dominant role in deciding the sign of the values of H^E. In the case of DBE and benzene mixtures, the positive values of H^E over the whole composition range suggest that the energy released by electron donor/acceptor interactions is less than the energy gained by the system due to disruption of the orientational order of the pure components. At low mole fractions of DBE, the orientational disorder of DBE will be maximum, whereas at high mole fractions of DBE the orientational order of the aromatic hydrocarbons will be disrupted. It appears that the energy associated with DBE order is less than that of aromatic hydrocarbons. Furthermore, the energy effects of electron-donor/acceptor interactions outweigh the energy effects of DBE disorder, whereas the energy effects of aromatic hydrocarbons are more than those of electron-donor/acceptor interactions. Therefore, H^{E} at low mole fractions of DBE is negative and at high mole fractions is positive.

Because the shape and size of the two components of the mixtures is different, it was considered worthwhile to examine our data in terms of Flory's statistical theory which allows for the shape and the size of the molecule.

FLORY'S STATISTICAL THEORY

According to Flory's theory [6,7], V^{E} and H^{E} values for binary mixtures are given by

$$V^{\mathrm{E}} = \tilde{V}^{\mathrm{E}}_{\mathrm{cal}}(X_1V_1^* + X_2V_2^*) \tag{2}$$

$$H^{\mathrm{E}} = X_1P_1^*V_1^*\left(\tilde{V}_1^{-1} - \tilde{V}_{\mathrm{cal}}^{-1}\right) + X_2P_2^*V_2^*\left(\tilde{V}_2^{-1} - \tilde{V}_{\mathrm{cal}}^{-1}\right) + X_1V_1^*\theta_2\tilde{X}_{12}\tilde{V}_{\mathrm{cal}}^{-1} \tag{3}$$

where X_1 and X_2, and V_1^* and V_3^* denote the mole fractions and characteristic volumes of components 1 and 2 respectively of the binary mixtures. $\tilde{V}^{\mathrm{E}}_{\mathrm{cal}}$ is given by

$$\tilde{V}^{\mathrm{E}}_{\mathrm{cal}} = \tilde{V}_0^{7/3}(4/3 - \tilde{V}^{\ominus\,1/3})^{-1}(\tilde{T} - \tilde{T}_0) \tag{4}$$

where $\tilde{V}^{\ominus}$, $\tilde{T}$ and $\tilde{T}_0$ are the ideal reduced volume, the reduced temperature and the ideal reduced temperature of the mixture defined by the following equations

$$\tilde{V}_0 = \phi_1\tilde{V}_1 + \phi_2\tilde{V}_2 \tag{5}$$

$$\tilde{T}_0 = \left(\tilde{V}_0^{1/3} - 1\right)/\tilde{V}_0^{4/3} \tag{6}$$

$$\tilde{V} = [1 + \alpha(T/3)/(1 + \alpha T)]^3 \tag{7}$$

$$V_1^* = \tilde{V}_1/\tilde{V}_2 \tag{8}$$

$$\phi_1 = 1 - \phi_2 = N_1V_1^*/(N_1V_1^* + N_2V_2^*) \tag{9}$$

The equations have the same significance as has been described by Flory. α is the coefficient of volume expansion of the pure component. The reduced temperature, $\tilde{T}$, of the mixture is given by

$$\tilde{T} = \frac{\phi_1P_1^*\tilde{T}_1 + \phi_2P_2^*\tilde{T}_2}{\phi_1P_1^* + \phi_2P_2^*}\left(1 - \frac{\phi_1\theta_2\chi_{12}}{\phi_1P_1^* + P_2^*\phi_2}\right)^{-1} \tag{10}$$

where P_1^* is a characteristic pressure defined by

$$P_1^* = \alpha_1 T \tilde{V}_1^2/(K_T)_{\mathrm{i}} \tag{11}$$

where $(K_T)_{\mathrm{i}}$ denotes the isothermal compressibility, χ_{12} is a pair potential and θ_2 is the site fraction and is given by

$$\theta_2 = \frac{X_2}{(X_2 + X_1\gamma_1 S_1/\gamma_2 S_2)} \tag{12}$$

where S_1 denotes the contact sites in each segment of a molecule, considered to be made up of γ_1 segments. To calculate $\gamma_1 S_1/\gamma_2 S_2$, it is assumed that the number of contact sites $\gamma_1 S_1$ per molecule is proportional to the surface area of a sphere of the same core volume. Thus

