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Thermodynamic properties of liquid mixtures containing 1,3-dioxolane and anilines: Excess molar volumes, excess molar enthalpies, excess Gibb's free energy and isentropic compressibilities changes of mixing

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ABSTRACT

Excess molar volumes V^E, excess molar enthalpies H^E, speeds of sound, u and vapour–liquid equilibrium data of 1,3-dioxolane (i) + aniline or N-methyl aniline or *o*-toluidine (j) binary mixtures have been measured as a function of composition at 308.15 K. Speeds of sound and vapour–liquid equilibrium data of (i + j) binary mixtures have been utilized to determine isentropic compressibilities changes of mixing, κ_S^E and excess Gibb's free energy G^E. The observed data have been analyzed in term of Graph theory which involves the topology of the mixture constituents. It has been observed V^E, H^E, κ_S^E and G^E values predicted by Graph theory compare well with their corresponding experimental values.

1. Introduction

Non-ideality of liquid mixtures has been attributed [1] to either physical intermolecular force or to chemical reaction occurring between the components of liquid mixtures. The process of mixture formation may trigger inter and intramolecular changes in either one or all the components in liquid mixtures which in turn be reflected in their thermodynamic properties like excess molar volumes, excess molar enthalpies, excess Gibb's free energy, etc. In recent studies [2–6] topology of the constituents of binary or ternary mixtures has been employed to predict excess molar volumes, excess molar enthalpies and isentropic compressibility changes of mixing. An attempt has also been made to employ topology of a molecule to predict excess Gibb's free energy of binary mixture. In continuation of our studies [7,8] on mixtures containing 1,3-dioxolane, we report here excess molar volumes, excess molar enthalpies, isentropic compressibilities changes of mixing and excess Gibb's free energy of 1,3-dioxolane (i) + aniline or N-methyl aniline or *o*-toluidine (j) binary mixtures.

2. Experimental

1,3-Dioxolane **(D)** (Fluka, 99 mol.%), aniline **(A)** (Fluka, 99 mol.%), N-methyl aniline **(MA)** (Fluka, 98 mol.%), *o*-toluidine **(OT)** (Fluka, 99 mol.%) were purified by standard methods [9]. The purities of the purified liquids were checked by measuring their densities [recorded in Table 1] using bicapillary pycnometer at 298.15 ± 0.01 K and these agreed to within ±0.05 kg m^{-3} with their literature values [9,10]. Excess molar volumes, V^E for the binary mixture were measured dilatometrically as described elsewhere [11]. The change in liquid level of dilatometer capillary was measured with a cathetometer that could read to ±0.001 cm. The uncertainties in the measured V^E values are 0.5%.

Excess molar enthalpies, H^E for the studied mixtures were measured by a 2-drop calorimeter (model, 4600) supplied by the Calorimeter Sciences Corporation (CSC), USA at 308.15 K in a manner described elsewhere [2]. The uncertainties in the measured H^E values are 1%.

Speeds of sound, u (at frequency 2 MHz) in binary mixtures were measured using a variable path interferometer (Model M 84, Mittal Enterprises, India) and a measuring cell. The measuring cell was a specially designed cell in which water was circulated through the cell to maintain the desired temperature. The speeds of sound values for the purified liquids at 298.15 ± 0.01 K (recorded in

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Table 1
Comparison of densities speeds of sound, u, and vapour pressure of pure liquids with their literature values at 298.15 K.

Liquids	u/m s^{-1}		ρ/kg m^{-3}		P/Torr	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
1,3-Dioxolane	1388	1388.8 [12]	1047.2	1047.3 [10]	161.3[a]	161.4[a] [18]
Aniline	1635	1634 [13]	1017.2	1017.4 [9]	0.7	0.67 [19]
N-methyl aniline	1572	1573 [14]	982.4	982.2 [9]	0.5	0.453 [20]
o-Toluidine	1602	–	994.2	994.3 [9]	0.3	0.317 [21]

[a] Value at 308.15 K.

Table 1) compare well with their corresponding experimental values [12–14]. The uncertainties in the measured sound speeds value is 1 ms^{-1}.

Total vapour pressure of the various (i + j) mixtures was measured as a function of the liquid-phase mole fraction of (i), x_i at 308.15 ± 0.01 K by a static method [15] in the manner described elsewhere [16]. The height of the mercury in the manometer was corrected to 273.15 K and standard gravity. The composition of the liquid phase was determined interferometrically using Carl Zeiss interferometer in the manner described earlier [17]. The measured vapour pressures were reproducible to ±0.18 Torr or better while uncertainties in the liquid-phase composition were about 0.01 mol.%. The errors in the vapour pressure determinations were estimated to be 0.3 mm. Our measured vapour pressures (Table 1) at 298.15 K for aniline, N-methyl aniline, and *o*-toluidine compare well within the experimental uncertainties with their corresponding literature [18–21] at 298.15 K and 1,3-dioxolane values at 308.15 K.

3. Results

Excess molar volumes, V^E, excess molar enthalpies, H^E, and speeds of sound, u data of **D** (i) + **A** or **MA** or **OT** (j) binary mixtures measured as a function of composition at 308.15 K are recorded in Tables 2–4 respectively. The isentropic compressibilities, κ_S for various (i + j) mixtures were determined from their speeds of sound data using relation:

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

The densities, ρ_{ij} of binary mixtures were evaluated from their excess molar volumes data by employing Eq. (2)

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

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

$$\kappa_S^E = \kappa_S - \kappa_S^{id} \tag{3}$$

κ_S^{id} values were obtained as suggested by Benson and Kiyohara [22]

$$\kappa_S^{id} = \sum_{i=i}^{j} \phi_i \left[\kappa_{S,i} + \frac{T v_i \alpha_i^2}{C_{p,i}} \right] - T \left(\sum_{i=i}^{j} x_i v_i \right) \frac{\left(\sum_{i=i}^{j} \phi_i \alpha_i \right)^2}{\left(\sum_{i=i}^{j} x_i C_{p,i} \right)} \tag{4}$$

where ϕ_i is the volume fraction of component (i) in the mixed state; $\kappa_{S,i}$, v_i, α_i and $C_{p,i}$ are isentropic compressibility, molar volume, thermal expansion coefficient and molar heat capacity respectively of the pure component (i). The values of α_i and $C_{p,i}$ were taken from

