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Molecular interactions in binary mixtures containing *o*-toluidine

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Abstract

Molar excess volumes, V^E and molar excess enthalpies, H^E of binary mixtures formed by *o*-toluidine (*i*) and benzene or toluene or *o*- or *p*- or *m*-xylene (*j*) mixtures have been determined dilatometrically and calorimetrically as a function of composition at 308.15 K. The observed data have been estimated using graph theory (which in turn depends upon the topology of the constituents in pure and mixed states). Predicted values compare well with their corresponding experimental values. IR studies lend further credence to the nature and extent of interaction of the proposed structures of molecular species in these mixtures.

Keywords: *o*-Toluidine; Molar excess enthalpies, H^E; Molar excess volumes, V^E; Connectivity parameter of third degree, $^3\xi$; Interaction parameters, χ

1. Introduction

In our systematic investigations of thermodynamic properties of mixtures, we have reported [1–8] molar excess volumes, molar excess enthalpies and excess isentropic compressibilities of binary and ternary mixtures containing constituents differing in shape, size and polarity. The analysis of the observed data with topology of the constituents of the mixtures has provided knowledge about the molecular interactions and the nature of state of components in pure and mixture state. In the present paper continuing with our study, we report molar excess volumes and molar excess enthalpies of binary mixtures formed by *o*-toluidine with aromatic hydrocarbons at 308.15 K.

2. Experimental

o-Toluidine [Fluka], benzene, toluene and *o*-, *p*- and *m*-xylenes (AR grade) were purified by standard methods [9]. The purities of the samples were checked by measuring their densities at 298.15 ± 0.01 K and these agree to within ±0.05 kg m^{-3} with their corresponding literature values [9].

Molar excess volumes, V^E for the binary $(i+j)$ mixtures were determined in a V-shaped dilatometer that has been described elsewhere [10]. The uncertainties in the measured V^E values are about 0.5%.

Samples for IR studies were prepared by mixing (*i*) and (*j*) components in 1:1 (w/w) ratio and their IR spectra were recorded on PerkinElmer-Spectrum RX-I, FTIR spectrometer.

Molar excess enthalpies, H^E for binary mixtures were measured by two-drop calorimeter (model, 4600) supplied by the Calorimetry Sciences Corporation (CSC), USA as described below.

2.1. Construction

The main parts of the two-drop calorimeter (shown in Fig. 1) includes; the access door, the access door latch, the computer interface cable, the reference and sample chambers, the syringe, the syringe-retaining clip, the plunger retaining thumb screw and pressure sensor needle. It also includes a reaction vessel (Fig. 2), a rapid responding thermoelectric device (TED) as the heat measuring sensor, an electrical heater for calibration and burette system for addition of sample. The heat flow between the reaction vessel and a constant temperature block is detected by TED sensor, amplified and converted from an analogue signal to a digital signal in data collection system. The temperature of the constant temperature block is actively controlled using block control TEDs.

2.2. Calibration of the calorimeter

The calorimeter is calibrated at desired temperature by clicking calibrate button in the software. Clicking this button

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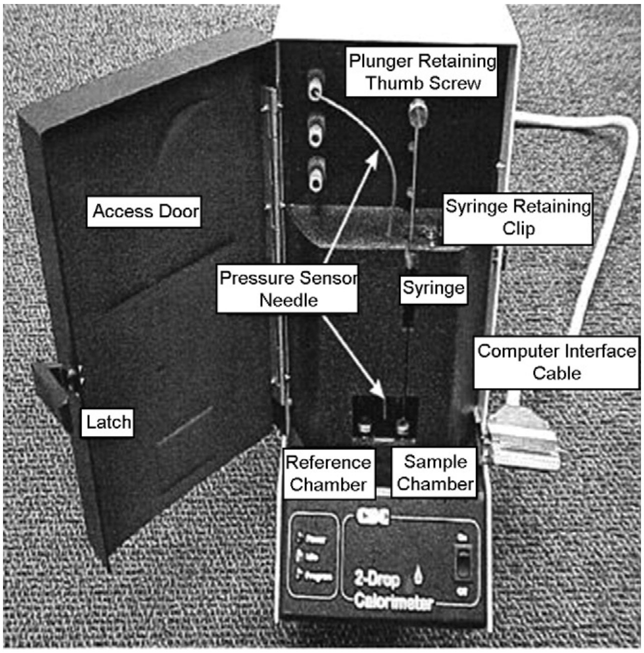


Fig. 1. The main parts of two-drop calorimeter.

performs a calibration of the calorimeter sensors using a built-in resistance calibration heater. At the end of the calibration, calibration factors (CF_1–CF_4) shown in the calibration table (provided in the software) are then employed in general instrument setting.

2.3. Working

Take a glass vial and pour known amount of liquid (*i*) with micro-syringe (supplied by CSC, capacity 50–250 μl). Also put 3 mm × 6 mm magnetic stirrer in it. Crimp a liner and seal onto vial and place it in the sample chamber. Load another vial with same amount of liquid (as taken in sample chamber vial) again crimp a liner and seal onto vial and keep it in the reference chamber. Now, take known amount of liquid (*j*) in the micro-syringe and clamp it in the syringe-retaining clip. Close and latch the access door.

