Molecular interactions in binary mixtures of non-electrolytes: Molar excess volumes and molar excess enthalpies

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Molar excess volumes and molar excess enthalpies for various $(i+j)$ binary m-nitrotoluene (i) + benzene, + toluene + $o-$, + $p-$ and m-xylene (j) mixtures have been determined as a function of composition at 308.15 K. The data have been analysed in terms of graph-theoretical approach which suggests that these mixtures are characterized by interactions between the π-electron cloud of aromatic hydrocarbons and the delocalized π-electron cloud over the nitrogen and the oxygen atoms of the nitro group of m-nitrotoluene.

A recent study[1] has shown that m-nitrotoluene + n-alkane mixtures are characterized by dipole-induced dipole interactions. It would be interesting to see how the replacement of n-alkanes by aromatic hydrocarbons would influence the nature of interactions between m-nitrotoluene and aromatic hydrocarbons in their binary mixtures. These considerations prompted us to determine molar excess volumes, V^E, and molar excess enthalpies, H^E, of m-nitrotoluene (i) + aromatic hydrocarbons (j) mixtures.

Materials and Methods

m-Nitrotoluene, benzene, toluene, $o-$, $m-$ and p-xylenes (AR Grade) were purified by standard methods[1-3]. The purities of the purified compounds were checked by measuring their densities at $298.15 \pm 0.01K$ and these agreed (within $\pm 5 \times 10^{-5}$ g cm^{-3}) with the corresponding literature values[4-7]. The density of m-nitrotoluene at 298.15K was calculated from the density versus temperature data. The necessary density data were taken from the literature[4].

Molar excess volumes were determined using a V-shaped dilatometer in the manner explained elsewhere[8]. The uncertainty in the measured V^E values is $\pm 0.5\%$.

Molar excess enthalpies for the various $(i+j)$ binary mixtures were measured at 308.15K using a flow microcalorimeter (LKB Broma, Sweden) in the manner described by Dahiya et al.[9]. The uncertainty in the measured H^E values is ~ 1%.

Results

Molar excess volumes, V^E, and molar excess

enthalpies, H^E, data for the various $(i+j)$ binary mixtures as function of composition at 308.15K (recorded in Tables 1 and 2 and shown graphically in Fig. 1) can be expressed as:

$$X^E(X = V \text{ or } H) = x_i(1 - x_i)[X^{(0)} + X^{(1)}(2x_i - 1) + X^{(2)}(2x_i - 1)^2] \qquad \dots (1)$$
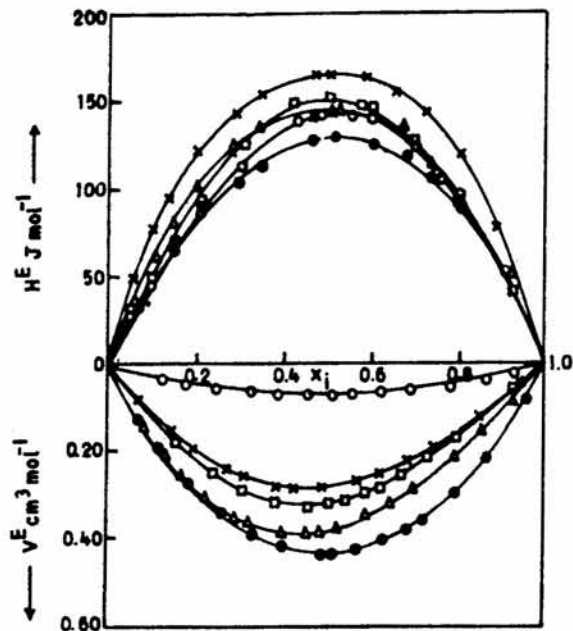

Fig. 1—Variation of V^E, H^E with mole fraction x_i, for
○ m-Nitrotoluene(i) + benzene(j),   □ m-Nitrotoluene(i) + toluene(j),   × m-Nitrotoluene(i) + o-xylene(j),   △ m-Nitrotoluene(i) + p-xylene(j),   ● m-Nitrotoluene(i) + m-xylene(j), mixtures at 308.15K.

