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Thermodynamic Properties of Binary Mixtures of Tetrahydropyran with Anilines at 308.15 K[†]

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Excess molar volumes, V^E, excess molar enthalpies, H^E, speeds of sound, u, and vapor−liquid equilibrium data of tetrahydropyran (1) + aniline or *N*-methylaniline or 2-methylaniline (2) binary mixtures have been measured over the entire mole fraction range at 308.15 K. Speeds of sound and vapor−liquid equilibrium data have been utilized to predict isentropic compressibility changes of mixing, κ_S^E, and excess Gibb's free energy, G^E. The observed V^E, H^E, κ_S^E, and G^E data have been analyzed in terms of Graph theory. It has been observed that V^E, H^E, κ_S^E, and G^E predicted by Graph theory compare well with their corresponding experimental values.

Introduction

Thermodynamic properties of liquid mixtures like excess molar volumes, V^E, excess molar enthalpies, H^E, isentropic compressibility changes of mixing, κ_S^E, and excess Gibb's free energy, G^E, have extensive applications in chemical engineering, design calculations for heat transfer, mass transfer and fluid flow,[1] process simulation, solution theory, and molecular dynamics. In recent studies,[2−4] 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 of binary liquid mixtures. An attempt has been made here to predict excess Gibb's free energy of binary mixtures by employing the topology of a molecule.

Experimental Section

Materials. Tetrahydropyran (THP) (Fluka, > 0.98 GC), aniline (A) (Fulka, > 0.98 GC), *N*-methylaniline (MA) (Fluka, > 0.98 GC), and 2-methylaniline (2MA) (Fluka, > 0.99 GC) were purified by standard methods.[5] The purities of the purified liquids were checked by measuring their densities [recorded in Table 1] using a bicapillary pycnometer at (298.15 ± 0.01) K, and these agreed to within ± 0.05 kg·m^{-3} with their literature values.[4,5]

Apparatus and Procedure. Excess molar volumes, V^E, excess molar enthalpies, H^E, and speeds of sound, u, were determined by a dilatometer, 2-drop calorimeter, and interferometer, respectively, in the manner described elsewhere.[6,3,7] The uncertainties in the measured V^E, H^E, and u values are 0.5 %, 1 %, and 1 ms^{-1}, respectively. The uncertainty in the mole fraction of mixtures used for measuring V^E, H^E, and κ_S^E is 10^{-4}.

Total vapor pressures of various binary mixtures were measured as a function of the liquid-phase mole fraction of (1), x_1, at (308.15 ± 0.01) K by a static method[8] in the manner described elsewhere.[9] The composition of the liquid phase was determined interferometrically using a Carl Zeiss interferometer in the manner described earlier.[10] The uncertainties in the liquid phase composition were about 0.01 mol %. The errors in the vapor pressure determinations were estimated to be ± 0.01 kPa. Our measured vapor pressures (Table 1) for THP, A, MA, and 2MA compare well with their corresponding literature[11−14] values at 298.15 K within the experimental uncertainties.

Table 1. Comparison of Densities, Speeds of Sound, *u*, and Vapor Pressure of Pure Liquids with Their Literature Values at 298.15 K

	ρ/kg·m^{-3}		u/m·s^{-1}		P/Pa	
liquids	exptl	lit.	exptl	lit.	exptl	lit.
THP	868.6	868.8[b]	1388	1388.8[b]	9525	9536[e]
A	1017.2	1017.4[a]	1635	1634[c]	93	89[f]
MA	982.4	982.2[a]	1572	1573[d]	66	60[g]
2-MA	994.2	994.3[a]	1602	_	41	42[h]

[a] Ref 5. [b] Ref 4. [c] Ref 17. [d] Ref 18. [e] Ref 11. [f] Ref 12. [g] Ref 13. [h] Ref 14.

Results and Discussion

Excess molar volumes, V^E, excess molar enthalpies, H^E, and speeds of sound, u, data of THP (1) + A or MA or 2MA (2) mixtures measured as a function of composition at 308.15 K are plotted in Figures 1 and 2 and reported in Table 2, respectively. The isentropic compressibilities, κ_S, and isentropic compressibilities changes of mixing, κ_S^E, for (1 + 2) mixtures were determined by employing their speeds of sound data and the Benson and Kiyohara equation[15] in the manner described elsewhere. Such κ_S and κ_S^E values for the investigated mixtures are recorded in Table 2. Measured vapor pressures for THP (1) + A or MA or 2MA (2) binary mixtures at 308.15 K over the entire composition range are reported in Table 3. The measured vapor pressures were then coupled with the corresponding liquid-phase composition of (1) to predict excess Gibb's free energy, G^E, and activity coefficient of the mixtures, assuming[16] that G^E data can be expressed by eq 1

$$G^E/RT = x_1 x_2 \sum_{n=0}^{2} [G^n (x_1 - x_2)^n] \qquad (1)$$

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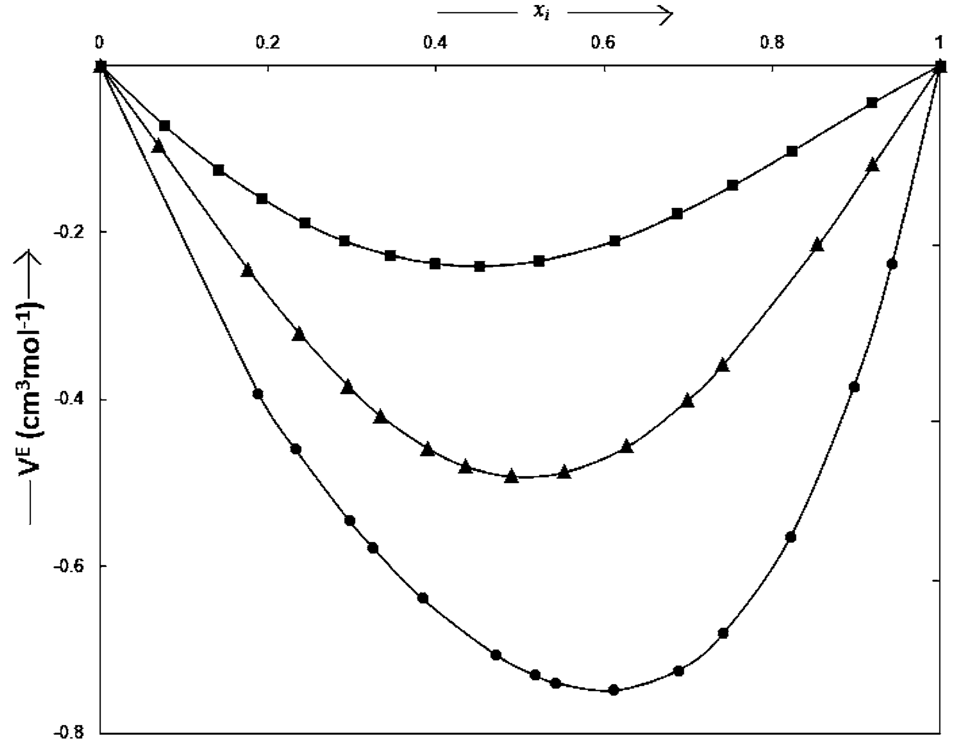


