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Excess volumes of mixing and excess enthalpies of mixing of *n*-butyl chloride with aromatic hydrocarbons at 298.15 K

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Abstract

The excess volumes and enthalpies of mixing of binary mixtures of *n*-butyl chloride with benzene, toluene, *o*-xylene, *m*-xylene and *p*-xylene have been measured experimentally over the whole composition range at 298.15 K. The data have been analysed qualitatively in terms of the specific interactions of electron donor–acceptor type and of the disruption of molecular order in the pure components.

Flory's theory correctly predicts the sign and to an acceptable extent the magnitude of the H^E values although the agreement for V^E values is not good. However, the Graph theory correctly predicts the sign as well as the magnitude of the V^E and H^E values.

INTRODUCTION

Our earlier studies [1–3] of the excess enthalpies and excess volumes of 1,2-dibromoethane or ethyl iodide plus aromatic hydrocarbon mixtures demonstrated the existence of weak specific interactions of electron donor–acceptor type between the components, in which the aromatic hydrocarbon behaves as an electron donor. These studies also provided evidence for the disruption of the molecular order of the pure components. Similar results have been obtained for 1-bromoalkanes and 1-chloroalkane plus *n*-alkane mixtures [4,5].

In the present studies, V^E and H^E data for *n*-butyl chloride plus benzene, toluene, *o*-xylene, *m*-xylene and *p*-xylene at 298.15 K have been investigated in order to understand the nature of the molecular interactions and the physicochemical behaviour of these binary mixtures. The data have also been examined critically in terms of Flory's [6,7] statistical theory and the Graph theoretical approach [8–10].

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EXPERIMENTAL

n-Butyl chloride, benzene, toluene, *o*-xylene, *m*-xylene and *p*-xylene (BDH, AnalaR grade) were purified by standard procedures [11]. The purity of the final samples was checked by density determinations at 25 ± 0.01° C. The experimental values agreed with literature values [12] to within 5×10^{-5} g cm^{-3}.

TABLE 1

Experimentally measured excess volumes of mixing for *n*-butyl chloride (i) + aromatic hydrocarbon (j) mixtures at 298.15 K

Mole fraction, x_i	V_m^E (cm^3 mol^{-1})	Mole fraction, x_i	V_m^E (cm^3 mol^{-1})
n-Butyl chloride (i) + benzene (j)			
0.0955	0.0473	0.6310	0.0766
0.1713	0.0757	0.6552	0.0671
0.2620	0.0997	0.7060	0.0581
0.3026	0.1067	0.7275	0.0530
0.3847	0.1127	0.8230	0.0390
0.4724	0.1089	0.8927	0.0259
0.6027	0.0821		
n-Butyl chloride (i) + toluene (j)			
0.1393	−0.0634	0.6454	−0.1881
0.2791	−0.1267	0.6985	−0.1680
0.3014	−0.1515	0.8009	−0.1353
0.3818	−0.1846	0.8289	−0.1206
0.5085	−0.1998		
n-Butyl chloride (i) + *o*-xylene (j)			
0.1223	−0.1193	0.5520	−0.2656
0.1535	−0.1410	0.5943	−0.2611
0.2229	−0.2024	0.7517	−0.2065
0.2695	−0.2142	0.9089	−0.1015
0.4085	−0.2600		
n-Butyl chloride (i) + *m*-xylene (j)			
0.1740	−0.1114	0.4340	−0.1906
0.2160	−0.1206	0.5539	−0.1749
0.2236	−0.1344	0.6266	−0.1500
0.2613	−0.1597	0.7924	−0.0749
0.3436	−0.1834	0.8973	−0.0380
n-Butyl chloride (i) + *p*-xylene (j)			
0.0958	−0.0841	0.4732	−0.2593
0.2229	−0.1692	0.6087	−0.2394
0.2836	−0.1959	0.7604	−0.1773
0.2934	−0.2237	0.8578	−0.1144
0.3824	−0.2393		

The excess volumes of mixing, as a function of composition, were measured dilatometrically as described earlier [13]. The temperature of the water bath was controlled to ±0.01 K. A continuous flow calorimeter (LKB-2107, LKB, Broma, Sweden) was used in the manner described by Monk and Wadso [14]. The uncertainty in the H^E values is 1–2%.