Table 1—Measured V^E values at 308.15K for the various $(i+j)$ mixtures as functions of x_i, the mole fraction of component i; also included are the various $V^{(n)}$ (n = 0-2) parameters along with standard deviation $\sigma(V^E)$

x_i	V^E (cm³ mol⁻¹)	x_i	V^E (cm³ mol⁻¹)
	m-Nitrotoluene(i) + benzene(j)		
0.0502	− 0.019	0.5104	− 0.073
0.1251	− 0.039	0.5568	− 0.069
0.1785	− 0.045	0.6219	− 0.066
0.2507	− 0.060	0.6915	− 0.060
0.3251	− 0.068	0.7801	− 0.052
0.3894	− 0.074	0.8602	− 0.037
0.4569	− 0.073	0.9217	− 0.019

$V^{(0)} = -0.292;\ V^{(1)} = 0.031;\ V^{(2)} = -0.041;\ \sigma(V^E) = 0.002$

	m-Nitrotoluene(i) + toluene(j)		
0.0729	− 0.087	0.5469	− 0.320
0.1615	− 0.182	0.5908	− 0.307
0.2408	− 0.253	0.6250	− 0.287
0.3108	− 0.293	0.6698	− 0.260
0.3824	− 0.325	0.7315	− 0.219
0.4609	− 0.335	0.7965	− 0.170
0.5106	− 0.328	0.8654	− 0.113

$V^{(0)} = -1.320;\ V^{(1)} = 0.272;\ V^{(2)} = 0.322;\ \sigma(V^E) = 0.003$

	m-Nitrotoluene(i) + o-xylene(j)		
0.0712	− 0.085	0.5299	− 0.286
0.1457	− 0.159	0.5694	− 0.277
0.1956	− 0.204	0.6256	− 0.259
0.2698	− 0.249	0.6912	− 0.230
0.3106	− 0.261	0.7456	− 0.202
0.3895	− 0.284	0.8509	− 0.126
0.4269	− 0.292	0.9456	− 0.049
0.4895	− 0.291		

$V^{(0)} = -1.160;\ V^{(1)} = 0.205;\ V^{(2)} = 0.021;\ \sigma(V^E) = 0.002$

	m-Nitrotoluene(i) + p-xylene(j)		
0.0825	− 0.149	0.4895	− 0.394
0.1290	− 0.211	0.5269	− 0.385
0.1695	− 0.263	0.5896	− 0.357
0.2225	− 0.313	0.6459	− 0.329
0.2895	− 0.362	0.6985	− 0.292
0.3265	− 0.374	0.7896	− 0.219
0.3987	− 0.390	0.8569	− 0.159
0.4562	− 0.397	0.9290	− 0.083

$V^{(0)} = -1.560;\ V^{(1)} = 0.423;\ V^{(2)} = -0.039;\ \sigma(V^E) = 0.002$

	m-Nitrotoluene(i) + m-xylene(j)		
0.0745	− 0.132	0.5749	− 0.437
0.1215	− 0.201	0.6312	− 0.410
0.1895	− 0.280	0.6841	− 0.384
0.2659	− 0.350	0.7215	− 0.364
0.3326	− 0.397	0.7952	− 0.303
0.4016	− 0.425	0.8659	− 0.220
0.4856	− 0.440	0.9564	− 0.081
0.5126	− 0.442		

$V^{(0)} = -1.760;\ V^{(1)} = -0.002;\ V^{(2)} = -0.197;\ \sigma(V^E) = 0.002$

$V^{(n)}$ (n = 0-2) and $\sigma(V^E)$ are in cm³ mol⁻¹

Table 2—Measured H^E values at 308.15K for the various $(i+j)$ mixtures as functions of x_i, the mole fraction of component i; also included are the various $H^{(n)}$ (n = 0-2) parameters alongwith standard deviation $\sigma(H^E)$

x_i	H^E (J mol⁻¹)	x_i	H^E (J mol⁻¹)
	m-Nitrotoluene(i) + benzene(j)		
0.0521	27.1	0.5504	141.1
0.0982	45.6	0.6012	139.2
0.1482	64.6	0.6981	124.2
0.2105	85.1	0.7601	109.5
0.3012	112.1	0.8012	92.2
0.4297	136.6	0.9127	50.3
0.4812	141.3		

