



Topological and thermodynamic investigations of molecular interactions of aniline and *o*-toluidine with chloroform

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ARTICLE INFO

Article history:

Received 6 December 2007

Received in revised form 27 February 2008

Accepted 29 February 2008

Available online 18 March 2008

Keywords:

Molar excess enthalpies, H^E

Molar excess volumes, V^E

Isentropic compressibility changes of

mixing, κ_S^E

Connectivity parameter of third degree, ${}^3\xi$

Interaction parameter, χ

ABSTRACT

Molar excess volumes, V^E , molar excess enthalpies, H^E , and speeds of sound data, u , of chloroform (*i*) + aniline or *o*-toluidine (*j*) binary mixtures have been measured as a function of composition at 308.15 K. Isentropic compressibility changes of mixing, κ_S^E have been determined by employing speed of sound data. Topological investigations of V^E data reveals that aniline, chloroform and *o*-toluidine are associated entities and these (*i* + *j*) mixtures contain a 1:1 molecular complex. The IR studies lend further support to the nature and extent of interaction for the proposed molecular entity in the mixtures. H^E and κ_S^E values have also been calculated by employing Moelwyn-Huggins concept [Polymer 12 (1971) 387] taking topology of the constituents of the mixtures. It has been observed that calculated H^E and κ_S^E values compare well with their corresponding experimental values. The observed V^E , H^E and κ_S^E data have also been analyzed in terms of Flory theory.

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1. Introduction

Molar excess enthalpy of liquid mixtures is an important basic property used in chemical industry designs. The measurement, correlation, and theoretical calculation of the molar excess enthalpy are the subject of active research [1–8]. Further molar excess volumes data of the liquid mixtures are required, for instance, for relating excess enthalpy and excess free energy values. From a practical point of view, the data are useful for the design of mixing, storage and process equipment. Anilines are known to be associated [9–11] in the pure state through bonding. The addition of a compound like chloroform to aniline or *o*-toluidine may tend either to rupture or enhance the self-association of aniline or *o*-toluidine or chloroform. As the state of aniline or *o*-toluidine or chloroform in pure as well mixture state may or may not be same, therefore, thermodynamic and topological studies of aniline or *o*-toluidine + chloroform mixtures can provide information about the state of aggregation of these compounds and the nature of species present in these mixtures. These considerations prompted us to study the thermodynamic properties molar excess volumes, molar excess enthalpies and isentropic com-

pressibility change of mixing of chloroform + aniline or *o*-toluidine mixtures.

2. Experimental

Aniline (A) [AR Grade], *o*-toluidine (OT) [Fluka], chloroform (AR Grade) were purified by standard methods [12]. The purities of the purified liquids were then checked by measuring their densities at 298.15 ± 0.01 K and these agreed to within ± 0.05 kg m⁻³ with their values reported in literature [12].

Molar excess volumes, V^E for the binary (*i* + *j*) mixtures were determined at 308.15 K as a function of composition in a V-shaped dilatometer that has been described elsewhere [13]. The uncertainties in the measured V^E values are $\pm 0.5\%$.

Molar excess enthalpies, H^E for binary mixtures were measured at 308.15 K by 2-drop calorimeter (model, 4600) supplied by the Calorimetry Sciences Corporation (CSC) USA in a manner as described elsewhere [14] and the uncertainties in the measured H^E values are $\pm 1\%$.

Speeds of sound in binary mixtures were measured at 308.15 ± 0.01 K using a variable path interferometer (Model-M 84, Mittal Enterprises, India) and a measuring cell. Water from the thermostat was circulated through the cell to maintain the desired temperature. The uncertainties in the measured speed of sound values are ± 1 ms⁻¹.

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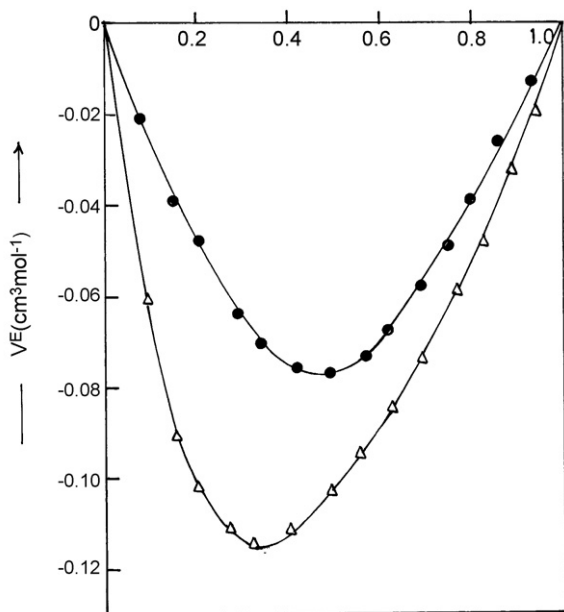


Fig. 1. Molar excess volumes, V^E , for chloroform (i) + aniline (j), (Δ) chloroform (i) + o-toluidine (j), and (\bullet) at 308.15 K.