$$(\gamma_1 S_1/\gamma_2 S_2) = (V_1^*/V_2^*)^{2/3} \tag{13}$$

The reduced temperature $\tilde{T}$ of the mixture is dependent on the adjustable parameter χ_{12}, which could be evaluated from the knowledge of some other excess function of the system. We have evaluated this parameter by using the experimental values of H^{E} at $X_1 = 0.5$ mixtures. These values of χ_{12} are given in Table 6 along with the V^{E} and H^{E} values at $X_1 = 0.1$, 0.3, 0.5, 0.7 and 0.9. The parameters of the pure components were evaluated by using isothermal compressibilities values reported in the literature [17,18]. The values of the coefficient of volume expansion were calculated from the molar volumes of components at different temperatures.

Examination of Tables 5 and 6 reveals that the calculated values of V^{E} and H^{E} are not in agreement with the experimental values. The signs of the V^{E} calculated values do not agree with the experimental values, except for the *o*-xylene + 1,2-dibromoethane mixtures. A reasonably good agreement in H^{E} values for the benzene + DBE system is obtained. Positive values of H^{E} are obtained for other systems, except for *p*-xylene + 1,2-dibromoethane mixtures over the whole composition range.

It seems that the Flory theory is not able to correctly predict the excess functions when there is a change in sign with variation in composition of the mixture.

THE SANCHEZ AND LACOMBE THEORY

V^{E} and H^{E} can be expressed in terms of Sanchez and Lacombe's theory as

$$V^{\mathrm{E}} = \left[1/\tilde{\rho}_{\mathrm{mix}} - (\phi_1 V_1 + \phi_2 V_2)\right]\gamma_{\mathrm{mix}} V_{\mathrm{mix}}^* \tag{14}$$

$$H^{\mathrm{E}} = 2\phi_1\phi_2\gamma_{\mathrm{mix}}\tilde{\rho}_{\mathrm{mix}}(\epsilon_{11}^* + \epsilon_{22}^* - 2\epsilon_{12}^*) + RT\gamma_{\mathrm{mix}}\left[\frac{\tilde{\rho}_1\phi_1^{\ominus} - \phi_1\tilde{\rho}_{\mathrm{mix}}}{\tilde{T}_1} + \frac{\tilde{\rho}_2\phi_2^{\ominus} - \phi_2\tilde{\rho}_{\mathrm{mix}}}{\tilde{T}_2}\right] \tag{15}$$

TABLE 5

Comparison of the measured V^E values for 1,2-dibromoethane (1) + aromatic hydrocarbons (2) at 298.15 K with their corresponding V^E values as evaluated from the theories of Flory and of Sanchez and Lacombe

Mole fraction of (1)	V^E (cm^3 mol^{-1})			
q	Exptl.	Flory	Sanchez and Lacombe	
1,2-Dibromoethane (1) + benzene (2)				
0.1	0.1075	0.0087	−0.0651	(0.0682)
0.3	0.2263	−0.0262	0.0827	(0.1201)
0.5	0.2550	−0.0417	–	–
0.7	0.1900	−0.0339	0.2262	(0.0256)
0.9	0.0750	−0.0023	0.2002	(0.3464)
1,2-Dibromoethane (1) + toluene (2)				
0.1	0.0350	−0.0017	−0.2141	(−0.1853)
0.3	0.0950	−0.0472	−0.0177	(−0.0244)
0.5	0.1362	−0.0638	–	–
0.7	0.1230	−0.0508	0.2597	(0.3087)
0.9	0.0585	−0.0082	0.3457	(0.4804)
1,2-Dibromoethane (1) + *o*-xylene (2)				
0.1	0.0710	0.0239	−0.1204	(0.1542)
0.3	0.1835	0.0086	0.0877	(0.0546)
0.5	0.2550	0.0011	–	–
0.7	0.2425	0.0030	0.4059	(0.4577)
0.9	0.1100	0.0143	0.5341	(0.6537)
1,2-Dibromoethane (1) + *m*-xylene (2)				
0.1	0.0625	0.0070	−0.1694	(−0.2116)
0.3	0.1700	−0.0523	0.4303	(0.0119)
0.5	0.2525	−0.0518	–	–
0.7	0.2425	−0.0437	0.3915	(0.4515)
0.9	0.1100	−0.0060	0.5373	(0.6691)
1,2-Dibromoethane (1) + *p*-xylene (2)				
0.1	0.0350	−0.0430	−0.2788	(−0.3144)
0.3	0.1025	−0.1488	−0.0550	(−0.0873)
0.5	0.1625	−0.1854	–	–
0.7	0.1525	−0.1457	0.3038	(0.3561)
0.9	0.0725	−0.0508	0.4550	(0.5765)