Figure 1. Excess molar volumes, V^E, at 308.15 K: ▲, THP (1) + A (2); ■, THP (1) + MA (2); ●, THP (1) + 2MA (2).

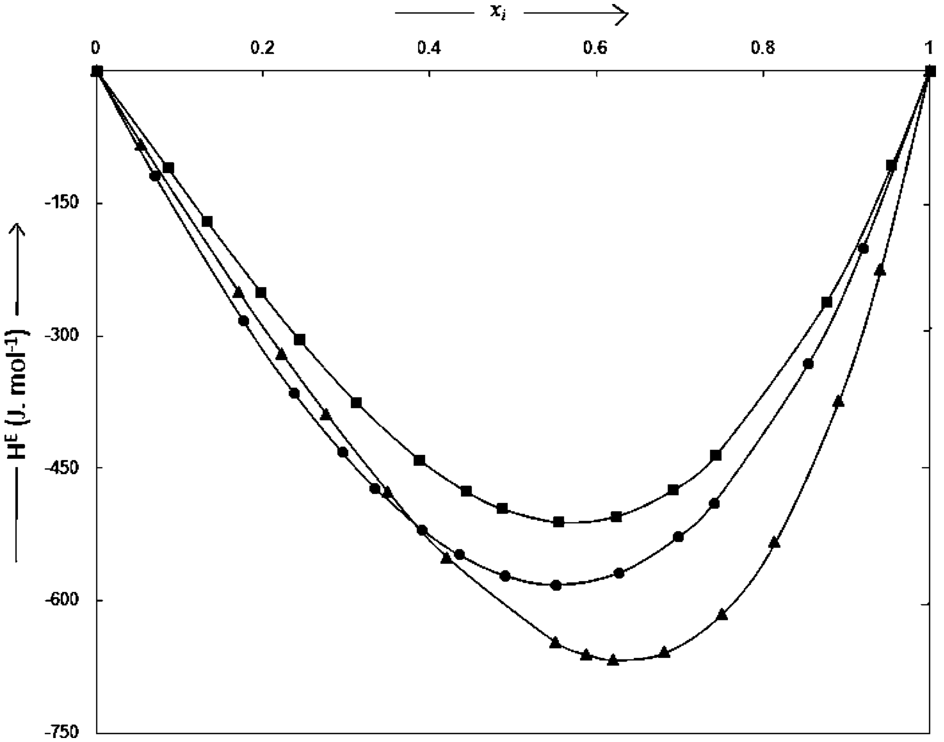


Figure 2. Excess molar enthalpies, H^E, at 308.15 K: ▲, THP (1) + A (2); ■, THP (1) + MA (2); ●, THP (1) + 2MA (2).

All second virial coefficients, β_{12}, were zero. These G^n ($n = 0$ to 2) parameters along with G^E values are recorded in Table 3. V^E, H^E, and κ_S^E data were fitted to eq 2

$$X^E\ (X = V \text{ or H or } \kappa_S) = x_1x_2[X^{(0)} + X^{(1)}(2x_1 - 1) + X^{(2)}(2x_2 - 1)^2] \quad (2)$$

where $X^{(n)}$ ($n = 0$ to 2), etc., are the parameters characteristic of (1 + 2) mixtures. These parameters were evaluated by least-squares methods and are recorded along with standard deviations, $\sigma(X^E)$ ($X = V$ or H or κ_S), in Tables 2 and 4.

We are unaware of any V^E, H^E, κ_S^E, and G^E data of the studied mixtures with which to compare our results. However, speeds of sound values for the purified liquids at (298.15 ± 0.01) K (recorded in Table 1) compare well with their corresponding experimental values.[4,17,18] V^E, H^E, κ_S^E, and G^E data of these mixtures are negative over entire mole fraction range. While H^E data for an equimolar mixture vary in the order MA > 2MA > A, V^E data vary as MA > A > 2MA. Further, $\kappa_S{}^E$ and G^E

Table 2. Speeds of Sound, u, Isentropic Compressibilities, κ_S, and Isentropic Compressibility Changes of Mixing, κ_S^E, for the Various (1 + 2) Mixtures As a Function of Mole Fraction, x_1, of Component (1) at 308.15 K