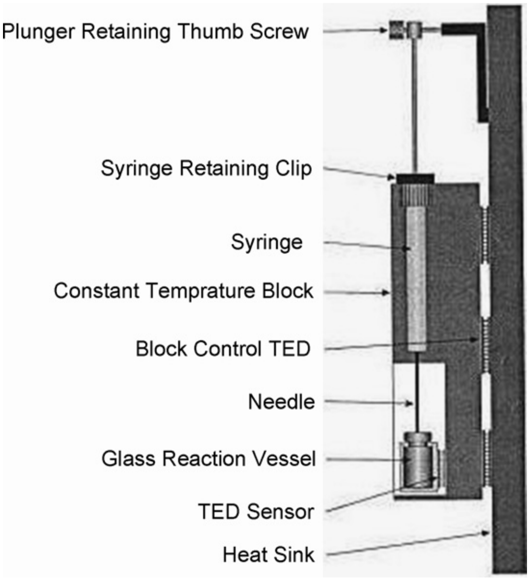


Fig. 2. Reaction vessel.

Desired experimental temperature is then set up by clicking on the down arrow next to temperature in the experimental set-up tab. The desired temperature attained in the set-up is indicated by a constant line in temperature scale. After the temperature is set; the required information on the experimental set-up screen is filled. The information involves, (i) injection time of liquid (which is 10 min, when a heat pulse is run before the injection); (ii) the heat pulse before injection (after 1 min with a size roughly same as we expect for ($i + j$) binary mixture); and (iii) heat pulse after injection (after 25 min). Typically, calibration heat pulses should be approximately the same size as the heat expected from the chemical reaction.

By pressing the appropriate run button on the toolbar, programme gets started and after certain selected duration, liquid (*j*) from the micro-syringe is then injected into liquid (*i*) placed in sample chamber. Such injection of liquid is controlled by software provided by CSC. After an experiment is finished the data are automatically transferred to the experimental results tab. Results involve, (i) pre-injection calibration heater pulse area which shows the integrated area of the calibration heater pulse that occurred before injection; (ii) injection area which reflects the integrated area of the chemical injection peak; (iii) post-injection calibration heat pulse area of the calibration heat pulse that occur after the injection; and (iv) temperature at which the experiment was run at.

The injection area (in cal) is then calculated by software provided by CSC. This area represents molar excess enthalpy H^E. An injection area (−0.0438 cal) evaluated by software for 1,3-dioxolane (*i*) + benzene (*j*) mixture at $x_i = 0.5608$ is shown in Fig. 3.

The reliability of the instrument was checked by measuring the H^E values for 1,3-dioxolane (*i*) + benzene (*j*) mixture at 298.15 K and they agree (Fig. 4) with the corresponding experimental values [11]. The uncertainty in measuring H^E values is 1%.

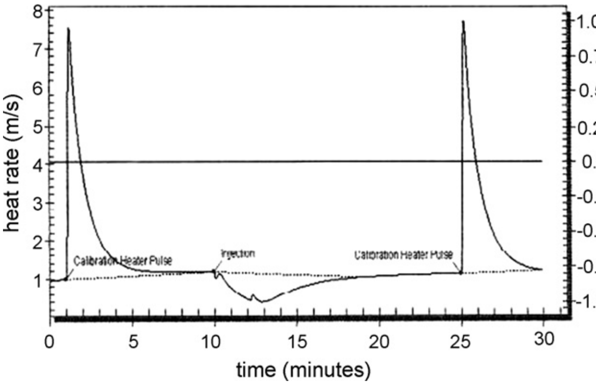


Fig. 3. Injection area evaluated by software for 1,3-dioxolane (*i*) + benzene (*j*) ($x_i = 0.5608$) at 298.15 K.

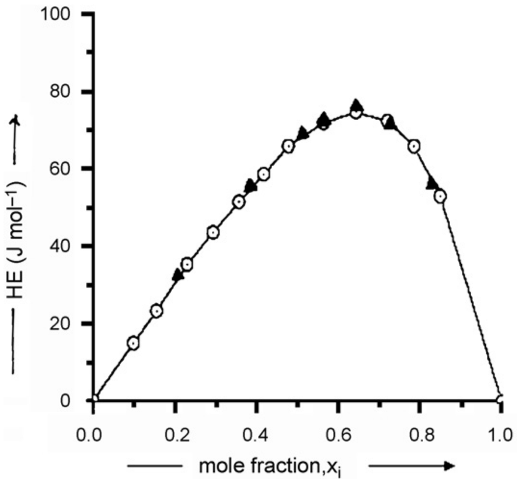


Fig. 4. Molar excess enthalpy, H^E of 1,3-dioxolane (i) + benzene (j) mixture at 298.15 K. (◯) Literature value; (▲) this work.

3. Results

Molar excess volumes, V^E and molar excess enthalpies, H^E, data for o-toluidine (i) + benzene or toluene or o- or p- or m-xylene (j) mixtures have been determined as a function of composition at 308.15 K (recorded in Tables 1 and 2 and plotted in Figs. 5 and 6) were expressed as

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

where x_i is the mole fraction of component (i) and $X^{(n)}$ (n = 0–2) are parameters characteristic of (i + j) binary mixtures. These parameters were determined by fitting X^E data to Eq. (1) by least square optimization and are recorded together with the standard