where

$$\phi_1 = m_1(\rho_1^*)^{-1}/\sum(m_i/\rho_1^*) \tag{16}$$

$$m_1 = X_1 M_1\left[\sum(X_1 m_1)\right]^{-1} \tag{17}$$

$$\gamma = \sum X_1\gamma_1 \tag{18}$$

$$\gamma_i = r_1^0 V_1^*(V_{\text{mix}}^*)^{-1} \tag{19}$$

$$V_{\text{mix}}^* = \sum \phi_1^0 V_1^* \tag{20}$$

TABLE 6

Comparison of the measured H^E values for 1,2-dibromoethane (1) and aromatic hydrocarbons (2) at 298.15 K with their corresponding H^E values as evaluated from the Flory theory and the Sanchez and Lacombe theory

Mole fraction of (1)	H^E (cal mol^{-1})			
	Expt.	Flory	Sanchez and Lacombe	
1,2-Dibromoethane (1) + benzene (2)		$\chi_{12} = 6.6835$	$\epsilon_p = 0.9151$	
0.1	20.08	24.09	617.45	(45.42)
0.3	46.85	52.28	684.21	(53.27)
0.5	60.23	62.67	–	–
0.7	52.34	51.98	689.97	(64.39)
0.9	24.39	23.70	628.49	(68.08)
1,2-Dibromoethane (1) + toluene (2)		$\chi_{12} = 1.0785$	$\epsilon_p = 0.9291$	
0.1	−1.43	9.57	650.58	(−8.48)
0.3	3.23	19.17	656.48	(6.11)
0.5	20.08	22.77	–	–
0.7	29.40	19.95	585.30	(33.67)
0.9	15.42	10.27	519.34	(46.66)
1,2-Dibromoethane (1) + *o*-xylene (2)		$\chi_{12} = 0.2408$	$\epsilon_p = 0.9262$	
0.1	−8.60	4.48	769.84	(−26.65)
0.3	−7.17	6.71	732.07	(−71.67)
0.5	12.19	7.55	–	–
0.7	25.81	6.92	606.83	(29.53)
0.9	20.79	4.56	531.21	(46.79)
1,2-Dibromoethane (1) + *m*-xylene (2)		$\chi_{12} = 0.5474$	$\epsilon_p = 0.9276$	
0.1	−12.19	6.54	766.71	(−29.97)
0.3	−10.76	9.89	725.89	(−9.34)
0.5	10.76	13.51	–	–
0.7	31.19	12.08	597.70	(29.76)
0.9	22.23	6.90	521.75	(48.20)
1,2-Dibromoethane (1) + *p*-xylene (2)		$\chi_{12} = -1.7077$	$\epsilon_p = 0.9331$	
0.1	−15.06	−8.68	698.56	(−25.88)
0.3	−30.83	−25.42	662.66	(−5.81)
0.5	−12.91	−32.47	–	–
0.7	11.83	−27.63	546.59	(31.17)
0.9	14.34	−11.20	477.55	(48.49)

$$\phi_1^0 = m_1(\rho_1^* V_1^*)^{-1} / \sum m_1(\rho_1^* V_1^*)^{-1} \tag{21}$$

$$\tilde{V}_{\text{mix}} = 1/\tilde{\rho}_{\text{mix}} \tag{22}$$

All the terms have the same significance as described by Sanchez and Lacombe. The ϵ^*, V^*, γ, T^*, P^* and ρ^* values of pure aromatic hydrocarbons are the same as reported by Sanchez and Lacombe [8], whereas the values of the parameters of 1,2-dibromoethane were calculated from vapour pressure and densities at 10–132°C by the method described by Sanchez and Lacombe [8]. The vapour pressure [18] and densities [11] were taken from the literature. The values are 1.1654 kcal mol^{-1}, 9.71 cm^2 mol^{-1}, 8.0668, 586.5119 K, 4955 atm and 2.40 g cm^{-3} for ϵ^*, V^*, γ, T^*, P^* and ρ^* respectively. Evaluation of V^{E} and H^{E} values by this theory, therefore, requires a knowledge of the reduced density, $\tilde{\rho}_{\mathrm{mix}}$, of the mixture which in principle can be evaluated from the equation of state of the mixture, as follows