RESULTS

The V^E and H^E data for the binary mixtures of *n*-butyl chloride with benzene, toluene, *o*-xylene, *m*-xylene and *p*-xylene as a function of composition at 298.15 K are recorded in Tables 1 and 2 and shown graphically in Fig. 1 and Fig. 2 respectively. The equation

$$\frac{M^E}{x_1(1-x_1)} = A_m + B_m(2x_1 - 1) + C_m(2x_1 - 1)^2 \tag{1}$$

TABLE 2

Experimentally measured excess enthalpies of mixing for *n*-butyl chloride (i)+aromatic hydrocarbon (j) mixtures at 298.15 K

x_i	H_m^E (J mol^{-1})	x_i	H_m^E (J mol^{-1})
n-Butyl chloride (i)+benzene (j)			
0.0777	42.5	0.6793	177.5
0.1443	80.0	0.8040	116.6
0.2514	137.5	0.8109	105.9
0.4566	208.6	0.8949	62.0
n-Butyl chloride (i)+toluene (j)			
0.0947	−80.6	0.5070	−189.0
0.1739	−124.5	0.6719	−147.5
0.2610	−157.5	0.8367	−84.5
0.3468	−185.0	0.9124	−50.3
n-Butyl chloride (i)+ *o*-xylene (j)			
0.1092	−88.7	0.5454	−222.5
0.1928	−131.5	0.6992	−189.0
0.2816	−172.0	0.8532	−106.5
0.3759	−202.5	0.9203	−68.0
n-Butyl chloride (i)+ *m*-xylene (j)			
0.1109	−53.0	0.5799	−198.5
0.1957	−88.5	0.7030	−187.2
0.2910	−127.5	0.8555	−125.1
0.3802	−152.0	0.9216	−75.5
n-Butyl chloride (i)+ *p*-xylene (j)			
0.1042	−70.0	0.5440	−227.5
0.1963	−122.8	0.7038	−198.5
0.3150	−178.4	0.8559	−117.5
0.3811	−201.1	0.9219	−60.9

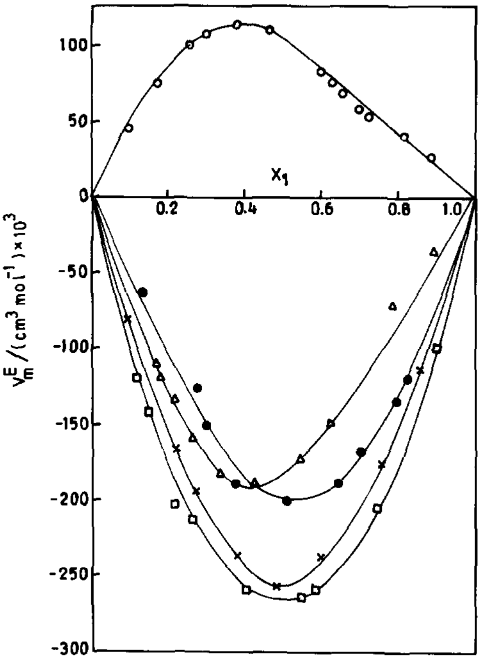

Fig. 1. Experimentally measured V_m^E at 298.15 K for *n*-butyl chloride (*i*)+benzene (○); +toluene (●); +*o*-xylene (□); +*m*-xylene (△) and +*p*-xylene (×).