$H^{(0)} = 561.2;\ H^{(1)} = 63.67;\ H^{(2)} = -6.33;\ \sigma(H^E) = 1.50$

	m-Nitrotoluene(i) + toluene(j)		
0.0482	22.2	0.5762	147.2
0.1011	47.5	0.6012	144.8
0.1472	68.1	0.7048	125.4
0.2098	93.2	0.7548	106.2
0.3093	125.1	0.8012	90.2
0.4210	148.9	0.9210	40.1
0.4991	152.5		

$H^{(0)} = 610.1;\ H^{(1)} = 10.48;\ H^{(2)} = -115.39;\ \sigma(H^E) = 1.84$

	m-Nitrotoluene(i) + o-xylene(j)		
		0.5068	166.0
0.0610	46.1	0.5912	162.1
0.1398	90.5	0.6574	156.0
0.2088	119.5	0.7271	143.5
0.2946	142.1	0.8062	120.0
0.3512	152.3	0.8918	79.5
0.4688	164.7		

$H^{(0)} = 660.0;\ H^{(1)} = 32.6;\ H^{(2)} = 233.2;\ \sigma(H^E) = 0.607$

	m-Nitrotoluene(i) + p-xylene(j)		
0.0514	35.2	0.4991	142.2
0.1041	60.6	0.5099	143.3
0.1471	80.1	0.6012	135.6
0.2017	101.3	0.6769	122.6
0.2836	124.2	0.7328	113.2
0.3437	135.1	0.8012	93.1
0.4611	140.2	0.9128	49.9

$H^{(0)} = 568.9;\ H^{(1)} = -39.68;\ H^{(2)} = 103.17;\ \sigma(H^E) = 1.43$

	m-Nitrotoluene(i) + m-xylene(j)		
0.0601	28.8	0.5096	128.0
0.1012	47.7	0.6021	124.2
0.1512	65.6	0.6761	115.9
0.2091	84.2	0.7319	104.2
0.2829	102.1	0.8006	88.1
0.3421	112.4	0.8861	75.3
0.4648	126.0	0.9012	51.9

$H^{(0)} = 508.0;\ H^{(1)} = 27.94;\ H^{(2)} = 0.197;\ \sigma(H^E) = 1.47$

$H^{(n)}$ (n = 0-2) and $\sigma(H^E)$ are in J mol⁻¹

where $X^{(n)}$ $(n = 0 - 2)$ are adjustable parameters and x_i is the mole fraction of component i in the mixture. These parameters were evaluated by fitting $X^E(X = V$ or $H)/x_i(1 - x_i)$ data to Eq. 1 by the method of least squares. Such parameters along-with the standard deviations $\sigma(X^E)$ of $X^E(X = V$ or $H)$ are given in Tables 1 and 2. The standard deviation $\sigma(X^E)$ is defined by,

$$\sigma(X^E) = [\Sigma(X^E_{Exptl} - X^E_{Calcd. Eq. 1})^2/(m - p)]^{0.5} \quad \dots (2)$$

(where X^E_{Exptl} is the experimentally measured value and $X^E_{Calcd. Eq. 1}$ is the value calculated from Eq. 1, m is the number of points and p is the number of adjustable parameters in Eq. 1).

Discussion

We are unaware of any V^E or H^E data for the *m*-nitrotoluene (i) + benzene or toluene or *o*- or *p*-or *m*-xylene (j) binary mixtures with which to compare our results. However, while V^E data for various (i + j) mixtures are negative, H^E data are positive over the entire range of compositions for all the mixtures. Further, while V^E data for equimolar composition vary in the order: benzene > *o*-xylene > toluene > *p*-xylene > *m*-xylene, H^E data for equimolar composition vary in the order: *o*-xylene > toluene ≃ *p*-xylene > benzene > *m*-xylene.