Table 2
Measured excess molar 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}
1,3-Dioxolane (i) + aniline (j)[a]			
0.0789	−0.134	0.5999	−0.493
0.1132	−0.188	0.6342	−0.477
0.2204	−0.330	0.7114	−0.418
0.3111	−0.428	0.8202	−0.294
0.4281	−0.497	0.8913	−0.190
0.4916	−0.516	0.9233	−0.138
0.5230	−0.517	0.9718	−0.0525
1,3-Dioxolane (i) + N-methyl aniline(j)[b]			
0.0709	−0.018	0.4912	−0.110
0.1771	−0.045	0.5531	−0.112
0.2387	−0.063	0.6272	−0.104
0.2958	−0.080	0.6992	−0.093
0.3349	−0.088	0.7417	−0.088
0.3916	−0.095	0.8545	−0.051
0.4361	−0.102	0.9213	−0.030
1,3-Dioxolane (i) + *o*-toluidine(j)[c]			
0.0549	−0.084	0.5889	−0.512
0.1721	−0.251	0.6218	−0.497
0.2239	−0.312	0.6831	−0.466
0.2769	−0.375	0.7523	−0.407
0.3510	−0.443	0.8147	−0.328
0.4217	−0.486	0.8916	−0.216
0.5518	−0.512	0.9407	−0.123

Also included are various $V^{(n)}$ (n = 0–2) parameters along with standard deviations, $\sigma(V^E)$.

[a] $V^{(0)} = -2.055$, $V^{(1)} = -0.088$, $V^{(2)} = 0.239$; $\sigma(V^{(E)}) = 0.005$ cm^3 mol^{-1}.

[b] $V^{(0)} = -0.435$, $V^{(1)} = -0.091$, $V^{(2)} = 0.135$; $\sigma(V^{(E)}) = 0.001$ cm^3 mol^{-1}.

[c] $V^{(0)} = -2.046$, $V^{(1)} = -0.337$, $V^{(2)} = 0.178$; $\sigma(V^{(E)}) = 0.005$ cm^3 mol^{-1}.

Table 3
Measured excess molar 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}
1,3-Dioxolane (i) + aniline (j)[a]			
0.0613	−161.6	0.5812	−896.2
0.1622	−413.5	0.6223	−873.3
0.2241	−547.6	0.6816	−817.1
0.2774	−650.8	0.7519	−715.1
0.3503	−768.5	0.8127	−586.7
0.4231	−848.4	0.8928	−371.3
0.5511	−900.3	0.9514	−182.2
1,3-Dioxolane (i) + N-methyl aniline (j)[b]			
0.0853	−382.3	0.6432	−387.7
0.1423	−543.3	0.7123	−313.4
0.2533	−678.2	0.7943	−234.8
0.3765	−652.4	0.8543	−171.3
0.4531	−590.4	0.8912	−134.5
0.5123	−531.6	0.9321	−93.2
0.5976	−440.2	0.9721	−37.4
1,3-Dioxolane (i) + *o*-toluidine (j)[c]			
0.0754	−220.5	0.6112	−826.6
0.1632	−464.0	0.6979	−696.2
0.2424	−646.8	0.7432	−608.7
0.3213	−786.1	0.8080	−466.7
0.4001	−872.8	0.8831	−281.1
0.4843	−906.1	0.9311	−163.3
0.5655	−871.2	0.9621	−86.8

Also included are various H^n (n = 0–2) parameters along with standard deviations, $\sigma(H^E)$.

[a] $H^{(0)} = -3584.5$, $H^{(1)} = -621.2$, $H^{(2)} = 285.3$; $\sigma(H^E) = 9.0$ J mol^{-1}.

[b] $H^{(0)} = -2183.9$, $H^{(1)} = 2116.0$, $H^{(2)} = -1430.8$; $\sigma(H^E) = 5.0$ J mol^{-1}.

[c] $H^{(0)} = -3612.1$, $H^{(1)} = 360.5$, $H^{(2)} = 1025.6$; $\sigma(H^E) = 9.0$ J mol^{-1}.

Table 4
Speeds of sound, u, isentropic compressibilities, κ_S, and isentropic compressibilities changes of mixing, κ_S^E for the various (i + j) mixtures as a function of mole fraction, x_i of component (i) at 308.15 K.

x_i	u/ms^{-1}	κ_S/TPa^{-1}	κ_S^E/TPa^{-1}
1,3-Dioxolane (i) + aniline (j)[a]			
0.0812	1587	391.9	−7.1
0.1413	1576	396.6	−11.2
0.2212	1557	404.5	−15.3
0.2916	1539	412.8	−18.4
0.3488	1523	420.3	−20.1
0.4621	1489	437.5	−22.4
0.5219	1470	447.8	−22.6
0.5928	1447	461.1	−22.6
0.6414	1431	470.9	−21.8
0.7131	1406	486.8	−20.4
0.8001	1374	508.3	−16.8
0.8715	1347	528.1	−12.4
0.9213	1327	543.3	−8.4
0.9711	1307	559.7	−3.2
1,3-Dioxolane (i) + N-methyl aniline (j)[b]			
0.0415	1521	442.8	−1.6
0.1211	1511	446.5	−5.1
0.2001	1501	450.7	−8.3
0.2754	1490	455.5	−10.8
0.3512	1477	461.3	−13.1
0.4222	1463	467.8	−14.5
0.4943	1447	475.7	−15.1
0.5421	1436	481.7	−15.2
0.6213	1415	492.8	−14.4
0.7003	1393	505.7	−12.6
0.7832	1367	521.1	−10.1
0.8632	1341	537.7	−6.6
0.9011	1329	546.1	−5.1
0.9632	1307	560.8	−1.9
1,3-Dioxolane (i) + *o*-toluidine (j)[c]			
0.1122	1539	425.7	−3.7
0.1891	1526	431.0	−6.9
0.2413	1516	435.1	−8.8
0.2911	1506	439.1	−10.8
0.3212	1500	441.7	−11.9
0.4011	1484	449.5	−14.5
0.4513	1473	455.2	−15.7
0.5651	1444	470.4	−17.1
0.6637	1415	487.1	−16.3
0.6989	1404	493.5	−15.8
0.7512	1386	504.4	−14.2
0.8319	1358	522.8	−11.1
0.9071	1330	542.3	−6.8
0.9713	1306	560.9	−2.4

Also included are various $\kappa_S{}^n$ (n = 0–2) parameters along with standard deviations, σ (κ_S^E).