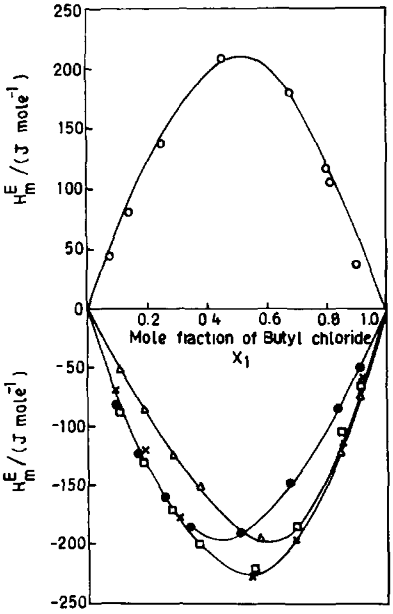

Fig. 2. Experimentally measured H_m^E at 298.15 K for *n*-butyl chloride (*i*)+benzene (○); +toluene (●); +*o*-xylene (□); +*m*-xylene (△) and +*p*-xylene (×).

TABLE 3

Values of adjustable parameters of eqn. (1) and the standard deviation σ (V_m^E) of the molar excess volumes of various ($i + j$) mixtures at 298.15 K

System	A_m (cm^3 mol^{-1})	B_m (cm^3 mol^{-1})	C_m (cm^3 mol^{-1})	$\sigma(V_m^E)$ (cm^3 mol^{-1})
Butyl chloride (i) + benzene (j)	0.3969	−0.2123	−0.0037	0.0056
Butyl chloride (i) + toluene (j)	−0.7988	−0.1966	0.2256	0.0073
Butyl chloride (i) + *o*-xylene (j)	−1.0747	−0.0403	−0.1486	0.0058
Butyl chloride (i) + *m*-xylene (j)	−0.7352	0.2332	0.2780	0.0071
Butyl chloride (i) + *p*-xylene (j)	−1.0236	0.0262	0.1317	0.0069

TABLE 4

Values of adjustable parameters A_m, B_m and C_m of eqn. (1) and standard deviations, $\sigma(H_m^E)$, of the molar excess enthalpies of various binary mixtures at 298.15 K

System	A_m (J mol^{-1})	B_m (J mol^{-1})	C_m (J mol^{-1})	$\sigma(H_m^E)$ (J mol^{-1})
n-Butyl chloride (i) + benzene (j)	819.9	51.1	−339.2	5.01
n-Butyl chloride (i) + toluene (j)	−740.2	187.7	−69.8	4.46
n-Butyl chloride (i) + *o*-xylene (j)	−888.9	−25.9	23.3	5.58
n-Butyl chloride (i) + *m*-xylene (j)	−745.6	−342.0	149.7	5.26
n-Butyl chloride (i) + *p*-xylene (j)	−919.5	−119.3	194.5	5.43

was fitted to the data, where x_1 is the mole fraction of *n*-butyl chloride, 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, $\sigma(M^E)$, in Tables 3 and 4 for V^E and H^E respectively.

DISCUSSION

We are unaware of any previous data with which to compare our present results for these mixtures. The plots of V^E and H^E against x_1 are slightly skewed towards high mole fractions of *n*-butyl chloride. The V^E and H^E values were found to be negative for mixtures of *n*-butyl chloride with toluene, *o*-xylene, *m*-xylene or *p*-xylene, and positive for *n*-butyl chloride and benzene mixtures over the whole composition range; for equimolar mixtures, values were found to vary in the following order: *n*-butyl chloride + benzene > + *m*-xylene > + toluene > + *p*-xylene and > + *o*-xylene. The variation in V^E and H^E values of these mixtures can be attributed to the following factors.

(i) Specific interactions of the electron donor–acceptor type between *n*-butyl chloride and aromatic hydrocarbons where the aromatic hydrocarbon behaves as an electron donor.

(ii) The disruption in the molecular order of the pure components.

The former factor leads to negative values of V^E and H^E, while the latter acts in the opposite direction. As the V^E and H^E values for all the studied systems are negative (except for *n*-butyl chloride–benzene), the contribution of factor (i) to the excess functions is more than that of factor (ii). If it is assumed that the energy associated with molecular order for all pure aromatic hydrocarbons is of the same magnitude, then the variation in V^E and H^E values for these mixtures will be due to the variation in magnitude of the specific interaction energy in these mixtures.