At the simplest qualitative level, the present H^E data may be explained if it is assumed that the *m*-nitrotoluene + benzene mixture is characterized by interactions between the π-electron cloud of benzene with the delocalized π-electron cloud over the nitrogen and oxygen atoms[10] (of the nitro group of *m*-nitrotoluene) resulting in the formation of weak *p*-complex[11]. The introduction of CH_3 group in benzene, as in toluene, would then lower the tendency of the toluene to accept the π-electron of the nitro group, so that H^E for *m*-nitrotoluene + toluene mixtures should be more positive than that of *m*-nitrotoluene + benzene mixture. The experimental H^E values for these mixtures support this viewpoint. The introduction of two CH_3 groups in benzene, as in xylenes, would further increase the π-electron density of the aromatic ring suggesting that H^E values for *m*-nitrotoluene + *o*-, + *m*- or *p*-xylene mixtures should be more positive than that for the *m*-nitrotoluene + toluene mixture. This is indeed true for the *m*-nitrotoluene + *o*-xylene mixture only; H^E data for the *m*-nitrotoluene + *p*-xylene and + *m*-xylene mixtures, however, suggest that for these mixtures some interactions other than those mentioned above are important.

The V^E and H^E data of the present mixtures were then analysed in terms of an approach[12,13]

that utilizes the graph theoretical connectivity parameters of the third degree[14], $^3\xi$, of the constituents of these mixtures.

Since the $^3\xi$ parameters of the constituents of (i + j) mixtures depend on the valencies of the various verticies in their molecular graphs, the addition of j to i would cause structural changes in their topologies so that V^E of such (i + j) mixtures would reflect changes in the topologies of i and or j. With assumption of no particular molecular state for i and j, V^E according to this approach[13] is given by Eq. 3,

$$V^E = \alpha_{ij} [\Sigma(x_i(\xi_i)_m)^{-1} - \Sigma x_i/^3\xi_i] \quad \dots (3)$$

$(^3\xi_i)_m$ and $^3\xi_i$ in Eq. 3 denote, respectively, the $^3\xi$ values of i in mixture and in the pure state, x_i is the mole fraction of i, $^3\xi$ etc. are defined[14] by Eq. 4,

$$^3\xi = \sum_{m < n < 0 < p} (\delta^v_m \delta^v_n \delta^v_0 \delta^v_p)^{-0.5} \quad \dots (4)$$

and have the same significance as described elsewhere[13]. Further, δ^v_m etc. in Eq. 4 reflect explicitly[14] the valency of the mth etc. vertex in the molecular graph of i in forming bonding and are related[15,16] to the maximum valency, Z_m, and the number of hydrogen atoms, h_m attached to the mth etc. vertex by the relation $\delta^v_m = Z_m - h_m$. α_{ij} in Eq. 3 is a constant, characteristic of (i + j) mixture.

Again, as the degree of association in j is not known with certainty and as no theoretical method is available to evaluate $(^3\xi_i)_m$ of i in the (i + j) mixtures, we regard $(^3\xi_i)_m$, $(^3\xi_j)_m$, $^3\xi_i$ and $^3\xi_j$ as adjustable parameters and have evaluated them by fitting experimental data to Eq. 3. Only those $(^3\xi_i)_m$ and $^3\xi_i$ values were retained that best reproduced the experimental V^E data, i.e., for which the variance of fit, ρ, defined by $\rho = [\Sigma(V_{exptl.} - V_{calcd.})^2/(Q-P)]^{0.5}$, (where (Q-P) is the number of degrees of freedom) was minimum. Such $(^3\xi_i)_m$ and $(^3\xi_i)$ values (i = i or j), together with V^E values calculated in the manner at various x_i are recorded in Table 3.

A number of structures were then assumed for the i and j in the pure and in the (i + j) mixture states and their $^3\xi'$ values evaluated from structural considerations. These $^3\xi'$ values were next compared with the corresponding values obtained from Eq. 3 and any structure or a combination of structures that yielded value that compared well with the corresponding $^3\xi$ value was taken to be a sufficiently representative structure of that component.