[a] $\kappa_S^{(0)} = -90.5, \kappa_S^{(1)} = -11.9, \kappa_S^{(2)} = -18.9; \sigma(\kappa_S^E) = 0.1\ \ \text{TPa}^{-1}$.

[b] $\kappa_S^{(0)} = -60.3, \kappa_S^{(1)} = -6.3, \kappa_S^{(2)} = 14.9; \sigma(\kappa_S^E) = 0.1\ \ \text{TPa}^{-1}$.

[c] $\kappa_S^{(0)} = -65.3, \kappa_S^{(1)} = -24.0, \kappa_S^{(2)} = 6.3; \sigma(\kappa_S^E) = 0.1\ \ \text{TPa}^{-1}$.

the literature [23]. α_i for **D** was evaluated in the same manner as described elsewhere [24]. Such κ_S^E values for the investigated mixtures are recorded in Table 4. V^E, H^E and κ_S^E values for the investigated (i + j) mixtures are plotted in Figs. 1–3.

Measured vapour pressure of **D** (i) + **A** or **MA** or **OT** (j) binary mixtures are recorded in Table 5. The measured vapour pressure of the various (i + j) mixtures were then coupled with the corresponding liquid-phase composition of (i) to predict excess Gibb's free energy, G^E and activity coefficients of the components of mixtures (γ_i and $\gamma)_j$, assuming [25] that G^E data can be expressed by Eq. (5)

$$\frac{G^E}{RT} = x_A x_B \sum_{n=0} \left[G^n (x_A - x_B)^n \right] \qquad (5)$$

and that all second virial coefficients, β_{ij}'s are zero. These G^n (n = 0–2) parameters along with G^E values are recorded in Table 5 and plotted in Fig. 4.

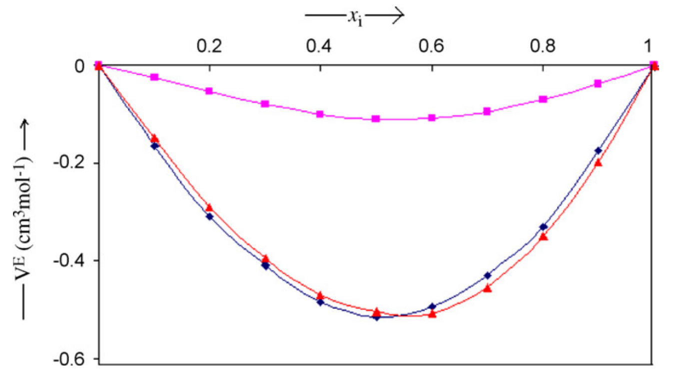


Fig. 1. Excess molar volumes, V^E at 308.15 K of 1, 3-dioxolane (i) + aniline (j) (♦); 1,3-dioxolane (i) + N-methylaniline (j) (■); 1,3-dioxolane (i) + *o*-toluidine (j) (▲).

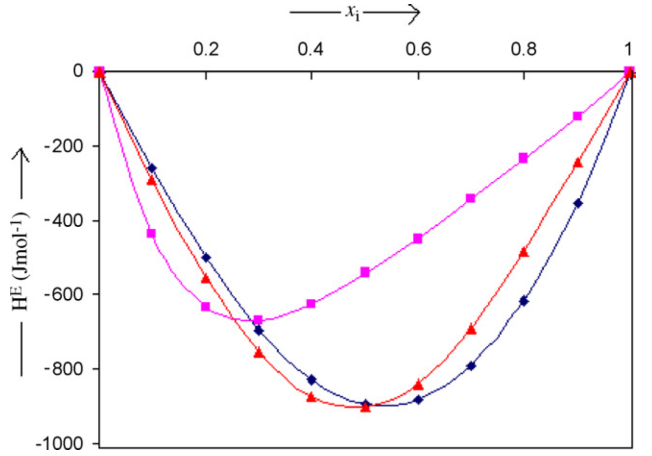


Fig. 2. Excess molar enthalpies, H^E at 308.15 K of 1,3-dioxolane (i) + aniline (j) (♦); 1,3-dioxolane (i) + N-methylaniline (j) (■); 1,3-dioxolane (i) + *o*-toluidine (j) (▲).

Excess molar volumes V^E, excess molar enthalpies, H^E and isentropic compressibilities changes of mixing, κ_S^E data were fitted to Eq. (6)

$$X^E(X = V \text{ or } H \text{ or } \kappa_S) = x_i x_j [X^{(0)} + X^{(1)}(2x_i - 1) + X^{(2)}(2x_i - 1)^2] \quad (6)$$

where $X^{(n)}(n = 0 - 2)$, etc. are the parameters characteristic of (i + j) mixtures. These parameters were evaluated by fitting $X^E(X = V$ or H or $\kappa_S)$ data to Eq. (6) by least squares methods and are recorded along with their standard deviations in Tables 2–4.

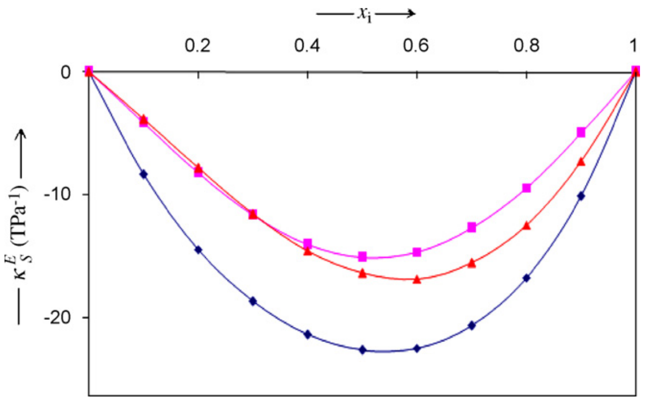


Fig. 3. Isentropic compressibilities of mixing, κ_S^E at 308.15 K of 1,3-dioxolane (i) + aniline (j) (♦); 1,3-dioxolane (i) + N-methylaniline (j) (■); 1,3-dioxolane (i) + *o*-toluidine (j) (▲).