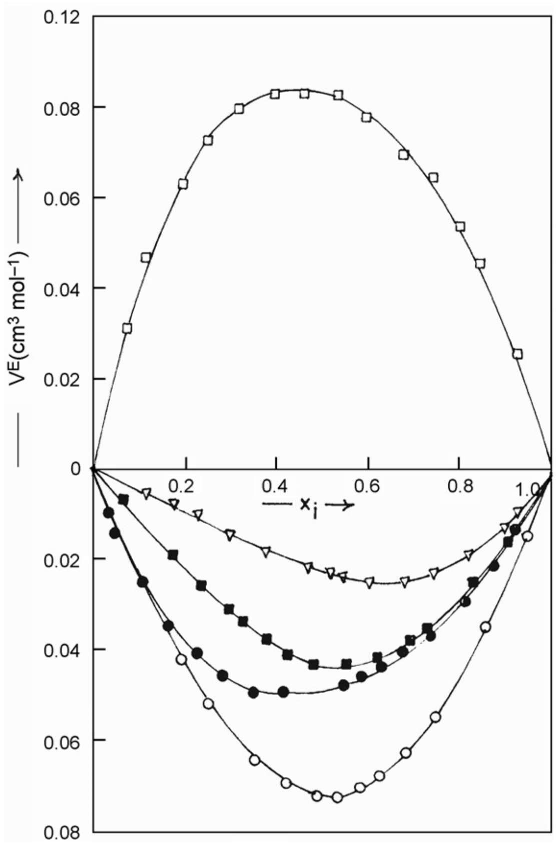


Fig. 5. Molar excess volumes, V^E for o-toluidine (i) + benzene (j) (●); o-toluidine (i) + toluene (j), (◯); o-toluidine (i) + o-xylene (j), (□); o-toluidine (i) + p-xylene (j), (■); o-toluidine (i) + m-xylene (i) (△).

Table 1
Measured molar excess volumes, V^E data for the various (i + j) mixtures as a function of mole fraction, x_i, of component (i) at 308.15 K

x_i	V^E (cm^3 mol^{-1})	x_i	V^E (cm^3 mol^{-1})
o-Toluidine (i) + benzene (j)[a]			
0.0540	−0.014	0.5962	−0.046
0.1710	−0.035	0.6263	−0.043
0.2274	−0.041	0.6805	−0.041
0.2866	−0.046	0.7432	−0.036
0.3557	−0.049	0.8164	−0.029
0.4203	−0.049	0.8822	−0.021
0.5564	−0.047	0.9315	−0.013
o-Toluidine (i) + toluene(j)[b]			
0.0426	−0.010	0.5375	−0.072
0.1067	−0.025	0.5873	−0.070
0.1952	−0.042	0.6268	−0.068
0.2576	−0.052	0.6923	−0.062
0.3571	−0.064	0.7534	−0.054
0.4265	−0.069	0.8642	−0.034
0.4989	−0.072	0.9483	−0.014
o-Toluidine (i) + o-xylene(j)[c]			
0.0687	0.031	0.5315	0.083
0.1145	0.047	0.5886	0.078
0.1876	0.064	0.6742	0.070
0.2425	0.073	0.7319	−0.064
0.3113	0.080	0.7982	0.054
0.3903	0.083	0.8382	0.046
0.4507	0.083	0.9214	0.026
o-Toluidine (i) + p-xylene(j)[d]			
0.0712	−0.007	0.4912	−0.043
0.1776	−0.019	0.5552	−0.043
0.2384	−0.026	0.6283	−0.042
0.2982	−0.031	0.6998	−0.038
0.3343	−0.034	0.7413	−0.035
0.3901	−0.038	0.8448	−0.024
0.4345	−0.041	0.9103	−0.015
o-Toluidine (i) + m-xylene(j)[e]			
0.1887	−0.008	0.5432	−0.023
0.2324	−0.010	0.6113	−0.024
0.2976	−0.014	0.6876	−0.023
0.3246	−0.015	0.7418	−0.022
0.3843	−0.018	0.8219	−0.018
0.4706	−0.021	0.8972	−0.012
0.5180	−0.023	0.9314	−0.009

[a] $V^{(0)} = -0.195$; $V^{(1)} = 0.040$; $V^{(2)} = -0.065$; $\sigma(V^{(E)}) = 0.001$ cm^3 mol^{-1}.
[b] $V^{(0)} = -0.287$; $V^{(1)} = -0.016$; $V^{(2)} = 0.018$; $\sigma(V^{(E)}) = 0.001$ cm^3 mol^{-1}.
[c] $V^{(0)} = 0.328$; $V^{(1)} = -0.066$; $V^{(2)} = 0.129$; $\sigma(V^{(E)}) = 0.001$ cm^3 mol^{-1}.
[d] $V^{(0)} = -0.171$; $V^{(1)} = -0.039$; $V^{(2)} = 0.036$; $\sigma(V^{(E)}) = 0.001$ cm^3 mol^{-1}.
[e] $V^{(0)} = -0.089$; $V^{(1)} = -0.056$; $V^{(2)} = 0.001$; $\sigma(V^{(E)}) = 0.001$ cm^3 mol^{-1}.