x_1	u / $m \cdot s^{-1}$	κ_S / TPa^{-1}	κ_S^E / TPa^{-1}
THP (1) + A (2)[a]			
10.0912	1564	410.0	−14.3
0.1516	1543	425.2	−23.6
0.2414	1510	448.8	−35.4
0.2990	1490	465.0	−42.1
0.3541	1470	481.4	−47.2
0.4417	1438	509.7	−52.5
0.5312	1404	541.8	−54.7
0.5943	1379	566.7	−53.6
0.6511	1357	590.6	−50.8
0.7344	1324	628.4	−43.8
0.8117	1294	666.2	−34.3
0.8830	1267	703.3	−23.0
0.9413	1245	735.2	−12.3
0.9812	1231	757.6	−4.1
THP (1) + MA (2)[b]			
0.0541	1509	453.0	−4.2
0.1321	1490	468.2	−12.2
0.2316	1468	486.9	−24.1
0.2811	1457	496.8	−29.6
0.3612	1437	514.4	−37.2
0.4112	1424	526.8	−40.5
0.4932	1400	550.3	−43.8
0.5638	1377	573.2	−43.8
0.6148	1360	591.8	−42.4
0.6919	1332	622.7	−37.4
0.7418	1313	644.4	−32.6
0.8141	1287	677.6	−24.4
0.8992	1257	718.8	−13.4
0.9514	1239	744.5	−6.1
THP (1) + 2-MA (2)[c]			
0.0832	1535	433.3	−11.2
0.1451	1505	453.5	−19.5
0.2102	1475	479.9	−28.1
0.2918	1441	502.2	−37.5
0.3581	1414	524.6	−43.8
0.4002	1399	539.1	−47.3
0.4981	1364	573.0	−52.8
0.5638	1343	596.1	−54.2
0.6118	1328	613.1	−54.0
0.7148	1299	650.3	−49.2
0.7981	1277	680.8	−40.8
0.8412	1267	696.8	−34.6
0.9003	1253	718.9	−23.8
0.9628	1240	742.6	−9.8

Also included are various κ_S^n ($n = 0$ to 2) parameters along with standard deviations, $\sigma(\kappa_S^E)$: [a] $\kappa_S^{(0)} = -217.4$, $\kappa_S^{(1)} = -30.0$, $\kappa_S^{(2)} = 28.8$; $\sigma(\kappa_S^E) = 0.1$ TPa^{-1}. [b] $\kappa_S^{(0)} = -175.9$, $\kappa_S^{(1)} = -30.8$, $\kappa_S^{(2)} = 85.3$; $\sigma(\kappa_S^E) = 0.1$ TPa^{-1}. [c] $\kappa_S^{(0)} = -211.9$, $\kappa_S^{(1)} = -71.6$, $\kappa_S^{(2)} = 5.3$; $\sigma(\kappa_S^E) = 0.1$ TPa^{-1}.

Table 3. Measured Vapor Pressure, P, and Derived Activity Coefficients γ_1 and γ_2 for the Various (1 + 2) Mixtures As a Function of Mole Fraction of Component, x_2, at 308.15 K

x_2	P / Pa	γ_1	γ_2	G^E / $J \cdot mol^{-1}$
THP (1) + A (2)[a]				
0.0000	13775	-	-	-
0.0502	12816	0.5492	0.9913	−81.0
0.1501	11510	0.6242	0.9842	−214.4
0.2510	9858	0.6941	0.9587	−312.9
0.3511	8153	0.7598	0.9226	−374.6
0.4504	6594	0.8195	0.8775	−413.6
0.5503	5062	0.8720	0.8247	−415.2
0.6513	3757	0.9172	0.7645	−385.0
0.7522	2438	0.9548	0.6963	−321.3
0.8511	1385	0.9827	0.6207	−221.4
0.9502	559	0.9979	0.5399	−84.3
1.0000	120	-	-	-
THP (1) + MA (2)[b]				
0.0000	13775	-	-	-
0.0511	12949	0.3713	0.9954	−132.8
0.1510	11230	0.5045	0.9634	−343.8
0.2522	9472	0.6128	0.9187	−472.9
0.3501	7660	0.7032	0.8672	−553.0
0.4531	6141	0.7689	0.8175	−586.5
0.5521	4729	0.8232	0.7641	−584.8
0.6501	3384	0.8743	0.6983	−545.8
0.7533	2145	0.9209	0.6182	−468.5
0.8502	1106	0.9651	0.5121	−336.1
0.9521	413	0.9951	0.3871	−136.1
1.0000	107	-	-	-
THP (1) + 2-MA (2)[c]				
0.0000	13775	-	-	-
0.0501	13002	0.5699	1.0005	−67.8
0.1541	11523	0.5795	0.9978	−213.2
0.2500	10058	0.6246	0.9788	−341.4
0.3541	8286	0.6934	0.9355	−438.6
0.4501	6528	0.7738	0.8695	−492.2
0.5511	4862	0.8551	0.7889	−496.6
0.6507	3397	0.9210	0.7049	−453.2
0.7511	2185	0.9706	0.6252	−358.1
0.8508	1265	0.9937	0.5708	−234.8
0.9521	453	1.0001	0.5439	−78.0
1.0000	67	-	-	-

Also included are various $G^{(n)}$ ($n = 0$ to 2) parameters: [a] $G^{(0)} = -0.653$, $G^{(1)} = 0.012$, $G^{(2)} = -0.032$ J·mol^{-1}. [b] $G^{(0)} = -0.921$, $G^{(1)} = -0.021$, $G^{(2)} = -0.240$ J·mol^{-1}. [c] $G^{(0)} = -0.782$, $G^{(1)} = 0.032$, $G^{(2)} = 0.211$ J·mol^{-1}.

values at equimolar composition follow the order: 2MA ≅ MA > A and A > 2MA > MA, respectively.

Graph Theory and Results

Excess Molar Volumes. According to Graph theory, excess molar volumes, V^E, for binary mixtures are given[19] by

$$V^E = \alpha_{12}\{[\sum_{i=1}^{2} x_i({}^3\xi_i)_m]^{-1} - [\sum_{i=1}^{2} x_i({}^3\xi_i)_m^{-1}]\} \quad (3)$$

where α_{12} is a constant characteristics of (1 + 2) mixtures. $({}^3\xi_i)$, $({}^3\xi_i)_m$ ($i = 1$ or 2), etc. are the connectivity parameters of the third degree of components (1) and (2) in the pure and mixed state and are defined by the relation

$${}^3\xi = \sum_{m<n<0<p} (\delta_m^\nu \delta_n^\nu \delta_o^\nu \delta_p^\nu)^{-0.5} \quad (4)$$

where δ_m^ν, etc. have the same significance as described elsewhere.[20] ${}^3\xi$, etc. parameters were determined by fitting experimental V^E data to eq 3, and only those values of $({}^3\xi_i)$ and $({}^3\xi_i)_m$ ($i = 1$ or 2) parameters were retained that best describe the experimental V^E data. These parameters, along with V^E values [predicted by employing eq 3], at various x_1 are recorded in Table 4. Examination of data in Table 4 reveals that V^E values compare well with their experimental values.