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.

3. Results

Molar excess volumes, V^E , molar excess enthalpies, H^E , and speeds of sound, u , data of chloroform (i) + A or OT (j) binary mixtures at 308.15 K over the whole composition range are recorded in Supplementary Tables 1–3 (plotted in Figs. 1 and 2), respectively. The isentropic compressibility, κ_S for binary mixtures were calculated using Eq. (1).

$$\kappa_S = (\rho_{ij} u^2)^{-1} \quad (1)$$

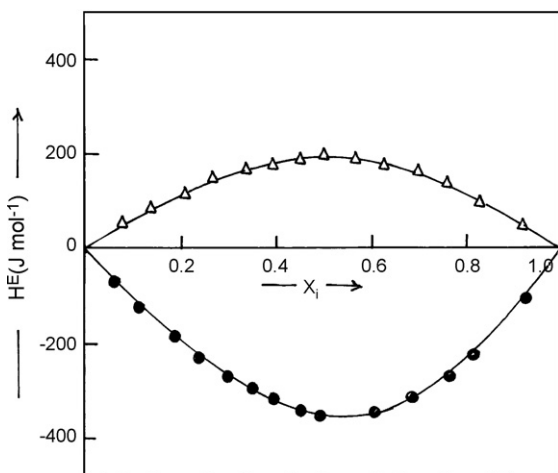


Fig. 2. Molar excess enthalpies, H^E for chloroform (i) + aniline (j), (Δ) chloroform (i) + o-toluidine (j), and (\bullet) at 308.15 K.

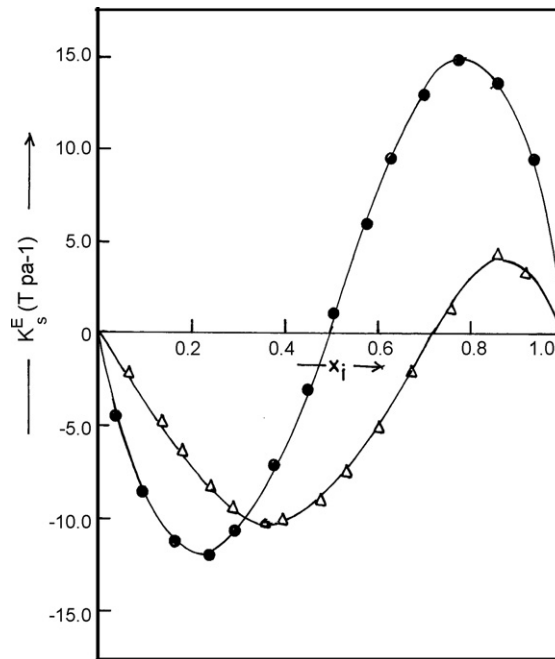


Fig. 3. Isentropic compressibility changes of κ_S^E for chloroform (i) + aniline (j), (Δ) chloroform (i) + o-toluidine (j), and (\bullet) at 308.15 K.

The densities, ρ_{ij} of the binary mixtures were calculated from their molar excess volume data using the relation:

$$V^E = \sum_{i=1}^j x_i M_i (\rho_{ij})^{-1} - \sum_{i=1}^j x_i M_i (\rho_i)^{-1} \quad (2)$$

where x_i , M_i , ρ_i are the mole fraction, molar mass and density of component (i) of (i+j) binary mixture. Isentropic compressibility changes of mixing, κ_S^E for (i+j) mixtures were determined by employing Eq. (3).

$$\kappa_S^E = \kappa_S - \sum_{i=1}^j \phi_i (k_S)_i \quad (3)$$

where ϕ_i and $(k_S)_i$, etc. are the volume fraction and isentropic compressibility of component (i). The resulting k_S and κ_S^E values (plotted in Fig. 3) for the binary mixtures are recorded in Supplementary Table 3.