Table 2
Measured molar excess enthalpies, H^E values for the various $(i+j)$ mixtures as a function of mole fraction, x_i, of component (i) at 308.15 K

x_i	H^E (J mol^{-1})	x_i	H^E (J mol^{-1})
o-Toluidine (i) + benzene(j)[a]			
0.0543	44.1	0.5159	444.7
0.1097	103.1	0.6015	424.8
0.1883	197.8	0.6999	355.7
0.2657	289.4	0.7564	297.6
0.3119	337.8	0.8008	289.6
0.3923	403.8	0.8580	170.7
0.4454	431.1	0.9110	102.1
o-Toluidine (i) + toluene(j)[b]			
0.0773	58.1	0.5661	457.9
0.1557	138.2	0.6339	447.7
0.2090	197.8	0.6983	415.7
0.2776	274.3	0.7380	385.0
0.3393	337.1	0.7997	257.2
0.4009	389.9	0.8561	247.1
0.4713	433.6	0.9222	142.6
o-Toluidine (i) + *o*-xylene(j)[c]			
0.0670	43.6	0.5059	437.1
0.1314	101.7	0.5897	454.4
0.1997	172.8	0.6365	449.0
0.2457	222.6	0.6913	427.7
0.3134	293.7	0.7412	394.0
0.3875	362.4	0.8013	334.9
0.4345	398.2	0.9014	191.9
o-Toluidine (i) + *p*-xylene(j)[d]			
0.0548	65.5	0.5113	478.4
0.1163	132.4	0.5778	512.6
0.1873	203.9	0.6442	529.7
0.2460	260.2	0.7013	525.8
0.3007	310.7	0.7776	484.7
0.3663	368.8	0.8417	319.4
0.4357	425.6	0.9333	217.6
o-Toluidine (i) + *m*-xylene(j)[e]			
0.0688	67.7	0.5008	454.4
0.1391	139.1	0.5693	481.4
0.1787	179.6	0.6457	488.2
0.2661	267.6	0.7315	458.8
0.3277	326.0	0.8007	400.0
0.3907	380.3	0.8559	326.5
0.4477	422.6	0.9170	213.8

[a] $H^{(0)} = 1776.0$; $H^{(1)} = 176.4$; $H^{(2)} = -956.3$; $\sigma(H^{(E)}) = 4.4$ J mol^{-1}.
[b] $H^{(0)} = 1781.2$; $H^{(1)} = 693.7$; $H^{(2)} = -533.3$; $\sigma(H^{(E)}) = 4.6$ J mol^{-1}.
[c] $H^{(0)} = 1738.8$; $H^{(1)} = 850.0$; $H^{(2)} = -407.3$; $\sigma(H^{(E)}) = 4.5$ J mol^{-1}.
[d] $H^{(0)} = 1885.3$; $H^{(1)} = 1285.6$; $H^{(2)} = 660.8$; $\sigma(H^{(E)}) = 5.3$ J mol^{-1}.
[e] $H^{(0)} = 1815.8$; $H^{(1)} = 1038.4$; $H^{(2)} = 182.7$; $\sigma(H^{(E)}) = 4.9$ J mol^{-1}.

deviation, $\sigma(X^E)$ defined by

$$\sigma(X^E) = \left[\frac{\sum[X^E_{\text{exptl}} - X^E_{\text{calc.}}]^2}{m-n}\right]^{0.5} \tag{2}$$

where m is the number of data points and n is the number of adjustable parameters of Eq. (1) in Tables 1 and 2.

3.1. Discussion

We are unaware of any V^E and H^E data at 308.15 K with which to compare our results. The H^E values are positive over the whole range of mixtures. However, V^E values for *o*-toluidine (i) + *o*-xylene (j) binary mixtures are positive, while those for *o*-toluidine (i) + benzene or toluene or *p*- or *m*-xylene (j) mixtures are negative over entire composition range. V^E data for an equimolar mixture vary in the order: *o*-xylene > *m*-xylene > *p*-xylene > benzene > toluene; H^E data vary as *p*-xylene > *m*-xylene > toluene ≅ *o*-xylene > benzene.

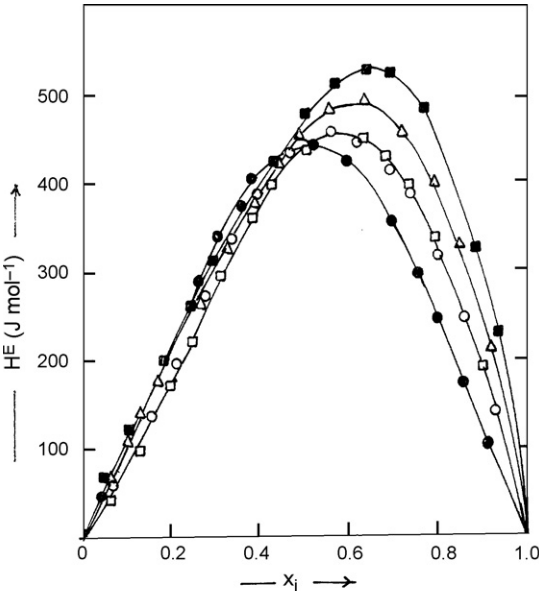


Fig. 6. Molar excess enthalpies, H^E for *o*-toluidine (i) + benzene (j), (●); *o*-toluidine (i) + toluene (j), (○); *o*-toluidine (i) + *o*-xylene (j), (□); *o*-toluidine (i) + *p*-xylene (j), (■); *o*-toluidine (i) + *m*-xylene (j), (△).