Table 3—Comparison of V^E and H^E values (calculated from appropriate equations (see text) with the corresponding experimental values at 308.15K for the various i + j mixtures as functions of x_i, mole fraction of i; also included are the various interaction energies, x_{ij} parameters

Property	x_i							
	0.1	0.2	0.3	0.4	0.6	0.7	0.8	0.9
				m-Nitrotoluene(i) + benzene(j)				
V^E (exptl)	− 0.310	− 0.052	− 0.065	− 0.072	− 0.069	− 0.060	− 0.046	− 0.026
V^E (calcd)	− 0.300	− 0.053	− 0.067	− 0.074	− 0.068	− 0.058	− 0.042	− 0.023
H^E (exptl)	60.0	100.7	126.3	139.4	135.6	119.6	93.2	54.3
H^F (calcd)	44.8	82.5	112.6	133.8	145.6	133.3	106.5	62.9

$^3\xi_i = (^3\xi_i)_m = 1.022, \ ^3\xi_j = (^3\xi_j)_m = 0.666, \ \alpha_{ij} = 1.324 \ cm^3 \ mol^{-1}; \ X_{ij} = 479.97 \ J \ mol^{-1}$

				m-Nitrotoluene(i) + toluene(j)				
V^E (exptl)	− 0.120	− 0.219	− 0.289	− 0.327	− 0.301	− 0.244	− 0.167	− 0.081
V^E (calcd)	− 0.119	− 0.218	− 0.284	− 0.319	− 0.305	− 0.261	− 0.194	− 0.106
H^E (exptl)	47.5	39.9	123.3	144.8	145.8	125.1	92.0	49.1
H^E (calcd)	51.5	92.4	132.5	143.7	149.1	133.0	103.4	59.3

$^3\xi_i = (^3\xi_i)_m = 1.0122, \ ^3\xi_j = (^3\xi_j)_m = 0.84, \ \alpha_{ij} = 31.92 \ cm^3 \ mol^{-1}; \ X_{ij} = 558.11 \ J \ mol^{-1}$

				m-Nitrotoluene(i) + o-xylene(j)				
V^E (exptl)	− 0.118	− 0.204	− 0.260	− 0.288	− 0.268	− 0.226	− 0.165	− 0.088
V^E (calcd)	− 0.092	− 0.163	− 0.228	− 0.269	− 0.288	− 0.261	− 0.207	− 0.119
H^E (exptl)	70.5	115.9	143.7	159.1	162.2	149.2	122.2	75.2
H^E (calcd)	68.8	102.6	148.7	164.0	153.2	129.8	95.8	52.3

$^3\xi_i = (^3\xi_i)_m = 1.011, \ ^3\xi_j = (^3\xi_j)_m = 1.426, \ \alpha_{ij} = 11.82 \ cm^3 \ mol^{-1}; \ X_{ij} = 795.46 \ J \ mol^{-1}$

				m-Nitrotoluene(i) + m-xylene(j)				
V^E (exptl)	− 0.170	− 0.293	− 0.376	− 0.424	− 0.426	− 0.380	− 0.297	− 0.170
V^E (calcd)	− 0.149	− 0.269	− 0.359	− 0.416	− 0.429	− 0.381	− 0.281	− 0.169
H^E (exptl)	47.7	82.6	106.7	121.3	124.0	111.4	88.1	51.9
H^E (calcd)	45.7	81.2	106.6	121.9	121.9	106.7	81.3	45.8

$^3\xi_i = (^3\xi_i)_m = 1.0122, \ ^3\xi_j = (^3\xi_j)_m = 1.174, \ \alpha_{ij} = 107.32 \ cm^3 \ mol^{-1}; \ X_{ij} = 507.44 \ J \ mol^{-1}$

				m-Nitrotoluene(i) + p-xylene(j)				
V^E (exptl)	− 0.173	− 0.292	− 0.364	− 0.395	− 0.354	− 0.293	− 0.211	− 0.112
V^E (calcd)	− 0.134	− 0.240	− 0.319	− 0.378	− 0.379	− 0.336	− 0.260	− 0.148
H^E (exptl)	45.5	83.3	112.3	131.6	137.7	123.0	95.6	54.8
H^E (calcd)	53.9	94.6	122.6	138.3	134.8	116.5	87.7	48.7

$^3\xi_i = (^3\xi_i)_m = 1.10, \ ^3\xi_j = (^3\xi_j)_m = 1.25, \ \alpha_{ij} = 114.71 \ cm^3 \ mol^{-1}; \ X_{ij} = 607.58 \ J \ mol^{-1}$