$$\tilde{\rho}_{\mathrm{mix}}^2 + (RT/\epsilon_{\mathrm{mix}}^*)\left[\tilde{\rho}_{\mathrm{mix}}(1-\gamma_{\mathrm{mix}}^{-1}) + \ln(1-\tilde{\rho}_{\mathrm{mix}})\right] + \tilde{P} = 0 \tag{23}$$

where

$$\epsilon_{\mathrm{mix}}^* = \sum \phi_1 \epsilon_{11}^* - RT \sum\sum \phi_1 \phi_2 \chi_{12}^0 \tag{24}$$

$$\chi_{12}^0 = \epsilon_{11}^* + \epsilon_{22}^* - 2\epsilon_{12}^* \tag{25}$$

$$\tilde{P} = PV_{\mathrm{mix}}^*/\epsilon_{\mathrm{mix}}^* \tag{26}$$

provided that the interaction energy ϵ_{12}^* for the binary mixture is known. However, such information is not available in most cases. Therefore, the interaction energy ϵ_{12}^* was calculated from its V^{E} value at $X = 0.5$ through eqns. (14) and (23), (16–22) and (24–26). This value of ϵ_{12}^* for the mixture was then used to evaluate $\tilde{\rho}_{\mathrm{mix}}$ and, hence, V^{E} and H^{E} for the mixture at any composition through eqns. (16) and (23). Such V^{E} and H^{E} values for all the mixtures at $X = 0.1$, 0.3, 0.7 and 0.9 are recorded in column 4 in Tables 5 and 6 respectively and are also compared with their corresponding experimental values. The poor agreement between the calculated and experimental V^{E} and H^{E} values for these mixtures may be attributed to failure of these mixtures to satisfy the equation of state (eqn. (23)).

The extent to which a binary mixture deviated from eqn. (23) was evaluated by using the V^{E} and H^{E} values for an equimolar mixture and to calculate $\tilde{\rho}_{\mathrm{mix}}$ and ϵ_{12}^* and, hence, the R.H.S. of eqn. (23). It was observed that the R.H.S. of eqn. (23) varied from 0.0234 to 0.0289 for these binary mixtures. Once the R.H.S. of eqn. (23) was established, the reduced density $\tilde{\rho}_{\mathrm{mix}}$ for the mixture at any other composition was calculated by numerically solving eqn. (23). This value of $\tilde{\rho}_{\mathrm{mix}}$ was then used to calculate V^{E} and H^{E} at other compositions; such V^{E} and H^{E} values are recorded in parentheses in Tables 5 and 6.

Examination of Table 6 reveals that the change of sign of H^{E} with increase of mole fraction is correctly predicted by the theory. The magnitude of H^{E} calculated values also agrees with the experimental H^{E} values to some extent.

The calculated V^{E} values are in poor agreement with the corresponding experimental V^{E} values for all the systems studied. At low mole fractions of 1,2-dibromoethane, the calculated V^{E} is less than the experimental V^{E}, whereas at high mole fractions, the reverse is true.

CONCLUSION

There is a disruption of the orientational order of the pure components when they are mixed. There are weak specific electron-donor/acceptor interactions between DBE and the aromatic hydrocarbons. The energy associated with these interactions is more than the favourable orientational order energy of 1,2-dibromoethane, whereas the interaction energy is less than the orientational energy of the aromatic hydrocarbons.

The Flory theory is not able to correctly predict the V^E and H^E values of the studied systems. However, the Sanchez and Lacombe theory does correctly predict the change of sign of the H^E values with the change of mole fraction. The H^E values calculated by this theory are of the same order as the experimental H^E values. The calculated V^E values are in poor agreement with the corresponding experimental V^E values.

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