The observed V^E and H^E data for these mixtures can qualitatively be explained if it be assumed that: (i) *o*-toluidine is an associated molecular entity; (ii) there is interaction between hydrogen atom of *o*-toluidine (i) and π-electron cloud of aromatic ring of benzene, toluene and *o*- or *p*- or *m*-xylenes (j) to form weak *p*-complex [12]; (iii) interactions between (i) and (j) components of $(i+j)$ mixture then weaken *i*–*i* interactions which leads to its depolymerization; (iv) monomers of (i) and (j) then under goes specific interaction to from *i*:*j* molecular entity; (v) there is steric repulsion between *o*-toluidine and xylenes due to the presence of bulky –CH_3 group.

The positive values of H^E for *o*-toluidine (i) + benzene (j) mixtures suggest that contribution to H^E values due to factor (iii) far outweigh the contribution due to factors (ii) and (iv). The introduction of one –CH_3 group into benzene (as in toluene) would increase the π-electron donating capacity of benzene and hence there would be strong interaction between hydrogen atom of *o*-toluidine and π-electron cloud of aromatic ring of toluene. This is supported by less positive H^E values for *o*-toluidine + toluene than for *o*-toluidine + benzene mixtures. When two –CH_3 group are introduced (as in xylenes), there is further increase π-electron donating capacity of ring and thus interaction between *o*-toluidine and xylene would be stronger than that in case of toluene; however at the same time there exist a steric hindrance between *o*-toluidine and xylene molecule due to the presence of two methyl groups of xylenes. Higher H^E values for *o*-toluidine (i) + *o*- or *p*- or *m*-xylene mixtures than

Table 3
Comparison of V^E and H^E values calculated from Eqs. (4) and (9) with their corresponding experimental values at 308.15 K along with various $(^3\xi_i)$ and $(^3\xi_i)_m$ ($i = i$ or j); α_{ij} parameters for the various ($i + j$) mixtures as a function of, x_i, mole fraction of component (i)

	x_i								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
o-Toluidine (i) + benzene (j)[a]									
V^E(exptl)	−0.025	−0.039	−0.046	−0.049	–	−0.045	−0.039	−0.031	−0.019
V^E(graph)	−0.021	−0.035	−0.044	−0.048	–	−0.044	−0.035	−0.027	−0.015
H^E(exptl)	81.8	193.9	302.2	381.3	–	398.3	331.8	227.8	107.2
H^E(graph)	125.9	233.2	319.3	–	–	418.1	384.0	307.7	247.5
o-Toluidine (i) + toluene (j)[b]									
V^E(exptl)	−0.025	−0.044	−0.059	−0.068	–	−0.069	−0.059	−0.046	−0.026
V^E(graph)	−0.029	−0.050	−0.064	−0.067	–	−0.068	−0.057	−0.043	−0.024
H^E(exptl)	79.6	187.7	297.9	389.1	–	455.7	414.4	320.9	179.5
H^E(graph)	101.4	207.0	306.4	–	–	465.3	439.7	359.4	215.7
o-Toluidine (i) + *o*-xylene (j)[c]									
V^E(exptl)	−0.042	−0.066	−0.078	−0.083	–	−0.077	−0.068	−0.053	−0.032
V^E(graph)	−0.031	−0.053	−0.071	−0.077	–	−0.078	−0.067	−0.052	−0.027
H^E(exptl)	71.8	173.1	280.1	372.6	–	454.2	422.9	336.3	194.2
H^E(graph)	92.4	187.4	280.3	–	–	478.2	481.5	424.7	278.9
o-Toluidine (i) + *p*-xylene (j)[d]									
V^E(exptl)	−0.010	−0.021	−0.031	−0.039	–	−0.042	−0.038	−0.029	−0.016
V^E(graph)	−0.014	−0.026	−0.034	−0.040	–	−0.043	−0.038	−0.029	−0.017
H^E(exptl)	115.2	216.3	310.1	397.1	–	520.5	526.1	463.1	300.1
H^E(graph)	91.7	195.5	301.1	–	–	510.4	499.7	423.1	263.0
o-Toluidine (i) + *m*-xylene (j)[e]									
V^E(exptl)	−0.004	−0.009	−0.014	−0.019	–	−0.024	−0.023	−0.019	−0.012
V^E(graph)	−0.007	−0.014	−0.018	−0.021	–	−0.022	−0.020	−0.015	−0.009
H^E(exptl)	99.2	201.4	300.2	387.7	–	487.4	474.7	400.7	248.7
H^E(graph)	94.5	224.9	298.4	–	–	485.5	469.8	393.3	241.8

α_{ij} is in cm^3 mol^{-1}; χ'_{ij} and χ_{12} are in J mol^{-1}.

[a] $(^3\xi_i) = (^3\xi_i)_m = 1.010$; $(^3\xi_i) = (^3\xi_i)_m = 0.666$; $\alpha_{ij} = 0.952$; $\chi'_{ij} = 712.2$; $\chi_{12} = 63.2$.

[b] $(^3\xi_i) = (^3\xi_i)_m = 1.102$; $(^3\xi_i) = (^3\xi_\mathrm{i})_m = 0.840$; $\alpha_{ij} = 3.830$; $\chi'_{ij} = 1375.7$; $\chi_{12} = -420.1$.

[c] $(^3\xi_i) = (^3\xi_i)_m = 1.601$; $(^3\xi_i) = (^3\xi_i)_m = 1.426$; $\alpha_{ij} = 37.273$; $\chi'_{ij} = 800.9$; $\chi_{12} = 97.9$.

[d] $(^3\xi_i) = (^3\xi_i)_m = 1.001$; $(^3\xi_i) = (^3\xi_i)_m = 1.250$; $\alpha_{ij} = 0.874$; $\chi'_{ij} = 1284.2$; $\chi_{12} = -460.3$.