Table 5
Measured vapour pressure, P and derived activity coefficients γ_i and γ_j for the various (i + j) mixtures as a function of mole fraction of component (j) at 308.15 K.

x_j	P (Torr)	γ_i	γ_j	G^E (J mol^{-1})
1,3-Dioxolane (i) + aniline (j)[a]				
0.0000	161.3	–	–	–
0.1324	130.3	0.5204	0.9623	−344.8
0.2421	108.9	0.6319	0.9155	−469.8
0.3453	84.5	0.7403	0.8512	−548.3
0.4443	65.4	0.8079	0.7974	−563.9
0.5216	54.2	0.8513	0.7541	−550.6
0.6211	39.8	0.8990	0.6934	−502.4
0.7435	25.2	0.9422	0.6190	−413.1
0.8435	12.2	0.9793	0.5223	−266.9
0.9041	7.0	0.9870	0.4900	−211.1
1.0000	0.9	–	–	–
1,3-Dioxolane (i) + *o*-toluidine (j)[b]				
0.0000	161.3	–	–	–
0.1123	130.8	0.5127	0.9714	−331.0
0.2222	111.8	0.5931	0.9366	−455.4
0.3343	91.1	0.6753	0.8871	−548.5
0.4543	67.1	0.7686	0.8109	−602.0
0.5256	54.2	0.8153	0.7627	−600.8
0.6543	34.4	0.8862	0.6706	−548.2
0.7543	19.2	0.9426	0.5709	−436.9
0.8432	8.6	0.9832	0.4616	−260.9
0.9001	7.9	0.9862	0.4484	−236.1
1.0000	0.5	–	–	–
1,3-Dioxolane (i) + N-methyl aniline (j)[c]				
0.0000	161.3	–	–	–
0.1532	138.8	0.4091	0.9615	−395.3
0.2432	112.6	0.5507	0.8962	−601.2
0.3553	91.2	0.6177	0.8545	−679.6
0.4432	74.2	0.6932	0.7945	−744.5
0.5556	60.2	0.7576	0.7267	−758.5
0.6671	46.4	0.8093	0.6574	−731.2
0.7432	32.0	0.8822	0.5353	−633.3
0.8654	17.0	0.9417	0.4096	−480.7
0.9010	8.1	0.9721	0.3296	−349.7
1.0000	0.8	–	–	–

Also included are various $G^{(n)}$ (n = 0–2) parameters.

[a] $G^{(0)} = -0.878$, $G^{(1)} = -0.088$, $G^{(2)} = -0.173$ J mol^{-1}.

[b] $G^{(0)} = -1.039$, $G^{(1)} = 0.0211$, $G^{(2)} = -0.1031$ J mol^{-1}.

[c] $G^{(0)} = -1.183$, $G^{(1)} = -0.101$, $G^{(2)} = -0.402$ J mol^{-1}.

4. Discussion

We are unaware of any V^E, H^E, κ_S^E and G^E data of the studied (i + j) mixtures with which to compare our results. V^E, H^E, κ_S^E and G^E data of **D** (i) + **A** or **MA** or **OT** (j) mixtures are negative over entire composition range. While H^E and κ_S^E data for an equimolar mixture vary in the order: **MA** > **OT** > **A**; V^E data vary as **MA** > **A** ≅ **OT**. However G^E data for the investigated mixtures at an equimolar composition vary in the order: **A** > **OT** > **MA** respectively.

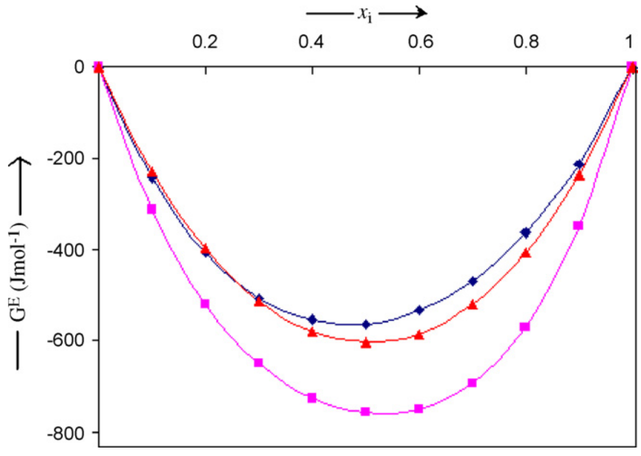


Fig. 4. Gibb's free energy at 308.15 K of 1,3-dioxolane (i) + aniline (j) (♦); 1,3-dioxolane (i) + N-methylaniline (j) (■); 1,3-dioxolane (i) + *o*-toluidine (j) (▲).

At the simplest qualitative level, H^E data of these mixtures can be explained, if it be assumed that (1) **D** (i) and **A** or **MA** or **OT** (j) are associated molecular entities; (2) there is interaction between lone pair of electrons on oxygen atom of **D** and hydrogen atom of **A** or **MA** or **OT**; (3) there is interactions between i_n and j_n molecules that leads to depolymerization of i_n or j_n to form their respective monomers; (4) monomers of i and j then undergo specific interactions to form i:j molecular complex. Negative H^E values of **D** (i) + **A** (j) mixtures suggest that contribution to H^E due to factors (2) and (4) far outweigh the contribution due to factor (3). The replacement of hydrogen atom by –CH_3 group in –NH_2 of **A** (as in **MA**) will increase the π-electron density on nitrogen atom, which in turn would lead to strong interaction between hydrogen atoms of **MA** with oxygen atom of **D**. Thus H^E for **D** (i) + **MA** (j) mixtures should be higher (more negative) than those for H^E **D** (i) + **A** (j) mixtures. This is not true. High H^E values for **D** (i) + **MA** (j) mixtures than those for **D** (i) + **A** (j) mixtures suggest that contribution to H^E due to depolymerization of **MA** is less than that of aniline. Further introduction of –CH_3 group in benzene ring of **A** (as in **OT**) would also increase the electron density on nitrogen atom of **OT** and will be less as compared to **MA**. Thus H^E values for **D** (i) + **OT** (j) should be higher than those for **D** (i) + **A** (j) mixtures. This is indeed true.