The electron-donating power of benzene is known [15] to increase with the introduction of methyl groups into the ring as in toluene: consequently electron donor–acceptor interactions will also increase and the V^E and H^E values for toluene mixtures will be less than those of benzene mixtures. This is supported by our experimental results for *n*-butyl chloride plus benzene or toluene mixtures (Figs. 1 and 2). The introduction of two methyl groups into the benzene ring, as in the xylenes, further enhances the electron-donating capacity of aromatic hydrocarbons. Therefore, the V^E and H^E values for xylene mixtures should be less than that of toluene mixtures: this is found to be true for *o*-xylene and *p*-xylene mixtures, but the *m*-xylene mixtures have slightly higher values than the toluene mixtures. This may be due to the unsymmetrical shape of the *m*-xylene molecule and it seems that the placement of the two methyl groups in the aromatic ring is such that they offer maximum steric hindrance to the chlorine atom of butyl chloride, which limits the interaction of the butyl chloride with the π-electron cloud of aromatic hydrocarbon. Amongst the xylenes, *p*-xylene is more symmetrical than the others; it offers little steric hindrance to the *n*-butyl chloride molecule and is the most electron-donating of the aromatic hydrocarbons under study. Thus the electron donor–acceptor interactions in its mixtures are stronger and hence it has the lowest values of V^E and H^E. Both our V^E and H^E data support this argument.

Because the shape and size of the two components in these mixtures are different, it was considered worthwhile to examine our data in terms of Flory's statistical theory [6,7] which takes into account the shape and size of the molecules. According to Flory's theory, V^E and H^E values for binary mixtures are given by

$$V^E = \tilde{V}^E_{\mathrm{cal}}(x_1V_1^* + x_2V_2^*) \tag{2}$$

$$H^E = x_1P_1^*V_1^*\left(\tilde{V}_1 - 1 - \tilde{V}_{\mathrm{cal}}^{-1}\right) + x_2P_2^*V_2^*\left(\tilde{V}_2^{-1} - \tilde{V}_{\mathrm{cal}}^{-1}\right) + x_1V_1^*\theta_2\chi_{12}\tilde{V}_{\mathrm{cal}}^{-1}, \tag{3}$$

where all the parameters used have been defined by Flory [6,7]. The adjustable parameter χ_{12} was evaluated by using experimental values of H^E at $x_1 = 0.5$ in the mixtures. These values of χ_{12} are given in Table 6 along with the H^E values at $x_1 = 0.1, 0.3, 0.5, 0.7$ and 0.9.

TABLE 5

Comparison of the measured V_m^E values for *n*-butyl chloride (i) + aromatic hydrocarbons (j) at 298.15 K with their corresponding V_m^E values as evaluated from the Flory theory and the Graph theoretical approach

x_i	V_m^E (cm^3 mol^{-1})		
	Exp.	Flory	Graph
n-Butyl chloride (i) + benzene (j)			
0.1	0.1023	0.7877	0.0788
0.3	0.2212	1.7166	0.1933
0.5	0.2422	1.9417	0.2422
0.7	0.1855	1.5702	0.2147
0.9	0.0717	0.6547	0.0974
n-Butyl chloride (i) + toluene (j)			
0.1	−0.0447	0.4779	−0.0582
0.3	−0.1437	1.1171	−0.1500
0.5	−0.1997	1.3450	−0.1997
0.7	−0.1767	1.1536	−0.3892
0.9	−0.0731	0.5097	−0.0941
n-Butyl chloride + *o*-xylene (j)			
0.1	−0.1024	0.4858	−0.0702
0.3	−0.2273	1.1707	−0.1899
0.5	−0.2687	1.4539	−0.2687
0.7	−0.2341	1.2888	−0.2782
0.9	−0.1082	0.5910	−0.1553
n-Butyl chloride + *m*-xylene (j)			
0.1	−0.0669	0.5195	−0.0503
0.3	−0.1646	1.2472	−0.1334
0.5	−0.1838	1.5439	−0.1838
0.7	−0.1255	1.3652	−0.1832
0.9	−0.0334	0.6250	−0.0965
n-Butyl chloride (i) + *p*-xylene (j)			
0.1	−0.0864	0.4429	−0.2475
0.3	−0.2121	1.0670	−0.2398
0.5	−0.2559	1.3240	−0.2559
0.7	−0.2083	1.1712	−0.3162
0.9	−0.0827	0.5356	−0.1367