[e] $(^3\xi_i) = (^3\xi_i)_m = 1.001$; $(^3\xi_i) = (^3\xi_i)_m = 1.174$; $\alpha_\mathrm{ij} = 3.729$; $\chi'_{ij} = 1244.1$; $\chi_{12} = -371.1$.

those for *o*-toluidine (i) + toluene or benzene (j) mixtures this suggest that contribution to H^E due to repulsion is more than that of interaction.

Negative values of V^E suggest interaction between *o*-toluidine and benzene or toluene or *p*-xylene or *m*-xylene mixtures. V^E is also a measure of assessing the compactness due to molecular arrangement of the constituents of mixtures. Lower values of V^E (more negative for *o*-toluidine + benzene or toluene mixture than those for *o*-toluidine + *p*-xylene or *m*-xylene mixtures) suggest that benzene or toluene gives more packed arrangement while *p*-xylene or *m*-xylene give relatively least packed arrangement in *o*-toluidine. However positive V^E values of *o*-toluidine (i) + *o*-xylene (j) mixtures suggest the *o*-toluidine and xylene are arranged in such a manner which leads to increase in volume and hence positive values of V^E.

4. Topology of the constituents of the mixtures and results

According to graph theory, if atoms in a structural formula of a molecule are represented by colored points and bonds joining

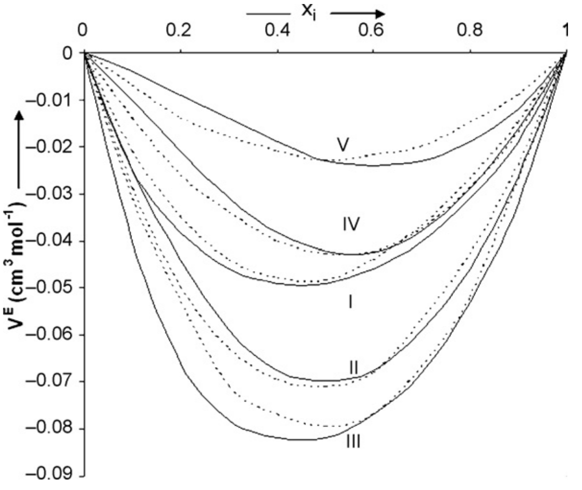
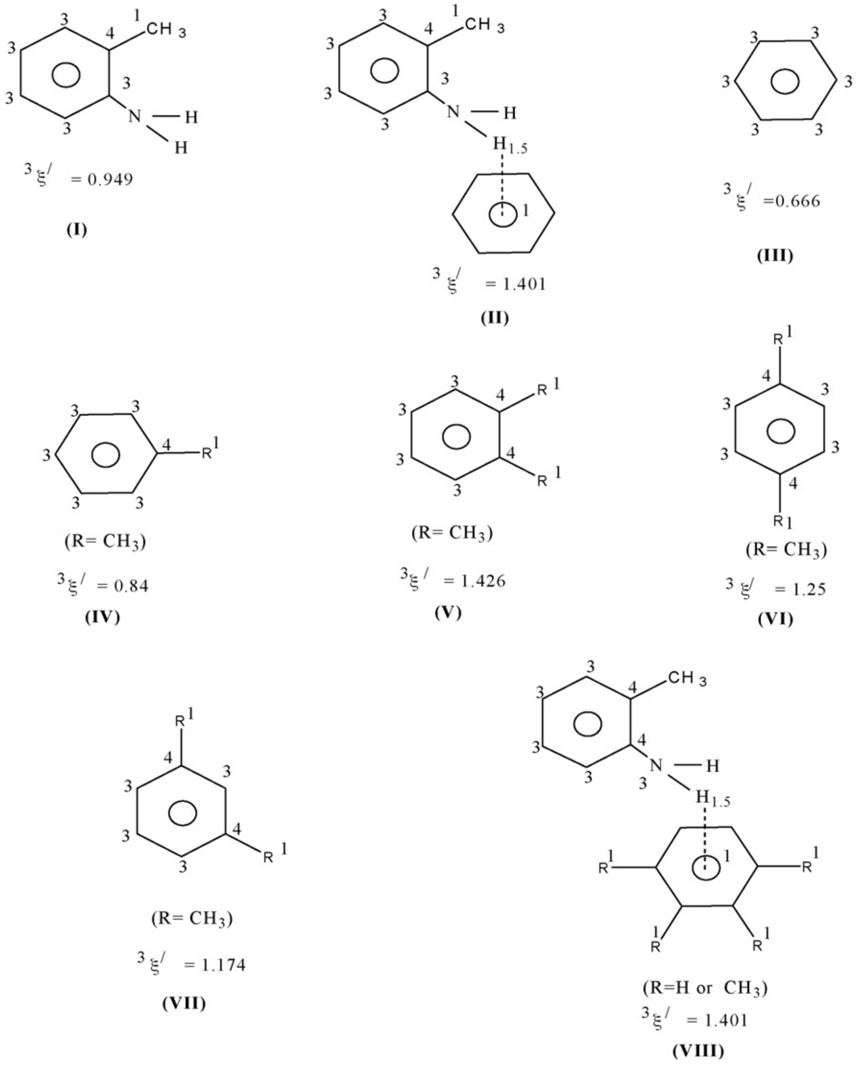


Fig. 7. Molar excess volumes, V^E at 308.15 K of (I) *o*-toluidine (i) + benzene (j); (II) *o*-toluidine (i) + toluene (j); (III) *o*-toluidine (i) + *o*-xylene (j); (IV) *o*-toluidine (i) + *p*-xylene (i); (V) *o*-toluidine (i) + *m*-xylene (j) mixtures. —: Experimental; – – –: graph theory.