V^E and κ_S^E data of the investigated mixtures suggest that **D** gives relatively more packed arrangement in aniline as compared to **MA** or **OT**. This may be due to the presence of –CH_3 group in **MA** or **OT** which restrict approach of **D** (i) molecules.

5. Graph theory and results

5.1. Excess molar volumes

According to Graph theory [26], excess molar volumes, V^E for a binary (i + j) mixture is given by

$$V^E = \alpha_{ij}\{[\sum x_i(^3\xi_i)_m]^{-1} - [\sum x_i(^3\xi_i)]^{-1}\} \qquad (7)$$

where x_i is the mole fraction of component (i).($^3\xi_i$), $(^3\xi_i)_m$ (i = i or j), etc. are the connectivity parameters of the third degree of a molecule in pure and mixed state and are defined by Eq. (8)

$$^3\xi = \sum_{m<n<o<p} (\delta_m^v \delta_n^v \delta_o^v \delta_p^v)^{-0.5} \qquad (8)$$

where δ_m^v, etc. have the same significance as described elsewhere [27]. ($^3\xi_i$) or $(^3\xi_i)_m$ (i = i or j) for the various of constituents, etc. parameters were predicted by fitting experimental V^E data to Eq. (7) and only those values of ($^3\xi_i$), $(^3\xi_i)_m$ (i = i or j) parameters were retained that best describe the experimental V^E data. Such parameters, together with V^E values [calculated via. Eq. (7)] at various x_i are recorded in Table 2 and compared with experimental V^E values. Examination of V^E data in Table 2 reveals that calculated V^E values compare well with their experimental values and thus these parameters can be relied upon to predict state of aggregation of components i/j in pure and mixed state.

A number of structures were then assumed for pure **D**, **A**, **MA**, **OT** and their $^3\xi'$ values were evaluated from their structural consideration [via. Eq. (9)]. $^3\xi'$ values were then compared with $^3\xi$ values (obtained via Eq. (7)) from V^E data. Any structure or combination of structures that yielded $^3\xi'$ value that compare well with $^3\xi_i$ value was taken to be representative structure of that component. For the investigated mixtures, we assumed that **D**, **A**, **MA** and **OT** exist as molecular entities **I–II**, **III–IV**, **V–VI** and **VII–VIII** respectively (Scheme 1) and their $^3\xi'$ values were then calculated to be 0.543, 1.364, 1.361, 1.890, 1.256, 1.814, 0.949 and 1.405 respec-

Table 6
Comparison of $V^{E,}$, H^E, κ_S^E values calculated from Eqs. (7) and (10) with their corresponding experimental values at 308.15 K for the various (i + j) mixtures as a function of x_i, mole fraction of component (i).

Property	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
1,3-Dioxolane (i) + aniline (j)[a]									
V^E (Exptl)	−0.165	−0.310	−0.410	−0.485	−0.515	−0.495	−0.430	−0.330	−0.175
V^E (Graph)	−0.138	−0.262	−0.369	−0.455	–	−0.540	−0.522	−0.444	−0.282
H^E (Exptl)	−260.1	−498.8	−694.0	−830.1	−895.0	−885.2	−792.9	−616.0	−352.1
H^E (Graph)	−255.1	−493.8	−690.1	–	−895.8		−796.6	−620.3	−355.5
κ_S^E (Exptl)	−8.3	−14.4	−18.6	−21.3	−22.6	−22.4	−20.6	−16.7	−10.1
κ_S^E (Graph)	−7.0	−13.1	−18.0	–	−22.8	–	−20.0	−15.5	−8.8
1,3-Dioxolane (i) + N-methyl aniline (j)[b]									
V^E (Exptl)	−0.025	−0.053	−0.079	−0.099	−0.109	−0.107	−0.094	−0.071	−0.038
V^E (Graph)	−0.030	−0.055	−0.078	−0.096	–	−0.115	−0.111	−0.095	−0.061
H^E (Exptl)	−435.9	−633.9	−672.7	−624.1	−543.2	−451.2	−342.2	−232.2	−121.1
H^E (Graph)	−412.2	−597.2	−650.1	–	−551.0	–	−338.1	−221.1	−106.7
κ_S^E (Exptl)	−4.1	−8.2	−11.6	−14.0	−15.1	−14.6	−12.7	−9.4	−4.9
κ_S^E (Graph)	−4.6	−8.7	−11.9	–	−14.9	–	−13.0	−10.0	−5.7
1,3-Dioxolane (i) + *o*-toluidine (j)[c]									
V^E (Exptl)	−0.148	−0.290	−0.396	−0.470	−0.506	−0.508	−0.455	−0.349	−0.198
V^E (Graph)	−0.138	−0.261	−0.366	−0.450	–	−0.528	−0.506	−0.426	−0.267
H^E (Exptl)	−291.9	−553.5	−754.4	−874.3	−903.0	−839.7	−693.7	−484.2	−240.0
H^E (Graph)	−358.8	−615.6	−784.5	–	−891.3	–	−722.7	−542.7	−301.3
κ_S^E (Exptl)	−3.9	−7.8	−11.1	−14.0	−16.5	−16.8	−15.8	−12.8	−7.0
κ_S^E (Graph)	−3.4	−7.4	−11.4	–	−16.3	–	−15.5	−12.3	−7.2

Also included are various $({}^3\xi_i)$ and $({}^3\xi_i)_m$ (i = i or j); α_{ij} and χ'_{ij}, etc. parameters.

[a] $({}^3\xi_i)=({}^3\xi_i)_m=0.601$; $({}^3\xi_j)=({}^3\xi_j)_m=1.500$; $\alpha_{ij}=2.403$; $\chi'_{ij}=-5017.5$ J mol^{-1}; $\chi_{12}=2510.8$ J mol^{-1}; $\chi'_{ij}=-124.0$ TPa^{-1}; $\chi_{12}=52.7$ TPa^{-1}.

[b] $({}^3\xi_i)=({}^3\xi_i)_m=0.601$; $({}^3\xi_j)=({}^3\xi_j)_m=1.801$; $\alpha_{ij}=0.483$; $\chi'_{ij}=-1523.3$ J mol^{-1}; $\chi_{12}=-4247.0$ J mol^{-1}; $\chi'_{ij}=-96.1$ TPa^{-1}; $\chi_{12}=48.8$ TPa^{-1}.