An examination of Tables 5 and 6 shows that Flory's theory correctly predicts the sign and to a good extent the magnitude of the H^E values for all mixtures. The deviations in H^E_{calc} values from those of experimentally determined values for *n*-butyl chloride plus benzene, toluene, *o*-xylene, *m*-xylene and *p*-xylene binary systems are not more than 56, 25, 20, 20 and 10 J mol^{-1} respectively at a particular mole fraction. However, the agreement for the V^E values is not good. Flory's theory is not able to predict the sign of the V^E values for all the systems except the *n*-butyl chloride plus

TABLE 6

Comparison of the measured H_m^E values for *n*-butyl chloride (i) and aromatic hydrocarbons (j) at 298.15 K with their corresponding H_m^E values as evaluated from the Flory theory and the Graph theoretical approach

x_i	H_m^E (J mol^{-1})		
	Exp.	Flory	Graph
n-Butyl chloride (i)+benzene (j)		$\chi_{ij} = 28.0350$ J mol^{-1}	
0.1	50.57	106.18	65.9
0.3	156.49	204.34	162.5
0.5	204.98	204.98	204.9
0.7	165.08	158.11	183.1
0.9	57.93	62.70	83.8
n-Butyl chloride (i)+toluene (j)		$\chi_{ij} = 6.7982$ J mol^{-1}	
0.1	−84.15	−59.80	−53.8
0.3	−173.56	−148.60	−173.4
0.5	−185.05	−185.05	−185.1
0.7	−142.03	−159.20	−140.9
0.9	−57.13	−68.90	−55.2
n-Butyl chloride (i)+ *o*-xylene (j)		$\chi_{ij} = 4.4668$ J mol^{-1}	
0.1	−78.10	−68.80	−77.9
0.3	−184.63	−174.30	−184.3
0.5	−222.48	−222.48	−222.5
0.7	−189.00	−196.60	−189.5
0.9	−81.84	−87.80	−82.4
n-Butyl chloride (i)+ *m*-xylene (j)		$\chi_{ij} = 7.1818$ J mol^{-1}	
0.1	−34.12	−54.00	−46.5
0.3	−122.98	−142.20	−128.2
0.5	−186.40	−186.40	−186.4
0.7	−180.45	−169.30	−201.1
0.9	−83.39	−76.90	−120.4
n-Butyl chloride (i)+ *p*-xylene (j)		$\chi_{ij} = 5.4965$ J mol^{-1}	
0.1	−62.97	−70.70	−72.4
0.3	−176.55	−177.40	−180.2
0.5	−229.88	−229.88	−229.9
0.7	−196.59	−198.90	−207.9
0.9	−80.15	−88.90	−96.5

benzene mixtures. The deviation is probably due to the errors in the coefficients of volume expansion (α) and in the isothermal compressibility (K_T) data of the pure components taken from the literature [16,17]. The K_T value for *n*-butyl chloride was evaluated using the following relation [18] as the value was not available in the literature:

$$\delta^2 = \alpha T / K_T \qquad (4)$$

where α is the coefficient of volume expansion and T is the temperature.

The solubility parameter δ was evaluated using the following relation:

$$\delta = \left(\frac{\Delta H - RT}{V}\right)^{1/2} \tag{5}$$

where ΔH is the heat of vaporisation, R is the gas constant and V is the molar volume.