A number of structures were then assumed for (1) and (2) components in pure and mixed states, and their ${}^3\xi'$ values were evaluated from their structural consideration (via eq 4). These ${}^3\xi'$ values were then compared with ${}^3\xi$ values obtained via eq 3. Any structure or combination of structures which provided ${}^3\xi'$ values comparing with the ${}^3\xi$ value was taken to be a representative structure of that component. Such an analysis

Table 4. Comparison of V^E, H^E, and κ_S^E Values Calculated from Equations 3 and 6 with Their Experimental Values (Calculated via Equation 2) at 308.15 K for the Various (1 + 2) Mixtures As a Function of x_1, Mole Fraction of Component (1)

	mole fraction of component (1), x_1								
properties	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
THP (1) + A (2)[a]									
V^E(exptl)	−0.140	−0.270	−0.395	−0.470	−0.490	−0.465	−0.400	−0.290	−0.150
V^E(graph)	−0.158	−0.288	−0.389	−0.458	–	−0.487	−0.440	−0.347	−0.202
H^E(exptl)	−150.6	−290.0	−418.1	−530.2	−616.8	−663.6	−651.4	−556.6	−350.6
H^E(graph)	−113.8	−255.3	−401.1	–	−623.4	–	−635.0	−523.4	−315.7
κ_S^E(exptl)	−15.8	−30.2	−41.8	−50.5	−54.8	−53.1	−47.1	−36.2	−20.0
κ_S^E(graph)	−16.7	−31.2	−42.5	–	−54.2	–	−48.2	−37.6	−21.6
THP (1) + MA (2)[b]									
V^E(exptl)	−0.092	−0.163	−0.215	−0.240	−0.241	−0.213	−0.169	−0.116	−0.058
V^E(graph)	−0.072	−0.132	−0.182	−0.217	–	−0.239	−0.220	−0.177	−0.106
H^E(exptl)	−140.8	−265.8	−370.9	−451.2	−500.4	−511.5	−476.5	−386.4	−231.2
H^E(graph)	−125.1	−251.5	−364.2	–	−502.9	–	−470.5	−374.4	−218.9
κ_S^E(exptl)	−12.0	−23.6	−32.8	−39.9	−43.1	−42.8	−38.1	−29.1	−16.8
κ_S^E(graph)	−12.7	−24.0	−32.2	–	−43.0	–	−38.5	−30.1	−17.3
THP (1) + 2-MA (2)[c]									
V^E(exptl)	−0.230	−0.410	−0.550	−0.650	−0.725	−0.740	−0.705	−0.600	−0.380
V^E(graph)	−0.238	−0.433	−0.581	−0.679	–	−0.713	−0.640	−0.500	−0.289
H^E(exptl)	−168.1	−316.3	−437.8	−526.0	−574.4	−576.6	−526.4	−417.5	−244.0
H^E(graph)	−165.0	−313.4	−436.4	–	−574.9	–	−525.1	−415.1	−241.6
κ_S^E(exptl)	−13.6	−26.8	−38.4	−47.1	−53.0	−54.3	−50.4	−40.5	−23.9
κ_S^E(graph)	−13.1	−26.1	−37.8	–	−52.9	–	−50.4	−40.6	−23.9

Also included are various $(^3\xi_i)$, $(^3\xi_i)_m$ ($i = 1$ or 2); X^n ($n = 0$ to 2); α_{12}; and χ'_{12} etc. parameters: [a] $(^3\xi_1) = (^3\xi_1)_m = 1.101$; $(^3\xi_2) = (^3\xi_2)_m = 1.500$; $\alpha_{12} = 26.404\ \mathrm{cm^3 \cdot mol^{-1}}$; $\chi'_{12} = -2376.0\ \mathrm{J \cdot mol^{-1}}$; $\chi^*_{12} = 1460.4\ \mathrm{J \cdot mol^{-1}}$; $\chi'_{12} = -167.5\ \mathrm{TPa^{-1}}$; $\chi^*_{12} = -9.9\ \mathrm{TPa^{-1}}$; $V^{(0)} = -1.970\ \mathrm{cm^3 \cdot mol^{-1}}$; $V^{(1)} = -0.070\ \mathrm{cm^3 \cdot mol^{-1}}$; $V^{(2)} = 0.568\ \mathrm{cm^3 \cdot mol^{-1}}$; $\sigma(V^{(E)}) = 0.005\ \mathrm{cm^3 \cdot mol^{-1}}$; $H^{(0)} = -2467.3\ \mathrm{J \cdot mol^{-1}}$; $H^{(1)} = -1388.6\ \mathrm{J \cdot mol^{-1}}$; $H^{(2)} = -495.5\ \mathrm{J \cdot mol^{-1}}$; $\sigma(H^E) = 6.0\ \mathrm{J \cdot mol^{-1}}$. [b] $(^3\xi_1) = (^3\xi_1)_m = 1.101$; $(^3\xi_2) = (^3\xi_2)_m = 1.801$; $\alpha_{12} = -5.566\ \mathrm{cm^3 \cdot mol^{-1}}$; $\chi'_{12} = -2058.9\ \mathrm{J \cdot mol^{-1}}$; $\chi^*_{12} = 873.3\ \mathrm{J \cdot mol^{-1}}$; $\chi'_{12} = -126.2\ \mathrm{TPa^{-1}}$; $\chi^*_{12} = 11.4\ \mathrm{TPa^{-1}}$; $V^{(0)} = -0.949\ \mathrm{cm^3 \cdot mol^{-1}}$; $V^{(1)} = 0.245\ \mathrm{cm^3 \cdot mol^{-1}}$; $V^{(2)} = 0.191\ \mathrm{cm^3 \cdot mol^{-1}}$; $\sigma(V^{(E)}) = 0.002\ \mathrm{cm^3 \cdot mol^{-1}}$; $H^{(0)} = -2001\ \mathrm{J \cdot mol^{-1}}$; $H^{(1)} = -627.9\ \mathrm{J \cdot mol^{-1}}$; $H^{(2)} = 101.8\ \mathrm{J \cdot mol^{-1}}$; $\sigma(H^E) = 5.0\ \mathrm{J \cdot mol^{-1}}$. [c] $(^3\xi_1) = (^3\xi_1)_m = 1.101$; $(^3\xi_2) = (^3\xi_2)_m = 1.401$; $\alpha_{12} = 62.028\ \mathrm{cm^3 \cdot mol^{-1}}$; $\chi'_{12} = -3860.8$; $\chi^*_{12} = -301.1\ \mathrm{J \cdot mol^{-1}}$; $\chi'_{12} = -177.3$; $\chi^*_{12} = 50.8\ \mathrm{TPa^{-1}}$; $V^{(0)} = -2.888\ \mathrm{cm^3 \cdot mol^{-1}}$; $V^{(1)} = -0.995\ \mathrm{cm^3 \cdot mol^{-1}}$; $V^{(2)} = -0.774\ \mathrm{cm^3 \cdot mol^{-1}}$; $\sigma(V^{(E)}) = 0.007\ \mathrm{cm^3 \cdot mol^{-1}}$; $H^{(0)} = -2297.6\ \mathrm{J \cdot mol^{-1}}$; $H^{(1)} = -527.2\ \mathrm{J \cdot mol^{-1}}$; $H^{(2)} = 12.5\ \mathrm{J \cdot mol^{-1}}$; $\sigma(H^E) = 6.0\ \mathrm{J \cdot mol^{-1}}$.