[c] $({}^3\xi_i)=({}^3\xi_i)_m=0.601$; $({}^3\xi_j)=({}^3\xi_j)_m=1.401$; $\alpha_{ij}=2.657$; $\chi'_{ij}=-3860.8$ J mol^{-1}; $\chi_{12}=-301.1$ J mol^{-1}; $\chi'_{ij}=-96.1$; $\chi_{12}=70.4$ TPa^{-1}.

tively. ${}^3\xi_i$ values of 0.601, 1.501, 1.801, 1.401 (Table 6) for **D**, **A**, **MA**, **OT** suggest that they exists as an associated molecular entities in pure state. Further to extract information about the state of **A** or **MA** or **OT** (i) in **D** (j), it was assumed that these binary mixtures may contain molecular entities **IX**–**XI**. In evaluating $({}^3\xi'_j)_m$ values for molecular entities IX–X it was assumed that only N–H edge of **A** or **MA** or **OT** is involved in interaction with oxygen atom of **D**. $({}^3\xi'_j)_m$ values for molecular entities **IX, X** and **XI** were then calculated to be 1.658, 1.389 and 1.658 respectively. $({}^3\xi_j)_m$ values of 1.500, 1.801 and 1.401 (Table 2) suggest that studied mixtures contain molecular entities **IX**–**XI**. The presence of molecular entities **IX**–**XI** in (i + j) mixtures suggest that addition of **A** or **MA** or **OT** (j) to **D** (i) should have influenced –N–H vibrations of **A** or **MA** or **OT** and C–O vibrations of **D**. For this purpose we analyzed the IR spectral data of pure **D** or **A** or **MA** or **OT** and equimolar mixtures of **D** (i) + **A** or **MA** or **OT** (j) binary mixtures. It was observed that while **D, A, MA** or **OT** in their pure state showed characteristic absorption at 1128 cm^{-1} (C–O vibration) and 3408, 3412, 3410 (N–H stretch) [28], the IR spectra of **D** (i) + **A** or **MA** or **OT (j)** equimolar mixtures showed characteristic absorption at 1150, 1148, 1155 cm^{-1} (C–O stretch)and 3430, 3422, 3428 cm^{-1} (N–H stretch) respectively. The IR data thus leads credence to the suggestion that of (j) to (i) does influence the C–O vibrations of **D** and N–H stretching vibrations of **A or MA** or **OT** which in turn support the existence of molecular entities **IX**–**XI**.

5.2. *Excess molar enthalpies and isentropic compressibilities changes of mixtures*

H^E and κ_S^E data of studied (i + j) mixtures were then analyzed in terms of Graph theory. For this purpose, it was assumed that in **D** (i) + **A** or **MA** or **OT** (j) binary mixtures formation involve processes; (1) the formation of unlike contact between i_n and j_n molecules; (2) unlike contact i_n–j_n formation then weakens i_n–j_n interactions and leads to the depolymerization of i_n and j_n to form their respective monomers; (3) the monomers of i and j then undergo specific interactions to form i:j molecular complex. If χ_{ij}, χ_{ii}, χ_{jj} and χ_{12} are molar interactions and molar compressibility interactions parameters for i–j, i–i, j–j contacts and specific interactions respectively, then change in molar thermodynamic property, ΔX ($X = H$ *or* κ_S) due to processes {1,2 and 3} would be given [29–32] by relations

$$X^E = \left[\frac{x_i x_j\left({}^3\xi_i/{}^3\xi_j\right)}{x_i + x_j\left({}^3\xi_i/{}^3\xi_j\right)}\right]\left[\chi_{ij} + x_i\chi_{ii} + x_i\chi_{jj} + x_j\chi_{12}\right] \tag{9}$$

For the studied mixtures, it is reasonable to assume that $\chi_{ij} \cong \chi_{12} = \chi'_{ij}$ and $\chi_{ii} = \chi_{jj} = \chi^{*'}$, the Eq. (9) can be expressed by

$$X^E = \left[\frac{x_i x_j\left({}^3\xi_i/{}^3\xi_j\right)}{x_i + x_j\left({}^3\xi_i/{}^3\xi_j\right)}\right]\left[\left(1 + x_j\right)\chi'_{ij} + 2x_i\chi^*\right] \tag{10}$$

Eq. (10) contains two unknown parameters and we evaluated these parameters by employing, H^E and κ_S^E data of the investigated (i + j) binary mixtures at two compositions. These parameters were then employed 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^* parameters are recorded in Table 6.

An examination of Table 6 data reveals that H^E and κ_S^E values compare well with their corresponding experimental values. This lends additional support to the assumptions made in deriving Eq. (10)