Molar excess volumes, V^E , molar excess enthalpies, H^E and Isentropic compressibility changes of mixing, κ_S^E data were fitted to Eq. (4)

$$X^E (X = V \text{ or } H \text{ or } \kappa_S) = x_i x_j [X^{(0)} + X^{(1)}(2x_i - 1) + X^{(2)}(2x_i - 1)^2] \quad (4)$$

where $X^{(n)}$ ($n=0, 2$), etc. are the parameters characteristic of (i+j) mixture and have been determined by fitting X^E data to Eq. (4) by the least squares method and are recorded along with standard deviation, $\sigma(X^E) [X=V \text{ or } H \text{ or } \kappa_S]$ defined by Eq. (5)

$$\sigma(X^E) = \left[\frac{\sum (X_{\text{exptl}}^E - X_{\text{Calc.Eq. (4)}}^E)^2}{m - p} \right]^{0.5} \quad (5)$$

[where m, n are the number of data points and adjustable parameters in Eq. (4)] in Supplementary Tables 1–3.

3.1. Discussion

The H^E data for chloroform (i)+A or OT (j) mixtures at 308.15 K have been reported in the literature [15]. Our H^E values for chloroform (i)+A (j) mixtures are in excellent agreement with the experimental values. However, for chloroform (i)+OT (j) mixture; H^E values differ by 2% in the range $0.6 \leq x_i \leq 0.8$. The general shapes of the curves of the mixtures are same. We are unaware of any V^E and κ_S^E data for ($i+j$) mixtures with which to compare our results. However, there is good agreement between the experimentally observed and literature values of speed of sound at 298.15 K for pure A: 1635.0 (1634.0) [16] and at 303.15 K for chloroform: 967.2 (968.0) [17]. While V^E data for the studied ($i+j$) mixtures are negative; H^E data are negative for chloroform (i)+OT (j) and are positive for chloroform (i)+A (j) mixtures over entire composition range. V^E and H^E data for an equimolar composition vary in the order: A > OT. Further κ_S^E values are negative for chloroform (i)+A (j) over whole composition range. However, κ_S^E values changes sign from negative to positive values for chloroform (i)+OT (j) mixtures with increase in mole fraction of chloroform.

The observed V^E and H^E data for studied ($i+j$) mixtures may be qualitatively explained, if it be assumed that (i) chloroform or A or OT are associated molecular entities; (ii) there is interaction between lone pair of electron on the nitrogen atom of A or OT and hydrogen atom of chloroform; (iii) interaction between i_n and j_n molecules then leads to depolymerization of i_n and j_n to yield their respective monomers; (iv) monomers of i and j then undergoes interaction to form $i:j$ molecular complex. The positive H^E values for chloroform (i)+A (j) mixtures suggest that contribution to H^E due to factor (iii) far outweigh the factor (iv). The addition of $-\text{CH}_3$ substituent in benzene ring of A (as in OT) increases the π -electron density of the benzene ring thereby allowing the lone pair of electron on the N-atom of OT to interact strongly as to compared to that of A with chloroform. Thus V^E and H^E values should be less for chloroform (i)+OT (j) mixtures as compared to chloroform (i)+A (j) mixtures. This is indeed true. The large interactions in chloroform (i)+OT (j) mixture than those for chloroform (i)+A (j) mixture is further supported, if we assume that H^E values are due to two factors (i) contribution due to size, H_{phys}^E and (ii) contribution arising from molecular interactions, H_{chem}^E . If H_{phys}^E values were taken be H_{expt}^E for cyclohexane + chloroform mixture [18], then H_{chem}^E values at an equimolar comparison for chloroform (i)+A or OT (j) mixtures are -434.4 and $-975.2 \text{ J mol}^{-1}$, respectively. The H_{chem}^E values thus support our viewpoint that OT interacts strongly with chloroform as compared to A.

The κ_S^E values for chloroform (i)+A or OT (j) mixtures suggest that A gives relatively more packed structure in chloroform as compared to OT. This is due to the presence of $-\text{CH}_3$ groups in OT which restrict the approach of OT to the chloroform molecules.