revealed that THP (molecular entities I to II, $^3\xi' = 1.078, 1.349$); A (molecular entities III to IV, $^3\xi' = 1.361, 1.890$); MA (molecular entities V to VI, $^3\xi' = 1.256, 1.814$); and 2MA (molecular entities VII to VIII, $^3\xi' = 0.949, 1.405$) exist as associated molecular entities (Scheme 1). $(^3\xi'_2)_m$ values were then calculated to extract information about the state of A or MA or 2MA (2) in THP (1). It was assumed that various (1 + 2) mixtures may contain molecular entities IX to XI. $(^3\xi'_2)_m$ values for molecular entities IX to XI were then calculated to be 1.735, 1.697, and 1.735. $(^3\xi_2)_m$ values of 1.500, 1.801, and 1.401 (Table 4) suggest the presence of molecular entities IX to XI in these mixtures. The existence of these molecular entities suggests that addition of A or MA or 2MA to THP should have influenced the C−O vibrations in cyclic ether and −N−H stretching in A or MA or 2MA of THP. In view of this, we analyzed IR spectra of pure THP or A or MA or 2MA and their equimolar THP (1) + A or MA or 2MA (2) mixtures. It was observed that THP, A, MA, and 2MA in their pure state show characteristic absorption at 1121 $\mathrm{cm^{-1}}$ (C−O vibration) and 3410, 3416, and 3412 $\mathrm{cm^{-1}}$ (N−H stretch).[21] On the other hand, IR spectra of equimolar THP (1) + A or MA or 2MA (2) mixtures show characteristic absorption at 1152, 1154, and 1160 $\mathrm{cm^{-1}}$ (C−O stretch) and 3435, 3424, and 3432 $\mathrm{cm^{-1}}$ (N−H stretch), respectively. The IR spectral data of the investigated mixtures thus suggest that addition of (2) to (1) does influence the C−O vibrations of THP and N−H stretching vibrations of A or MA or 2MA which in turn support the existence of molecular entities IX to XI.

Excess Molar Enthalpies and Isentropic Compressibilities Changes of Mixing. H^E and κ_S^E data of studied (1 + 2) mixtures were also analyzed in terms of Graph theory. For this purpose, it was assumed that THP (1) + A or MA or 2MA (2) binary mixture formation involves processes: (i) formation of unlike contact between 1_n and 2_n molecules; (ii) unlike contact 1_n−2_n formation then weakens 1_n−2_n interactions and leads to the depolymerization of 1_n and 2_n; and (iii) the monomers of 1 and 2 then undergo specific interactions to form a 1:2 molecular complex. If χ_{12}, χ_{11}, χ_{22}, and χ^*_{12} are molar interactions and molar compressibility interaction parameters for 1−2, 1−1, and 2−2 contacts and specific interactions, respectively, then change in molar thermodynamic properties, ΔX ($X = H$ or κ_S), due to processes (i) to (iii) would be given[4,22−24] by