Scheme 1. Connectivity parameters of various molecular entities.

them by lines, the resulting graph describes the topology of a molecule which in turn provides total information contained in that molecule [13–17]. If δ^v_m, δ^v_n, δ^v_o, etc. represent the degree of m, n, etc., vertices of the graph of a molecule, then connectivity parameter of third degree, is defined [18] by

$$^3\xi = \sum_{m<n<o<p} (\delta^v_m \delta^v_n \delta^v_o \delta^v_p)^{0.5} \qquad (3)$$

where δ^v_m, δ^v_n, δ^v_o, etc., is related to maximum valency, Z_m and number of hydrogen atoms, h_m attached to mth vertex by relation $\delta^v_m = Z_m - h_m$.

Molar excess volumes, V^E is packing effect, so the addition of benzene or toluene or *o*- or *p*- or *m*-xylenes (j) to *o*-toluidine (i) would cause change in topology of (j) or (i). Thus it would be of interest to analyze the V^E data of ($i+j$) mixtures in terms of graph theory [19], that employs the concept of the third degree. According to this approach, V^E is given as [19]

$$V^E = \alpha_{ij}\left\{\sum_{i=i}^{j}[x_i(^3\xi_i)_m]^{-1} - \sum_{i=i}^{j} x_i(^3\xi_i)^{-1}\right\} \qquad (4)$$

where x_i is the mole fraction of component (i) and ($^3\xi_i$) ($i = i$ or j) and ($^3\xi_i)_m$ ($i = i$ or j) are connectivity parameters of component (i) in pure and mixture state.

Since the degree of association of (j) is not known with certainty, we regarded these parameters as adjustable parameters and evaluated them by fitting V^E data to Eq. (4). Only those ($^3\xi_i$) ($i = i$ or j) and ($^3\xi_i)_m$ ($i = i$ or j) values were retained that best reproduced the experimental values. Such ($^3\xi_i$) ($i = i$ or j) and ($^3\xi_i)_m$ ($i = i$ or j) values along with V^E values (calculated using Eq. (4)) at various x_i are recorded in Table 3 (plotted in Fig. 7) and are also compared with their corresponding experimental values. Examination of Table 3 reveals that V^E values compare well with their corresponding experimental values and thus ($^3\xi_i$) ($i = i$ or j) and ($^3\xi_i)_m$ ($i = i$ or j) values can be relied upon to extract information about the state of component (i and j) in pure and mixture state. Structures were then assumed for (i) and (j) in pure and mixture states, and their ($^3\xi'$) values were determined by employing their topology. These ($^3\xi'$) values (obtained via Eq. (3)) were compared with ($^3\xi$) values (calculated from Eq. (4)). Any structure or combination of structures, that yielded ($^3\xi'$) values that compare well with $^3\xi$

values was taken to be a representative structure of that component.

For the present $(i+j)$ mixtures, we assumed that *o*-toluidine exist molecular entities as **I** and **II**. ${}^3\xi'$ Values for these entities were then calculated to be 0.949 and 1.401, respectively. ${}^3\xi_i$ values 1.001, 1.101, 1.601, 1.001 and 1.002 for *o*-toluidine (i) in these $(i+j)$ mixtures suggest that *o*-toluidine exists as an equilibrium mixture of monomer and dimmer $\{({}^3\xi') = 1.175\}$. ${}^3\xi'$ Values of 0.666, 0.840, 1.426, 1.250 and 1.174 for benzene, toluene, *o*-, *p*- and *m*-xylenes (Table 3) suggest that they exist as monomers (molecular entities **III**–**VII**) (Scheme 1).

$(3\xi'_i)_m$ Values were then calculated and utilized to extract information about the state of *o*-toluidine, in aromatic hydrocarbons. So it was assumed that these mixtures may contain molecular entity **VIII** $\{({}^3\xi') = 1.401\}$. In evaluating $({}^3\xi')$ for molecular entity **VIII**, it was assumed that molecular entity **VIII** is characterized by interaction between hydrogen atom of *o*-toluidine and π-electron could of aromatic ring of hydrocarbons. δ^v values for the various vertices are shown in molecular entities **I**–**VIII** $\delta^v(\pi = 1)$ [20] (where the π-electron cloud of molecule is involved in specific interaction with another molecule). $({}^3\xi_i)_m$ values of (1.001, 1.101, 1.601, 1.001 and 1.002; Table 3) suggest that $(i+j)$ mixtures are characterized by the presence of molecular entity **VIII** $({}^3\xi' = 1.401)$. The existence of molecular entity **VIII** in these mixtures then suggests that addition of i to j should have influence not only the ring vibration of (j) but should also have influenced the N–H stretching vibration of *o*-toluidine in mixture. For this purpose, we analyzed the IR data of pure *o*-toluidine, benzene and their equimolar mixture. It was observed while *o*-toluidine and benzene in the pure state show characteristic vibrations at 3454, 3369 cm^{-1} (symmetric and asymmetric N–H stretching) and 1580, 1498 and 1440 cm^{-1}, respectively (ring vibrations), the infrared spectrum data of the equilibrium mixtures of *o*-toluidine (i) + benzene (j) shows characteristic bands at 3458 and 3366 cm^{-1} (N–H symmetric and asymmetric stretching) [21] and 1616, 1518 and 1483 cm^{-1}, respectively. The IR spectra of *o*-toluidine (i) + benzene (j) mixture thus clearly suggest that addition of *o*-toluidine to benzene does influence N–H stretching vibration of *o*-toluidine and ring vibration of aromatic ring of benzene and thus lends support to the existence of molecular entity **VIII** in these mixtures.