The addition of chloroform (i) to A or OT (j) may cause change in the topology of i and/or j , which in turn must be reflected in the thermodynamic properties of ($i+j$) mixtures. Since, V^E , is a packing effect, and would be influenced by the change in topology of the molecules, it would, therefore, be worthwhile to analyze V^E data of chloroform (i)+A or OT mixtures in terms of Graph theory [19] that employs the theoretical concept of the connectivity parameters of third degree, ${}^3\xi$, of the constituents of ($i+j$) mixtures. According to this theory [19,20], V^E is given by

$$V^E = \alpha_{ij} [x_i ({}^3\xi_i)_m + x_j ({}^3\xi_j)_m]^{-1} - \sum x_i ({}^3\xi_i)^{-1} \quad (6)$$

where α_{ij} is a constant characteristic of ($i+j$) mixtures and $({}^3\xi_i)$ ($i=i$ or j), $({}^3\xi_i)_m$ ($i=i$ or j) are the connectivity parameters of third degree of components (i) and (j) in pure and mixture state and are defined

by Eq. (7)

$${}^3\xi = \sum_{m < n < o < p} (\delta_m^v \delta_n^v \delta_o^v \delta_p^v)^{-0.5} \quad (7)$$

where δ_m^v , etc. have the same significance as explained elsewhere [21].

We regarded $({}^3\xi_i)$ ($i=i$ or j), $({}^3\xi_i)_m$ ($i=i$ or j), etc. parameters as adjustable parameters as the degree of association of i and j is not known in pure and mixture state. These parameters were determined by fitting V^E data of ($i+j$) mixtures to Eq. (6). Only those $({}^3\xi_i)$ ($i=i$ or j), $({}^3\xi_i)_m$ ($i=i$ or j), etc. values were taken that best reproduced the experimental V^E data. Such $({}^3\xi_i)$ ($i=i$ or j), $({}^3\xi_i)_m$ ($i=i$ or j) values alongwith the V^E values (calculated using Eq. (6)) at various values of x_i are recorded in Table 1. Examination of data in Table 1 reveals that calculated V^E values compare well with their corresponding experimental values. Thus ${}^3\xi$ values for various components can be relied upon to extract information about their state in pure and mixed state. For this purpose, number of structures were assumed for chloroform, A, OT and their ${}^3\xi^l$ values were calculated from structural consideration [via Eq. (7)]. These ${}^3\xi^l$ values were next compared with ${}^3\xi$ values obtained from V^E data (Table 1). Any structure or a combination of structures for a component that give ${}^3\xi^l$ value which compared well with its ${}^3\xi$ values were taken to be a representative structure of that component.

For the analysis of present ($i+j$) mixtures, we assumed that chloroform, A and OT exist as molecular entities I, II–III, IV–V, respectively (Scheme 1). The ${}^3\xi^l$ values for these molecular entities were then calculated to 1.260, 1.361, 1.890, 0.949, and 1.401, respectively. ${}^3\xi$ values 1.251, 1.801, 1.802 for chloroform, A and OT suggest that they exist as dimers. In evaluating ${}^3\xi^l$ values of molecular entities III and V we assigned $\delta^v(\pi = 1)$. $({}^3\xi^l)_m$ values were next calculated to understand the state of A or OT in chloroform. It was assumed that studied ($i+j$) mixtures may contain molecular entity VI (${}^3\xi^l = 1.951$) and is characterized by interaction between lone pair of electron on nitrogen atom of A or OT with hydrogen atom of chloroform. $({}^3\xi_j)_m$ value of 1.801 and 1.803 (Table 1) for ($i+j$) mixtures suggest that ($i+j$) mixtures contain molecular entity VI.

The postulation of the existence of molecular entity VI in chloroform (i)+A or OT (j) mixtures suggest that addition of A or OT to chloroform should have influence the C–H vibrations of chloroform and C–N vibrations of A or OT. In view of this, we analyzed the IR spectra of pure chloroform, A or OT and equilibrium mixture of chloroform with A or OT. It was observed that while chloroform and A or OT in pure state showed characteristic absorption at 2887 cm^{-1} (C–H stretching), and 1383 and 1384 cm^{-1} (C–N stretching) [22], the IR spectra of equimolar mixtures of chloroform (i)+A or OT (j) showed absorption at 2914 and 2926 cm^{-1} (C–H stretching) and 1387 and 1389 cm^{-1} (C–N stretching), respectively. The IR spectra of chloroform (i)+A or OT (j) mixtures thus indicate that addition of chloroform to A or OT does influence the C–H and C–N vibrations of chloroform and A or OT. The IR studies thus lend additional support to the presence of molecular entity VI in ($i+j$) mixtures. These observations are in consistence with earlier observations made in explaining the qualitative discussion of thermodynamic data of these mixtures [15].