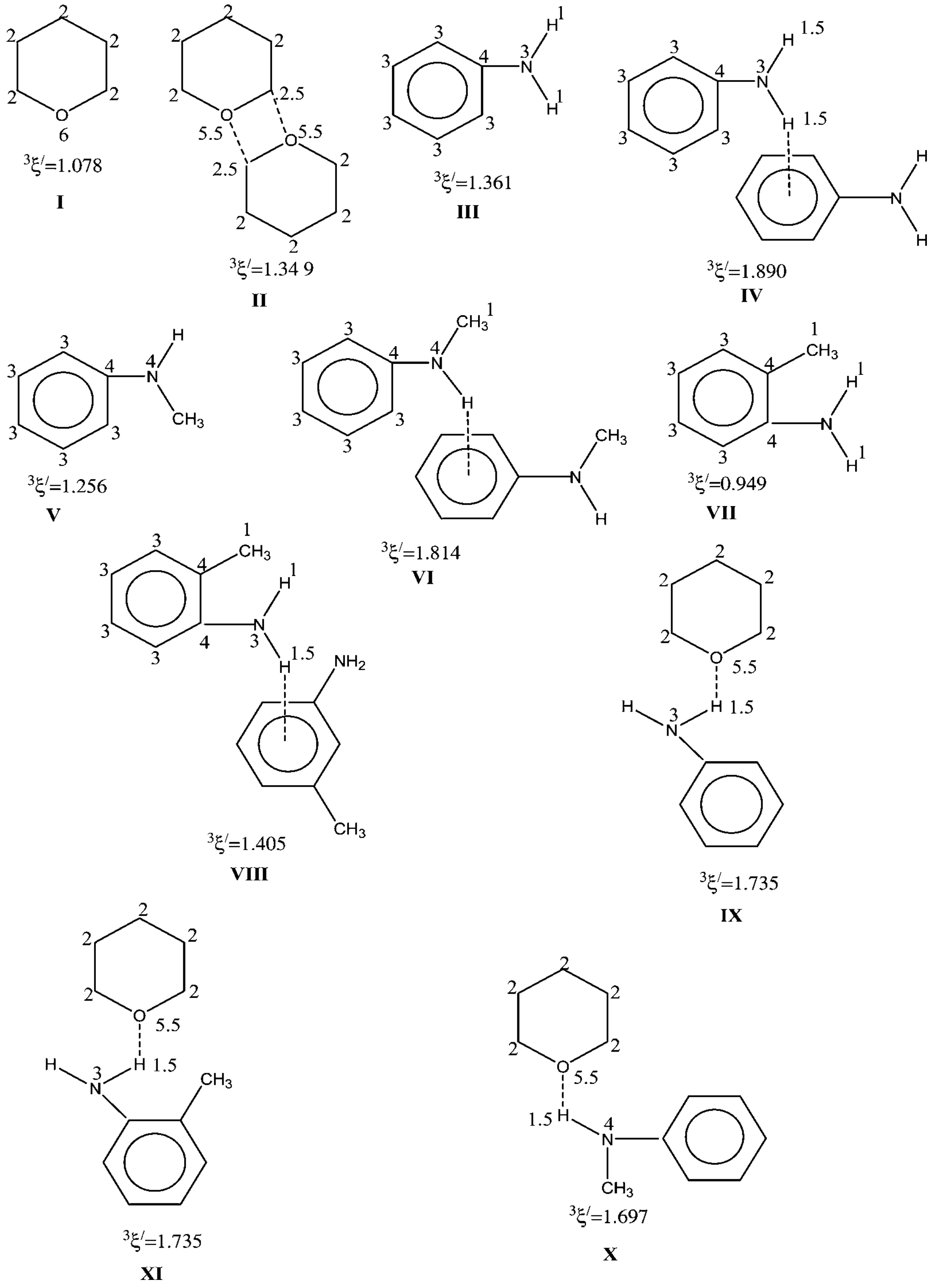
$$X^E = \left[\frac{x_1 x_2 (^3\xi_1/^3\xi_2)}{x_1 + x_2(^3\xi_1/^3\xi_2)}\right][\chi_{12} + x_1\chi_{11} + x_1\chi_{22} + x_2\chi^*_{12}] \tag{5}$$

For the studied mixtures, it is reasonable to assume that $\chi_{12} \cong \chi_{12} = \chi'_{12}$ and $\chi_{11} \cong \chi_{22} = \chi^*$, and then eq 5 can be expressed by

$$X^E = \left[\frac{x_1 x_2 (^3\xi_1/^3\xi_2)}{x_1 + x_2(^3\xi_1/^3\xi_2)}\right][(1 + x_2)\chi'_{12} + 2x_1\chi^*] \tag{6}$$

Equation 6 contains two unknown parameters, and these parameters were calculated by employing H^E and κ_S^E data of the investigated (1 + 2) binary mixtures at two compositions. These parameters were then employed to predict H^E and κ_S^E values at other values of x_1. Such H^E and κ_S^E data along with χ'_{12} and χ^* parameters are recorded in Table 4. An examination of Table 4 reveals that calculated H^E and κ_S^E values for various (1

Scheme 1. Connectivity Parameters of Various Molecular Entities



+ 2) mixtures compare well with their corresponding experimental values.

Excess Gibbs Free Energies. The activity coefficient, γ_1, of component 1 in a (1 + 2) binary mixture is a measure of molecular interactions between the components 1 and 2 and directly depends upon the effective surface fraction,[25] S_2, of 2 that comes into unlike contact. At the same time, thermal energy would influence the magnitude of unlike interaction energy so that γ_1 varies as some function of $(\chi_{12}^{**}/RT)S_2$, where χ_{12}^{**} is the interaction energy. On the basis of these considerations, activity coefficients of component 1 and 2, in (1 + 2) binary mixtures, can be expressed[26] by eqs 7 and 8

$$\ln \gamma_1 = \frac{\chi_{12}^{**} x_1 v_2}{RT \sum_{i=1}^{2} x_i v_i} \tag{7}$$

$$\ln \gamma_2 = \left(\frac{\chi_{12}^{**} v_2}{RT v_1}\right)\left[\ln \frac{\sum_{i=1}^{2} x_i v_i}{x_2 v_2} - \frac{x_1 v_1}{\sum_{i=1}^{2} x_i v_i}\right] \tag{8}$$

Equations 7 and 8 are valid for mixtures comprised of components having same molar volumes. In the investigated

Table 5. Comparison of G^E Values Calculated from Equations 11 to 13 with Their Experimental Values (Calculated via Equation 1) at 308.15 K as a Function of x_2, Mole Fraction of Component (2)