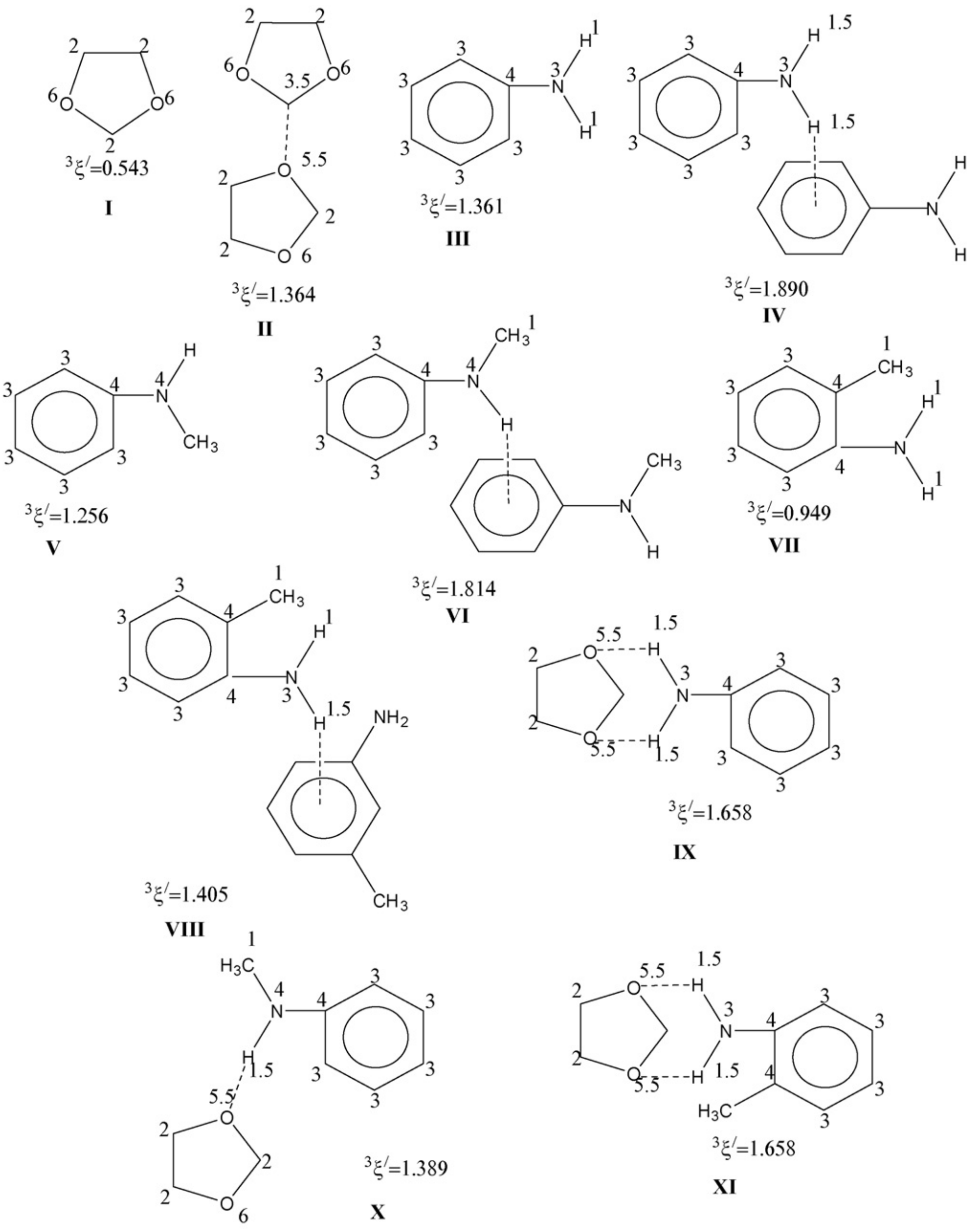
5.3. *Excess Gibb's free energy*

Excess Gibb's free energy of mixing at any temperature is given by

$$G^E = RT(x_i \ln\gamma_i + x_j \ln\gamma_j) \tag{11}$$

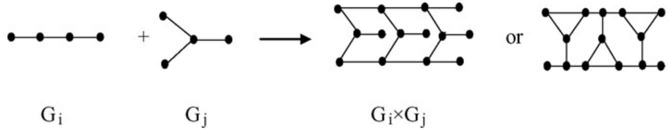
5.3.1.1. *Topological aspects of the activity coefficients of the components constituting a binary mixture*

According to mathematical discipline of graph theory, structural formula of chemists is actually a molecular graph [33] characterized by vertices (atoms) and edges (bonds) G (e, v). If the pure components i/j are represented by G_i (e_i, v_i) and G_j (e_j, v_j) respectively,then



Scheme 1. Connectivity parameters of various molecular entities.

molecular interactions in (i + j) mixture can be characterized by $G_i \times G_j$ molecular graph [34].



The activity coefficient, γ_i of components (i) in a (i + j) mixture varies $\gamma_i \to 1$ as $x_i \to 1$ and provides information about change in i–i interaction on the addition jth component in the mixture. Further, interactions between components of mixtures would depends upon (i) surface area of j that comes in to contact with surface area of i to form effective i–j contacts and (ii) the magnitude of molar interaction energy, χ'_{ij} among the constituents of mixtures. Based on this consideration, Singh et al. [35] expressed activity coefficient, γ_i in an (i + j) mixture by Eq. (12)

$$\ln \gamma_i = \frac{x_i \gamma_i \chi_{ij}}{RT \sum x_i \upsilon_i} \qquad (12)$$

where the standard state of i, is that of pure i; υ_i and χ_{ij} are molar volume of component (i) and molar interaction energy due to interaction between i and j respectively. The activity coefficients of jth component in (i + j) mixture was determined by employing Gibb's Duhem equation and expressed [36] by

$$\ln \gamma_j = \left[\frac{\chi_{ij}\upsilon_j}{RT\upsilon_i}\right]\left[\ln \frac{\sum x_i \upsilon_i}{x_j \upsilon_j} - \frac{x_i \upsilon_i}{\sum x_i \upsilon_i}\right] \qquad (13)$$

It has been assumed in deriving Eqs. (12) and (13) that components of mixture have nearly the same molar volume, so that on the addition of i to j there is no appreciable changes in their surroundings. As in the investigated (i + j) mixtures molar volumes of components i and j are not equal, so above equations are will not be valid to predict activity coefficients γ_i and γ_j. Consequently for these mixtures the activity coefficients of components (i) have been determined not by considering only the i–j molecular interactions but also by the work done in accommodating the jth component in to the matrix of ith component. If the effects due to i–j interaction

Table 7

Comparison of G^E values calculated from Eqs. (11), (16) and (17) with their corresponding experimental values at 308.15 K as a function of x_j, mole fraction of component (j).