We next employed Moelwyn-concept [23,24] of interactions between the surfaces of components of binary mixtures (using the concept of connectivity parameter of third degree, ${}^3\xi$ of a molecule which in turn depends on its topology) to evaluate molar excess enthalpies, H^E and isentropic compressibility changes of mixing, κ_S^E of the studied ($i+j$) mixtures. For this purpose it was assumed that mixture formation in chloroform (i)+A or OT mixtures involve processes; (1) establishment of unlike contacts between i_n and j_n molecules; (2) unlike contact formation then results in the depoly-

Table 1

Comparison of V^E , H^E and κ_S^E values calculated from appropriate equations with their corresponding experimental values at 308.15 K as a function of x_i , mole fraction of component (i)

	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Chloroform (i) + aniline (j)									
V^E (Exptl)	-0.069	-0.101	-0.110	-0.109	-	-0.092	-0.074	-0.054	-0.030
V^E (Graph)	-0.033	-0.060	-0.082	-0.097	-	-0.104	-0.095	-0.057	-0.044
V^E (Flory)	-0.147	-0.273	-0.377	-0.453	-	-0.499	-0.454	-0.351	-0.179
H^E (Exptl)	59.2	111.9	153.5	180.9	-	185.2	161.1	120.6	65.8
H^E (Graph)	63.6	115.8	155.2	-	-	187.1	166.0	128.2	73.1
H^E (Flory)	1.7	4.2	8.0	13	-	31.3	44.7	61.8	82.9
κ_S^E (Exptl)	-3.4	-7.1	-9.6	-10.2	-	-5.0	-0.6	3.3	4.4
κ_S^E (Graph)	-9.3	-13.1	-6.3	-	-	-2.1	1.3	3.3	3.1
κ_S^E (Flory)	-31.5	-59.4	-82.6	-100.3	-	-114.6	-107.6	-88.6	-53.8
$(^3\xi_i) = (^3\xi_i)_m = 1.251$; $(^3\xi_j) = (^3\xi_j)_m = 1.801$; $\alpha_{ij} = 4.735 \text{ cm}^3 \text{ mol}^{-1}$ $\chi_{ij}' = 344.0 \text{ J mol}^{-1}$; $\chi^* = 419.9 \text{ J mol}^{-1}$; $\chi_{ij}'' = 3.1 \text{ J mol}^{-1}$ $\chi_{ij}''' = 70.019 \text{ T Pa}^{-1}$; $\chi^* = -78.336 \text{ T Pa}^{-1}$									
Chloroform (i) + o-toluidine (j)									
V^E (Exptl)	-0.026	-0.050	-0.070	-0.078	-	-0.067	-0.054	-0.039	-0.020
V^E (Graph)	-0.024	-0.044	-0.044	-0.070	-	-0.076	-0.069	-0.055	-0.032
V^E (Flory)	-0.124	-0.233	-0.233	-0.399	-	-0.468	-0.453	-0.396	-0.285
H^E (Exptl)	-104.5	-195.4	-268.2	-318.8	-	-339.8	-305.1	-237.6	-136.1
H^E (Graph)	-105.1	-196.0	-268.5	-	-	-290.7	-305.9	-239.1	-137.8
H^E (Flory)	-25.5	-49.8	-72.6	-93.5	-	-127.9	-140.1	-148.1	-150.9
κ_S^E (Exptl)	-8.5	-11.8	-10.5	-7.5	-	0.5	12.9	15.0	11.6
κ_S^E (Graph)	-12.5	-14.4	-11.8	-	-	1.0	11.7	12.7	9.1
κ_S^E (Flory)	-28.6	-53.5	-73.7	-89.3	-	-101.8	-96.0	-79.5	-49.6
$(^3\xi_i) = (^3\xi_i)_m = 1.251$; $(^3\xi_j) = (^3\xi_j)_m = 1.803$; $\alpha_{ij} = 3.455 \text{ cm}^3 \text{ mol}^{-1}$ $\chi_{ij}' = -551.6 \text{ J mol}^{-1}$; $\chi^* = -849.4 \text{ J mol}^{-1}$; $\chi_{ij}'' = -4.0 \text{ J mol}^{-1}$ $\chi_{ij}''' = 129.39 \text{ T Pa}^{-1}$; $\chi^* = -83.10 \text{ T Pa}^{-1}$									

Also included are the various $(^3\xi_i)$ and $(^3\xi_j)_m$ ($i=i$ or j); α_{ij} parameters along with interaction energies χ_{ij} , χ_{12} , etc. parameters.