	mole fraction of component (2), x_2								
properties	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
THP (1) + A (2)[a]									
G^E(exptl)	−153.1	−269.5	−351.6	−400.9	−418.4	−403.9	−356.8	−275.5	−157.6
G^E(graph)	−117.2	−238.0	−342.8	−407.2	−	−383.3	−318.9	−237.0	−139.5
γ_1(exptl)	0.5877	0.6609	0.7288	0.7909	0.8468	0.8959	0.9376	0.9703	0.9921
γ_1(graph)	0.6648	0.6941	0.7366	0.7903	−	0.8969	0.9359	0.9644	0.9848
γ_2(exptl)	0.9927	0.9724	0.9413	0.9008	0.8519	0.7951	0.7306	0.6589	0.5808
γ_2(graph)	0.9945	0.9755	0.9416	0.8976	−	0.8099	0.7707	0.7280	0.6656
THP (1) + MA (2)[b]									
G^E(exptl)	−251.7	−418.2	−520.7	−574.8	−589.9	−569.6	−511.7	−407.8	−243.9
G^E(graph)	−186.0	−370.7	−516.7	−590.7	−	−534.9	−447.5	−337.7	−202.6
γ_1(exptl)	0.4410	0.5634	0.6626	0.7387	0.7985	0.8499	0.8984	0.9447	0.9830
γ_1(graph)	0.5290	0.5765	0.6430	0.7217	−	0.8629	0.9125	0.9496	0.9778
γ_2(exptl)	0.9819	0.9412	0.8922	0.8419	0.7902	0.7321	0.6599	0.5665	0.4502
γ_2(graph)	0.9901	0.9577	0.9058	0.8463	−	0.7401	0.6917	0.6361	0.5449
THP (1) + 2-MA (2)[c]									
G^E(exptl)	−143.3	−281.6	−395.7	−471.7	−500.9	−479.6	−409.5	−297.4	−155.1
G^E(graph)	−134.6	−274.2	−399.1	−481.0	−	−463.0	−386.0	−286.2	−167.7
γ_1(exptl)	0.5694	0.5989	0.6574	0.7336	0.8158	0.8975	0.9500	0.9852	0.9987
γ_1(graph)	0.6240	0.6530	0.6960	0.7525	−	0.8745	0.9218	0.9567	0.9817
γ_2(exptl)	1.0004	0.9908	0.9599	0.9044	0.8290	0.7438	0.6615	0.5940	0.5510
γ_2(graph)	0.9941	0.9731	0.9349	0.8837	−	0.7782	0.7318	0.6829	0.6136

Also included $(^3\xi_i)$ and $(^3\xi_i)_m$ ($i = 1$ or 2), β, and χ_{12}^{**} parameters for the various (1 + 2) mixtures. [a] $(^3\xi_1) = (^3\xi_1)_m = 1.101$; $(^3\xi_2) = (^3\xi_2)_m = 1.501$; $\beta = -2723.3$; $\chi_{12}^{**} = -461.3$ J·mol^{-1}. [b] $(^3\xi_1) = (^3\xi_1)_m = 1.101$; $(^3\xi_2) = (^3\xi_2)_m = 1.801$; $\beta = -2704.7$; $\chi_{12}^{**} = -834.4$ J·mol^{-1}. [c] $(^3\xi_1) = (^3\xi_1)_m = 1.101$; $(^3\xi_2) = (^3\xi_2)_m = 1.401$; $\beta = -3957.6$; $\chi_{12}^{**} = -516.6$ J·mol^{-1}.

(1 + 2) mixtures, molar volumes of the components 1 and 2 are not equal. In such cases, the activity coefficient, γ_1, can be predicted by taking into consideration (i) the molar interactions in (1 + 2) binary mixtures and (ii) work done in accommodating the second component into the matrix of the first component. The activity coefficients γ_1 and γ_2 taking into consideration these effects were then expressed[27] by

$$RT\ln(\gamma_1) = \frac{\chi_{12}^{**} x_2 \upsilon_2}{\sum_{i=1}^{2} x_i \upsilon_i} + \frac{\beta \upsilon_1 \upsilon_2^2 x_2^2 (1 - \upsilon_2/\upsilon_1)}{\sum_{i=1}^{2} (x_i \upsilon_i)^2} \tag{9}$$

$$RT\ln(\gamma_2) = \left[\chi_{12}^{**}\frac{\upsilon_2}{\upsilon_1}\right]\left[\ln\frac{\sum_{i=1}^{2} x_i\upsilon_i}{x_2\upsilon_2} - \frac{x_1\upsilon_1}{\sum_{i=1}^{2} x_i\upsilon_i}\right] + \frac{\beta x_1^2 \upsilon_1^2 \upsilon_2 (1 - \upsilon_2/\upsilon_1)}{\sum_{i=1}^{2} (x_i\upsilon_i)^2} \tag{10}$$

Since $\upsilon_2/\upsilon_1 = {^3\xi_1}/{^3\xi_2}$[28]

$$RT\ln\gamma_1 = \left[\frac{x_2\chi_{12}^{**}(^3\xi_1/^3\xi_2)}{x_1 + x_2(^3\xi_1/^3\xi_2)}\right] + \frac{\beta(1/^3\xi_1)(^3\xi_1/^3\xi_2)^2 x_2^2 (1 - {^3\xi_1}/{^3\xi_2})}{x_1^2 + x_2^2(^3\xi_1/^3\xi_2)^2} \tag{11}$$

$$RT\ln\gamma_2 = [\chi_{12}^{**}(^3\xi_1/^3\xi_2)]\left[\ln\left(\frac{x_1 + x_2(^3\xi_1/^3\xi_2)}{x_2(^3\xi_2/^3\xi_1)}\right) - \frac{x_1}{x_1 + x_2(^3\xi_1/^3\xi_2)}\right] + \frac{\beta x_1^2(1/^3\xi_2)(^3\xi_2/^3\xi_1)^2(1 - {^3\xi_1}/{^3\xi_2})}{x_1^2 + x_2^2(^3\xi_1/^3\xi_2)^2} \tag{12}$$

where β is a constant characteristic of the (1 + 2) mixture. Equations 11 and 12 contain two unknown parameters χ_{12}^{**} and β. The values of χ_{12}^{**} and β of a binary (1 + 2) mixture were evaluated using the activity coefficient data of components (1) and (2) at a single composition ($x_1 = 0.5$) These values were then subsequently utilized to predict the activity coefficients at other values of x_1. Excess Gibbs free energies of mixing, G^E, were then determined by employing the relation

$$G^E = RT(x_1 \ln\gamma_1 + x_2 \ln\gamma_2) \tag{13}$$

Such β values along with (γ_1,γ_2; x_1), χ_{12}^{**}, and G^E values (calculated via eqs 11 to 13) are recorded in Table 5 and also compared with their experimental values.

Examination of the data shows that (γ_1,γ_2; x_1) data for the components of the (1 + 2) mixtures, along with G^E data of the investigated mixture values, compare well with their corresponding experimental (γ_1,γ_2; x_1) and G^E values which in turn lend additional support to the assumptions made in deriving eqs 11 and 12.