In the present mixtures, we assumed that m-nitrotoluene can exist as molecular entities I and II. The $^3\xi'$ values for molecular entities I-II were then calculated to be 1.02 and 2.589 respectively. Since $^3\xi_i$ values of m-nitrotoluene in the m-nitrotoluene + benzene, + toluene, + o-, + p- and + m-xylene mixtures are 1.022, 1.012, 1.011, 1.0122 and 1.10 respectively (Table 3), they suggest that m-nitrotoluene exists as a monomer. Further, $^3\xi'$ values of 0.666, 0.84, 1.426, 1.174 and 1.25 for benzene, toluene, + o-, + p- and m-xylenes (Table 3) suggest that they exist as

monomers. Further, if m-nitrotoluene in its binary mixture with aromatic hydrocarbons is assumed to exist as a p-complex[11] (molecular entity III), then it should have a $^3\xi'$ value of 1.308. The $^3\xi$ values of 1.01-1.11 (Table 3) then suggest that these mixture contain molecular entity III. In evaluating $^3\xi'$ for molecular entities II and III, we assigned[12] $\delta^v(\pi = 1)$ and that the π-electron cloud of aromatic hydrocarbons is involved in interaction with the π-electron cloud over nitrogen and oxygen atoms in m-nitrotoluene.

To understand the energetics of the various in-

$(^3\xi' = 1.02)$

(I)

$(^3\xi' = 2.589)$

(II)

R=H or CH_3

$(^3\xi' = 1.308)$

(III)
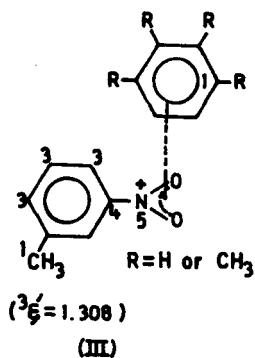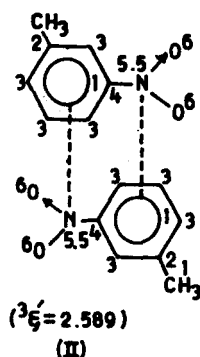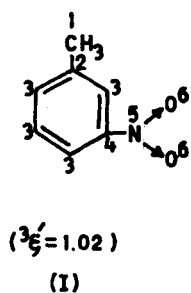
teractions that characterize these binary mixtures, the mixture formation may then be visualized to occur as follows:

Since *m*-nitrotoluene in the "pure state" in the present (i+j) mixtures exists as a monomer, the mixtures *m*-nitrotoluene (i) + benzene, + toluene, + *o*- , + *p*- or *m*-xylene (j) may be assumed to involve the formation of unlike i-j contacts between i and j. Thus, if X_{ij} is the enthalpy interaction parameter of unlike i-j contact formation then change in H^E would be given[17,18] by

$$H^E = x_i S_j X_{ij} \qquad \cdots (5)$$

where S_j is the surface fraction of j involved in the formation of i-j contacts. But S_j is defined[17] by,

$$S_j = x_j V_j / (x_i V_i + x_j V_j) \qquad \cdots (6)$$

so that

$$H^E = x_i x_j V_j X_{ij} / (x_i V_i + x_j V_j)$$

Further, $V_j / V_i = {}^3\xi_i / {}^3\xi_j$

$$H^E = x_i x_j ({}^3\xi_i / {}^3\xi_j) X_{ij} / [x_i + x_j ({}^3\xi_i / {}^3\xi_j)] \qquad \cdots (7)$$

Eq. 7 contains only one unknown parameter (X_{ij}) which was determined from H^E $(x_i = 0.5)$ data

and was subsequently used to determine H^E values at other compositions of the mixture. Such H^E values are recorded as $H^E_{(Calcd)}$ in Table 3 and are compared with the corresponding experimental values. Examination of Table 3 reveals that H^E values evaluated from Eq. 7 are in good agreement with the experimental values and that X_{ij} values vary in the order: *o*-xylene > *p*-xylene > toluene > *m*-xylene > benzene. This lends additional support to the qualitative analysis of the present V^E and H^E data.

Acknowledgement

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