merization of i_n and j_n to yield their respective monomers; (3) the monomers of (i) undergo interactions with monomers of (j) to form $i:j$ molecular complex, consequently, if χ_{ij} , χ_{ii} , χ_{jj} , and χ_{12} are molar energy and molar compressibilities parameters for $i-j$, $i-i$, $j-j$ contacts and specific interactions, respectively, then change in molar thermodynamic property X ($X=H$ or κ_S) due to processes (1, 2 (a, b) and 3) would be expressible [23–25] by Eqs. (8)–(11).

$$\Delta X_1(X=H \text{ or } \kappa_S) = x_i \chi_{ij} S_j$$

where S_j is the surface fraction of (j) defined [23] by

$$S_j = \frac{x_j v_j}{\sum x_i v_i}$$

so that

$$\Delta X_1(X=H \text{ or } \kappa_S) = \frac{x_i x_j \chi_{ij} v_j}{\sum x_i v_i} \quad (8)$$

$$\Delta X_2(X=H \text{ or } \kappa_S) = \frac{x_i^2 x_j \chi_{ii} v_j}{\sum x_i v_i} \quad (9)$$

$$\Delta X_3(X=H \text{ or } \kappa_S) = \frac{x_i^2 x_j \chi_{jj} v_j}{\sum x_i v_i} \quad (10)$$

$$\Delta X_4(X=H \text{ or } \kappa_S) = \frac{x_i x_j^2 \chi_{12} v_j}{\sum x_i v_i} \quad (11)$$

where v_i is the molar volume of component (i). The overall excess thermodynamic property, X^E ($X=H$ or κ_S) for ($i+j$) mixtures would then be given by Eq. (12)

$$X^E(X=H \text{ or } \kappa_S) = \sum_{i=1}^4 \Delta X_i = \left[\frac{x_i x_j v_j}{\sum x_i v_i} \right] [\chi_{ij} + x_i \chi_{ii} + x_i \chi_{jj} + x_j \chi_{12}] \quad (12)$$

since $v_j/v_i = ^3\xi_i/^3\xi_j$ [19]; consequently Eq. (12) reduces to Eq. (13)

$$X^E(X=H \text{ or } \kappa_S) = \left[\frac{x_i x_j (^3\xi_i/^3\xi_j)}{x_i + x_j (^3\xi_i/^3\xi_j)} \right] [\chi_{ij} + x_i \chi_{ii} + x_i \chi_{jj} + x_j \chi_{12}] \quad (13)$$

For the studied mixtures, if it be assumed that $\chi_{ij} \cong \chi_{12} = \chi_{ij}'$ and $\chi_{ii} \cong \chi_{jj} = \chi^*$, then Eq. (13) can be expressed by

$$X^E(X=H \text{ or } \kappa_S) = \left[\frac{x_i x_j (^3\xi_i/^3\xi_j)}{x_i + x_j (^3\xi_i/^3\xi_j)} \right] [(1 + x_j) \chi_{ij}' + 2x_i \chi^*] \quad (14)$$

Eq. (14) contains two unknown parameters (χ_{ij}' and χ^*) and these parameters were determined by employing H^E and κ_S^E data of the studied ($i+j$) mixtures at two compositions ($x_i=0.4$ and 0.5). These parameters were subsequently utilized to predict H^E and κ_S^E values at other values of x_i . Such H^E and κ_S^E values along with (χ_{ij}' and χ^*) are recorded in Table 1 and are also compared with their corresponding experimental values. A perusal of data in Table 1 reveals that H^E and κ_S^E values compare well their experimental values and thus basic arguments in deriving Eq. (14) are justified.

V^E , H^E and κ_S^E data of ($i+j$) mixtures have also been analyzed in terms of Flory's theory. According to this theory [26,27] V^E , H^E and κ_S^E are given by Eqs. (15)–(17)