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Literature Cited

(1) Ewing, M. B.; Levian, B. J.; Marsh, K. N. Excess enthalpies, excess volumes and excess Gibbs free energy for mixtures of cyclooctane +

cyclopentane at 288.15−298.15 and 308.15 K. *J. Chem. Thermodyn* **1970**, *2*, 689–691.

(2) Dimple; Yadav, J. S.; Singh, K. C.; Sharma, V. K. Molecular interaction in binary mixtures containing 2-methylaniline. *Thermochim. Acta* **2008**, *468*, 108–115.

(3) Yadav, J. S.; Sharma, D.; Sharma, V. K. Topological investigation of thermodynamic properties of binary mixtures containing 2-pyrrolidinone. *Thermochim. Acta* **2009**, *489*, 45–52.

(4) Siwach, R. K.; Dimple; Sharma, V. K. Thermodynamic properties of binary mixtures containing tetrahydropyan: excess molar volume, excess molar enthalipes and isentropic compressibilities changes of mixing. *Thermochim. Acta* **2010**, *506*, 1–7.

(5) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents, Physical properties and Methods of Purification*, 4th ed.: Wiley: New York, 1986.

(6) Singh, P. P.; Sharma, S. P. Molar excess volumes of ternary mixtures of non-electrolytes at 308. 15 K. *J. Chem. Eng. Data* **1985**, *30*, 477–479.

(7) Nath, J. Speeds of sound and isentropic compressibilities of (anisole + dichloromethane, or 1,2-dichloroethane, or trichloroethene, or tetrachloroethene, or cyclohexane) at $T = 303.15$ K. *J. Chem. Thermodyn.* **1996**, *28*, 481–490.

(8) Taha, A. A.; Grigsby, R. D.; Johnson, J. R.; Christian, S. D.; Affsprung, H. E. Manometric apparatus for vapour and solution studies. *J. Chem. Educ.* **1966**, *43*, 432–435.

(9) Khosla, M. P.; Mahl, B. S.; Chopra, S. L.; Singh, P. P. Excess free energy of mixing. *Z. Phys. Chem. (Leipzig)* **1972**, *251*, 129–136.

(10) Dahiya, H. P.; Singh, P. P.; Dagar, S. Thermodynamics of molecular interactions in aromatic hydrocarbon + o-chlorotoluene mixtures. *Fluid Phase Equilib.* **1987**, *33*, 191–205.

(11) Giner, B.; Villares, A.; Martin, S.; Lafuente, C.; Royo, F. M. Isothermal vapour-liquid equilibrium for cyclic ethers with 1-chloropentane. *Fluid Phase Equilib.* **2007**, *251*, 8–16.

(12) U.S. Environmental Protection Agency, *Health and Environmental Effects Profile for Aniline*. Environmental Criteria and Assessment Office, Office of Health and Environmental, Office of Research and Development: Cincinnati, OH, 1985.

(13) Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals Data Compilation*; Taylor and Francis: WA, 1989.

(14) U. S. Environmental Protection Agency. *Assessment tools for the evaluation of risk*; Environmental Research Laboratory: Duluth, MN, 1993.

(15) Benson, G. C.; Kiyohara, O. Evaluation of excess isentropic compressibilities and isochoric heat capacities. *J. Chem. Thermodyn.* **1979**, *11*, 1061–1064.

(16) Barker, J. A. Determination of activity coefficients from total pressure measurements. *Aust. J. Chem.* **1953**, *6*, 207–210.

(17) Deshpande, D. D.; Bhatgadde, L. G. Sound velocities, adiabatic compressiblites, and free volumes in aniline solutions. *J. Phys. Chem.* **1968**, *72*, 261–266.

(18) Katoch, A. Topological and Thermodynamic investigations of molecular interactions in binary and ternary mixtures of non-electrolytes. Ph.D. Thesis, M.D. University, Rohtak, India, 1997.

(19) Singh, P. P.; Sharma, V. K.; Sharma, S. P. Topological studies of the molecular species that characterize lower alkanol + methylene bromide mixtures: molar excess volumes and molar excess enthalpies. *Thermochim. Acta* **1986**, *106*, 293–307.

(20) Kier, L. B.; Yalkowasky, S. H.; Sinkula, A. A.; Valvani, S. C. *Physico-Chemical Properties of Drugs*; Mercel Dekker: New York, 1980.

(21) Rao, C. N. R. *Chemical Application of Infrared Spectroscopy*; Academic Press: London, 1963.

(22) Huggins, M. L. The thermodynamic properties of liquids, included solutions I. Intermolecular energies in monoatomic liquids and their mixtures. *J. Phys. Chem.* **1970**, *74*, 371–378.

(23) Huggins, M. L. The thermodynamic properties of liquids, included solutions: Part 2. Polymer solutions considered as diatomic system. *Polymer* **1971**, *12*, 389–399.

(24) Singh, P. P.; Bhatia, M. Energetics of molecular interactions in binary mixtures of non-electrolytes containing a salt. *J.Chem. Soc., Faraday Trans. I* **1989**, *85*, 3807–3812.

(25) Singh, P. P.; Maken, S. A model of non-electrolytic behaviour: activity coefficients. *Can. J. Chem.* **1992**, *70*, 1631–1634.

(26) Singh, P. P.; Dahiya, H. P.; Dagar, S. Thermodynamic and Topological investigations of binary mixtures of non-electrolytes: Activity coefficients, Molar excess Gibbs free energy of mixing and Molar excess enthalipies. *Z. Phys. Chem. (Leipzig)* **1988**, *269*, 817–831.

(27) Singh, P. P.; Maken, S. Topological aspects of molecular interactions in liquid mixtures of non-electrolytes. *Pure Appl. Chem.* **1994**, *66*, 449–454.

(28) Singh, P. P.; Nigam, R. K.; Singh, K. C.; Sharma, V. K. Topological aspects of the thermodynamics of binary mixtures of non-electrolytes. *Thermochim. Acta* **1981**, *46*, 175–190.

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