The energetic of the various $(\underline{i}+j)$ mixtures can be studied, if it is assumed that these mixtures formation involve: (i) *o*-toluidine is an associated molecular entity, (ii) the establishment of unlike contact between (i) and (j), (iii) unlike contact formation would then depolymerize (i_n) to form free (i) monomers, (iv) Monomers of (i) and (j) then undergoes specific interaction to form $i{:}j$ molecular entity. Consequently, if χ_{ii}, χ_{ij} and χ_{12} are the molar interaction parameters of i–i and i–j contacts and specific interactions, respectively, then enthalpy changes due to processes (ii)–(iv) are given by [22–24]

$$\Delta H_1 = \frac{x_i x_j \chi_{ij} \upsilon_j}{\sum x_i \upsilon_i} \tag{5}$$

$$\Delta H_2 = \frac{x_i^2 x_j \chi_{ii} \upsilon_j}{\sum x_i \upsilon_i} \tag{6}$$

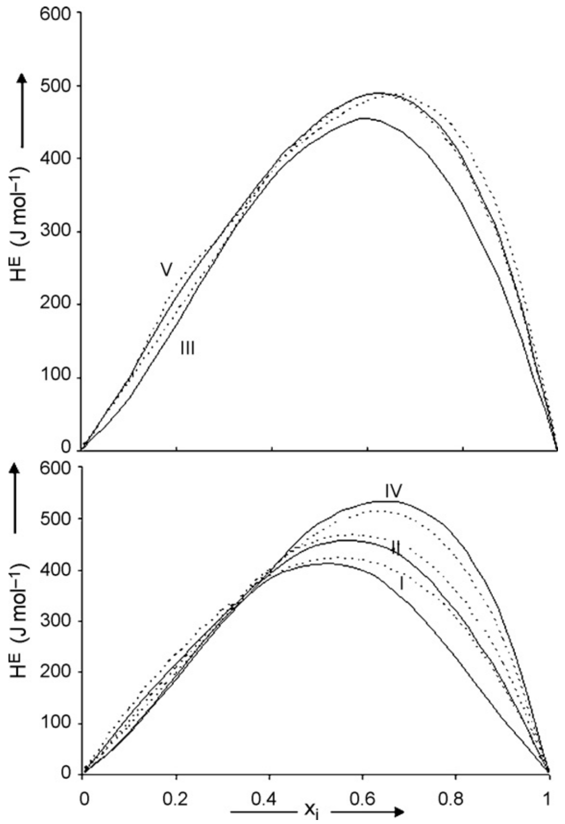


Fig. 8. Molar excess enthalpies, H^E at 308.15 K of (I) *o*-toluidine (i) + benzene (j); (II) *o*-toluidine (i) + toluene (j); (III) *o*-toluidine (i) + *o*-xylene (j); (IV) *o*-toluidine (i) + *p*-xylene (j); (V) *o*-toluidine (i) + *m*-xylene (j). —: Experimental; – – –: graph theory.

$$\Delta H_3 = \frac{x_i x_j^2 \chi_{12} \upsilon_j}{\sum x_i \upsilon_i} \tag{7}$$

where υ_j is molar volume component j. The overall changes in molar enthalpy due to processes (ii)–(iv) can then be expressed by

$$H^E = \sum_{i=1}^{3} \Delta H_i = \left[\frac{x_i x_j \upsilon_j}{\sum x_i \upsilon_i}\right][\chi_{ij} + x_i \chi_{ii} + x_j \chi_{12}] \tag{8}$$

For these mixtures, if it be assumed that $\chi_{ii} \cong \chi_{ij} = \chi'_{ij}$ then Eq. (8) reduces to

$$H^E = \left[\frac{x_i x_j \upsilon_j}{\sum x_i \upsilon_i}\right][(1 + x_i)\chi'_{ij} + x_j \chi_{12}] \tag{9}$$

since $\upsilon_j/\upsilon_i = {}^3\xi_i/{}^3\xi_j$ [25]; consequently Eq. (9) reduces to the following equation:

$$H^E = \{[x_i x_j({}^3\xi_i/{}^3\xi_j)]/[x_i + x_j({}^3\xi_i/{}^3\xi_i)]\}[(1 + x_i)\chi' + x_j \chi_{12}] \tag{10}$$

Eq. (10) contains two unknown parameters χ'_{ij} and χ_{12} and we employed H^E data at two compositions ($x_i = 0.4$ and 0.5) to evaluate them. These parameters were then utilized to predict H^E values at various values of x_i. Such H^E values along with χ'_{ij} and χ_{12} parameters are recorded in Table 3 (plotted in Fig. 8).

A persual of data in Table 3 reveals that H^E values compare well with their corresponding experimental values which lends additional support to the assumptions made in deriving Eq. (10).

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