Property	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
1,3-Dioxolane (i) + aniline (j)[a]									
G^E (Exptl)	−244.1	−406.9	−506.1	−554.9	−562.4	−533.3	−468.4	−363.8	−211.7
G^E (Graph)	−231.1	−431.3	−548.9	−582.9	–	−509.4	−433.4	−334.4	−204.7
γ_i (Exptl)	0.4500	0.5713	0.6740	0.7560	0.8207	0.8735	0.9188	0.9577	0.9875
γ_i (Graph)	0.4712	0.5557	0.6550	0.7472	–	0.8763	0.9185	0.9514	0.9779
γ_j (Exptl)	0.9830	0.9431	0.8931	0.8399	0.7855	0.7279	0.6625	0.5842	0.4900
γ_j (Graph)	0.9867	0.9384	0.8827	0.8311	–	0.7416	0.6939	0.6354	0.5496
1,3-Dioxolane (i) + N-methyl aniline (j)[b]									
G^E (Exptl)	−313.6	−519.6	−649.6	−725.0	−757.8	−749.8	−692.8	−569.1	−350.7
G^E (Graph)	−282.1	−487.5	−630.7	−719.5	–	746.1	−683.2	−562.2	−365.4
γ_i (Exptl)	0.3628	0.4899	0.5906	0.6656	0.7255	0.7825	0.8444	0.9113	0.9718
γ_i (Graph)	0.3836	0.4818	0.5712	0.6523	–	0.7917	0.8516	0.9058	0.9551
γ_j (Exptl)	0.9769	0.9276	0.8724	0.8185	0.7629	0.6951	0.6024	0.4775	0.3291
γ_j (Graph)	0.9842	0.9462	0.8943	0.8326	–	0.6854	0.5981	0.4938	0.3632
1,3-Dioxolane (i) + *o*-toluidine (j)[c]									
G^E (Expt)	−228.8	−396.7	−511.8	−579.9	−604.1	−585.1	−520.9	−407.1	−236.6
G^E (Graph)	−225.0	−414.5	−540.2	−598.1	–	−571.8	−506.7	−406.3	−258.8
γ_i (Expt)	0.4582	0.5526	0.6388	0.7163	0.7858	0.8486	0.9047	0.9522	0.9865
γ_i (Graph)	0.4687	0.5472	0.6334	0.7154	–	0.8440	0.8924	0.9334	0.9688
γ_j (Expt)	0.9876	0.9557	0.9109	0.8566	0.7941	0.7228	0.6415	0.5497	0.4489
γ_j (Graph)	0.9867	0.9498	0.8998	0.8472	–	0.7381	0.6746	0.5961	0.4843

Also included $(^3\xi_i)$ and $(^3\xi_i)_m$ (i = i or j); β and χ'_{ij} parameters for the various (i + j) mixtures.

[a] $(^3\xi_i) = (^3\xi_i)_m = 0.601$; $(^3\xi_j) = (^3\xi_j)_m = 1.501$; $\beta = -983.7$; $\chi'_{ij} = -1296.9\ \mathrm{J\,mol^{-1}}$.

[b] $(^3\xi_i) = (^3\xi_i)_m = 0.601$; $(^3\xi_j) = (^3\xi_j)_m = 1.801$; $\beta = 17.3$; $\chi'_{ij} = -3296.3\ \mathrm{J\,mol^{-1}}$.

[c] $(^3\xi_i) = (^3\xi_i)_m = 0.601$; $(^3\xi_j) = (^3\xi_j)_m = 1.401$; $\beta = -612.5$; $\chi'_{ij} = -1756.9\ \mathrm{J\,mol^{-1}}$.

(neglecting the difference in molar volumes of i and j) Eq. (12) and that due to difference in molar volumes of i and j are assumed to move independent contributions to the activity coefficients of the components of a binary (i + j), then Singh et al. [35], suggested that activity coefficients γ_i and γ_j can be expressed by

$$RT\ln(\gamma_i) = \frac{\chi_{ij}x_j v_j}{\sum x_i v_i} + \frac{\beta v_i v_j^2 x_j^2 (1 - v_j/v_i)}{\sum (x_i v_i)^2} \tag{14}$$

$$RT\ln(\gamma_j) = \left[\chi_{ij}\frac{v_j}{v_i}\right]\left[\ln\frac{\sum x_i v_i}{x_j v_j} - \frac{x_i v_i}{\sum x_i v_i}\right] + \frac{\beta x_i^2 v_i^2 v_j (1 - v_j/v_i)}{\sum (x_i v_i)^2} \tag{15}$$

Since $v_j/v_i = {}^3\xi_i/{}^3\xi_j$ [37]; Eqs. (14) and (15) reduces to

$$RT\ln(\gamma_i) = \left[\frac{x_j\chi_{ij}(^3\xi_i/^3\xi_j)}{x_i + x_j(^3\xi_i/^3\xi_j)}\right] + \frac{\beta(1/^3\xi_i)(^3\xi_i/^3\xi_j)^2 x_j^2(1 - {}^3\xi_i/^3\xi_j)}{x_i^2 + x_j^2(^3\xi_i/^3\xi_j)^2} \tag{16}$$

$$RT\ln(\gamma_j) = \left[\chi_{ij}(^3\xi_i/^3\xi_j)\right]\left[\ln\left(\frac{x_i + x_j(^3\xi_i/^3\xi_j)}{x_j(^3\xi_i/^3\xi_j)}\right) - \frac{x_i}{x_i + x_j(^3\xi_i/^3\xi_j)}\right] + \frac{\beta x_i^2(1/^3\xi_j)[1 - (^3\xi_i/^3\xi_j)]}{x_i^2 + x_j^2(^3\xi_i/^3\xi_j)^2} \tag{17}$$

where β is a constant characteristic of (i + j) mixture. Eqs. (16) and (17) contain two unknown parameters χ_{ij} and β. The values of χ_{ij} (calculated via Eq. (15) by employing H^E data) along with activity coefficient data of a component at single composition ($x_i = 0.5$) were utilized to predict β values which were subsequently employed to predict to γ_i and γ_j at other compositions. Such β values along with (γ_i, γ_j ; x_i) and G^E values (calculated via Eqs. (11), (16), (17)) are recorded in Table 7 and also compared with experimental values.

Examination of data in Table 7 shows that (γ_i, γ_j ; x_i) data for the components of the (i + j) mixtures, along with G^E data of the investigated mixtures values compare well with their corresponding experimental (γ_i, γ_j ; x_i) and G^E values which in turn lends additional support to the assumptions made in deriving Eqs. (16) and (17).

TS^E values for 1,3-dioxolane (i) + aniline, or N-methylaniline or *o*-toluidine (j) have also been estimated using Eq. $TS^E = (H^E - G^E)$ from the observed G^E and H^E and for an equimolar composition are −336, 212 and −238 $\mathrm{J\,mol^{-1}}$ respectively. Positive values of TS^E for **D** + **MA** in comparison to negative values of TS^E for **D** + **A** or **OT** may be due to the lesser self association of **MA** as compared to **A** or **OT**. These observations are consistent with the observations inferred from the qualitative interpretation of H^E data of the investigated mixtures.

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