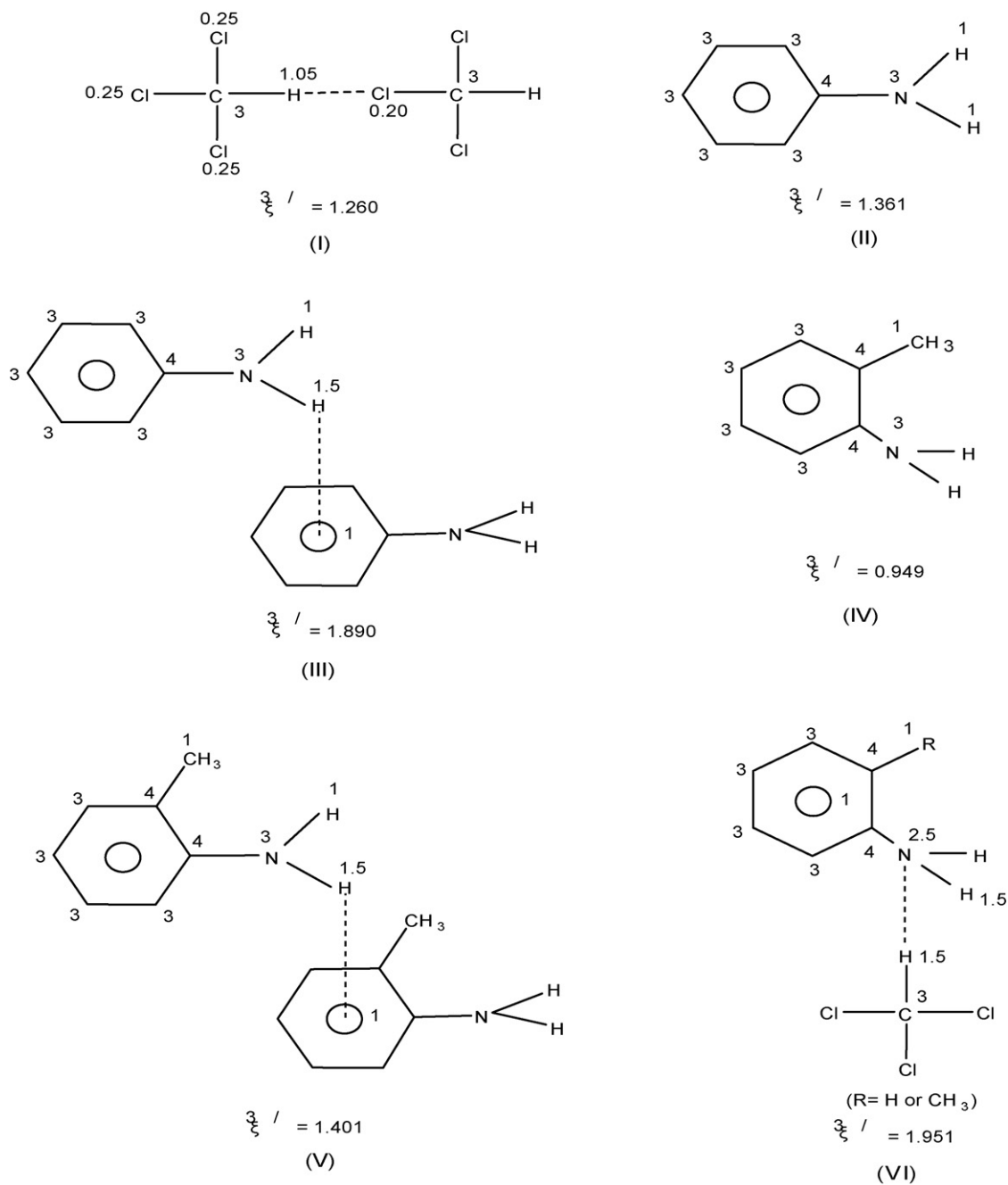
$$V^E = \bar{V}_{\text{cal}}^E \left[\sum_{i=1}^j x_i v_i^* \right] \quad (15)$$

$$H^E = \sum x_i P_i^* (\bar{v}_i^{-1} - \bar{v}_{\text{cal}}^{-1}) + x_i v_i^* \theta_j \chi_{ij}' / \bar{v}_{\text{cal}}^{-1} \quad (16)$$

$$\kappa_S^E = \kappa_S - \kappa_S^{\text{id}} \quad (17)$$

where

$$\bar{v}_i = [1 + \alpha_i(T/3)/(1 + \alpha_i T)^3]^3 \quad (18)$$



Scheme 1. Connectivity parameters of various molecular entities.