Our data were then analysed in terms of the Graph theoretical approach [8,9]. According to this theory

$$V^{\mathrm{E}} = \alpha_{ij}\left[\frac{1}{\sum x_i {}^3\xi_i} - \frac{x_j}{{}^3\xi_j}\right] \tag{6}$$

and

$$H^{\mathrm{E}} = x_i x_j K_{ij} \chi_{ij} \left({}^3\xi_i / {}^3\xi_j\right) / \left[x_i + x_j K_{ij}\left({}^3\xi_i / {}^3\xi_j\right)\right] \tag{7}$$

where x_i, x_j and ${}^3\xi_i$, ${}^3\xi_j$ are the mole fractions and the corresponding third-degree connectivity parameters for the i and j molecules respectively. The method of calculation of ${}^3\xi_i$ and ${}^3\xi_j$ is described elsewhere [8]. In eqn. (6), α_{ij} is a constant, characteristic of a particular mixture. Its value is calculated from the experimental value of V^{E} at 0.5 mole fraction; then the values of V^{E} at other mole fractions were evaluated using the same value of α and are presented in Table 5.

In eqn. (7) there are two unknown parameters, K_{ij} and χ_{ij}; they were evaluated by substituting H^{E} experimental values at two mole fractions, preferably 0.4 and 0.5, into eqn. (7). Then the H^{E} values at other mole fractions were calculated and are reported in Table 6. The values of V^{E} and H^{E} obtained from the Graph theoretical approach are reported in Table 6 and are compared with their corresponding experimental values: there is good agreement in the sign as well as in the magnitude of the values.

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REFERENCES

1 P. Verma, D.C. Spah, K.C. Kalra and K.C. Singh, J. Soln. Chem., 19 (1990) 85.
2 K.C. Singh, K.C. Kalra and Prakash Kumar, Indian J. Chem., 29A (1990) 124.
3 D.C. Spah, P.K. Verma, K.C. Singh and K.C. Kalra, Thermochim. Acta, 146 (1989) 187.
4 J. Valero, M. Gracia and C. Gutierrezlosa, J. Chem. Thermodyn., 12 (1980) 621.
5 J. Valero, M.C. Lopez, M. Gracia and C. Guttierrezlosa, J. Chem. Thermodyn., 12 (1980) 627.
6 P.J. Flory, J. Am. Chem. Soc., 87 (1965) 1833.
7 A. Abe and P.J. Flory, J. Am. Chem. Soc., 87 (1965) 1838.

8 P.P. Singh, R.K. Nigam, K.C. Singh and V.K. Sharma, Thermochim. Acta, 46 (1981) 175.
9 P.P. Singh, Thermochim. Acta, 66 (1983) 37.
10 P.P. Singh and Meenu Bhatia, Can. J. Chem., 68 (1990) 74.
11 Vogel's Textbook of Practical Organic Chemistry, ELBS, Longmans, London, 4th edn., 1978, pp. 266–267.
12 J. Timmerman, Physico-Chemical Constants of Pure Organic Compounds, Elsevier, Amsterdam, 1950, pp. 141, 152, 163, 165, 167, 261.
13 R.K. Nigam and P.P. Singh, Trans. Faraday Soc., 65 (1969) 950.
14 P. Monk and I. Wadso, Acta Chem. Scand., 22 (1968) 1842.
15 R.K. Nigam and K.C. Singh, J. Chem. Soc., Faraday Trans., 175 (1979) 1120.
16 J. Singh, H. Pflung and G.C. Benson, J. Phys. Chem., 72 (1968) 1939.
17 G.C. Benson and J. Singh, J. Phys. Chem., 72 (1968) 1345.
18 J.H. Hildebrand, J.M. Prausnitz and R.L. Scott, Regular and Related Solutions, Van Nostrand Reinhold, New York, 1970.