$$\bar{V}_{\text{cal}}^E = \bar{v}_0^{7/3} [(4/3) - (\bar{v}_0)^{1/3}]^{-1} [\bar{T} - \bar{T}_0] \quad (19)$$

$$\bar{v}_{\text{cal}} = \bar{v}_0 + \bar{V}_{\text{cal}}^E \quad (20)$$

$$\bar{T}_0 = \frac{\bar{v}_0^{1/3} - 1}{\bar{v}_0^{4/3}} \quad (21)$$

$$\bar{v}_i^* = \frac{V_i}{\bar{v}_i} \quad (22)$$

$$\bar{v}_0 = \sum \phi_i \bar{v}_i^* \quad (23)$$

$$\bar{T} = [\sum (\phi_i P_i^* \bar{T}_i / \sum \phi_i P_i^*)] [1 - (\phi_i \theta_j \chi_{ij}^{//}) (\sum \phi_i P_i^*)^{-1}]^{-1} \quad (24)$$

$$\bar{T}_i = \frac{\bar{v}_i^{1/3} - 1}{\bar{v}_i^{4/3}} \quad (25)$$

$$P_i^* = \sum \phi_i P_i^* - \sum \phi_i^* \theta_j \chi_{ij}^{//} \quad (26)$$

$$P_i^* = \alpha_i T \bar{v}_i^2 [(K_T)_i]^{-1} \quad (27)$$

The isentropic compressibility values, κ_S , were determined by employing relation:

$$\kappa_S = K_T - T v_m^* \alpha_p^2 / C_{p,m} \quad (28)$$

Isothermal compressibility, K_T , of a mixture (effectively at zero pressure) is given by relation

$$K_T = \left[\left(\frac{3\bar{v}_m^2}{p^*} \right) (\bar{v}_m^{1/3} - 1) / (4 - 3(\bar{v}_m^{1/3})) \right] \quad (29)$$

where

$$v_m^* = \sum_{i=1}^j \phi_i v_i^* \quad (30)$$

$$\bar{v}_m = \sum_{i=1}^j \phi_i v_i^* \quad (31)$$

$$\alpha_p = \frac{3(\bar{v}_m^{1/3} - 1)}{T(4 - 3(\bar{v}_m^{1/3}))} \quad (32)$$

$$C_{p,m} = \left(\frac{\partial H^E}{\partial T} \right) + \sum_{i=1}^j x_i C_{p,i} \quad (33)$$

$$p^* = \sum_{i=1}^j \phi_i p_i^* - \sum_{i=1}^j \phi_i \theta_j \chi_{ij}^{**} \quad (34)$$

$$\bar{v} = \frac{v}{v^*} \quad (35)$$

where P^* , \bar{T} , \bar{v} , $C_{p,i}^*$ denotes, respectively, the mole fraction and characteristic volume, characteristic pressure, reduced temperature, reduced volume and molar heat capacity of component (i) of ($i+j$) mixtures and have the same significance as described elsewhere [26,27].

Evaluation of V^E and H^E by Flory theory requires a knowledge of reduced temperature, \bar{T} , which in turn depends upon adjustable parameter χ_{ij}^{**} of binary mixtures. These parameters were determined by fitting their H^E value at $x_i = 0.5$ to Eq. (36).

$$H^E = \sum x_i P_i^* (\bar{v}_i^{-1} - \bar{v}_{cal}^{-1}) + x_i v_i^* \theta_j \chi_{ij}^{**} \bar{v}_{cal}^{-1} \quad (36)$$

Various parameters of pure components were determined using isothermal compressibility (K_T) reported in literature [12,28]. K_T values for those liquids which were not available in the literature were calculated by employing ΔH_V values in the manner as suggested by Hilderbrand [29]. H^E values for ($i+j$) mixtures at 298.15 K were determined in a manner described elsewhere [30]. κ_S^{id} values for the binary mixture were determined using Eq. (28) where κ_T^{id} , α_p^{id} and $C_{p,m}^{id}$ are taken volume fraction averages and mole fraction averages of pure components. Such V^E , H^E and κ_S^E values evaluated via Eqs. (15)–(36) by employing Flory theory alongwith χ_{ij}^{**} , etc. are recorded in (Table 1) and are also compared with their experimental values.

Examination of data in Table 1 has revealed that Flory theory correctly predicts the sign and order of V^E , H^E and κ_S^E values for the

studied ($i+j$) binary mixtures. However, qualitative agreement is poor. The failure of Flory theory to correctly predict the magnitude of V^E , H^E and κ_S^E may be due to various assumptions made in evaluating various parameters which were not reported in the literature but have been determined theoretically.

Acknowledgements

The authors are grateful to the Head, Chemistry Department and authorities of M.D. University, Rohtak, for providing research facilities.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2008.02.022.

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