Thermodynamic properties of binary mixtures containing tetrahydropyran: Excess molar volumes, excess molar enthalpies and isentropic compressibilities changes of mixing

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ABSTRACT

Excess molar volumes, V^E, excess molar enthalpies, H^E and speeds of sound, u data of tetrahydropyran (i) + cyclohexane or n-hexane or n-heptane (j) binary mixtures have been measured using dilatometer, calorimeter and interferometer over whole mole fraction range at 308.15 K. Speeds of sound data have been utilized to predict isentropic compressibilities changes of mixing, κ_S^E. The analysis of V^E in terms of Graph theory reveals that (i + j) mixtures are characterized by dipole–induced dipole interactions between THP and cyclo or n-alkanes to form 1:1 molecular complex. H^E and κ_S^E data of the investigated mixtures have also been analyzed in terms of Graph theory. V^E, H^E and κ_S^E data predicted by Graph theory compare well with their corresponding experimental values.

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1. Introduction

The systematic study of thermodynamic properties has greater importance to extract information about the molecular interactions among the constituents of mixtures. Knowledge of thermodynamic properties is also essential for the proper design of industrial processes. The nature and relative strength of molecular interactions operating among the components of liquid mixtures have been successfully predicted by measuring their thermodynamic properties like excess molar volumes, excess molar enthalpies, excess Gibbs free energies of mixing and isentropic compressibilities changes of mixing and analyzing them in terms of topology of constituents of mixtures, Homomorph concept, UNIFAC, EBGCM, Nagamachi models and Graph theory of liquid mixtures [1–8]. Cyclic ethers represent a class of technically important compounds frequently used as solvent in chemical industry. Tetrahydropyran is used in polymerization processes, pharmaceutical industries as a reaction intermediate [9]. A recent study [10] has shown that tetrahydropyran (i) + aromatic hydrocarbons (j) binary mixtures are characterized by interactions between dipole of tetrahydropyran and π-electron cloud of benzene ring of aromatic hydrocarbons to form 1:1 molecular complex. It would be of interest to see how

these interactions are influenced when aromatic hydrocarbons are substituted by cyclo or n-alkanes. These considerations prompted us to measure excess molar volumes, V^E, excess molar enthalpies, H^E and speeds of sound data of THP (i) + cyclohexane or n-hexane or n-heptane (j) binary mixtures.

2. Experimental

Tetrahydropyran (THP) (Fluka: >99.5 moles percent purity), cyclohexane (E. Merck: >99 moles percent), n-hexane (E. Merck: > 99.5 moles percent), n-heptane (E. Merck: >99 moles percent) were purified by standard methods [11]. The purities of the purified liquids were checked by measuring their densities using bi-capillary pycnometer (recorded in Table 1) at 298.15 ± 0.01 K and these agreed to within $\pm 5 \times 10^{-5}$ kg m^{-3} with their corresponding literature values [11]. Excess molar volumes, V^E for binary (i + j) mixtures were determined dilatometerically in the manner described elsewhere [12]. The change in liquid level of dilatometer capillary was measured with a cathetometer that could read to ± 0.001 cm. The uncertainties in our measured V^E values are $\pm 0.5\%$.

Excess molar enthalpies, H^E for the studied mixtures were measured by 2-drop calorimeter (model 4600) supplied by the Calorimetery Sciences Corporation (CSC), USA at 308.15 K in a manner described elsewhere [13]. The uncertainties in the measured H^E values are $\pm 1\%$.

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

Liquids	u (ms^{-1})		ρ (kg m^{-3})	
	Exptl	Lit.	Exptl	Lit.
Tetrahydropyran	1272	1271.1 [9]	877.23	877.20 [11]
n-Hexane	1079	1078.0 [14]	654.82	654.84 [11]
n-Heptane	1088	1087.6 [15]	679.49	679.46 [11]
Cyclohexane	1255	1254.4 [14]	773.94	773.89 [11]

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 double wall designed cell in which water was circulated to maintain the desired temperature. The speeds of sound values for the purified liquids at $(298.15 \pm 0.01\,\text{K})$ (recorded in Table 1) compare well with their corresponding experimental values [9,14,15]. The uncertainties in the measured speeds of sound values are $\pm 1\,\text{ms}^{-1}$.

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

3. Results

The measured excess molar volumes, V^E, excess molar enthalpies, H^E and speeds of sound, u data of tetrahydropyran (i) + cyclohexane, n-hexane and n-heptane (j) binary mixtures over entire composition range at 308.15 K are recorded in Tables 2–4. The isentropic compressibilities, κ_S for $(i+j)$ binary 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 (reported in Table 2) using 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 respectively of component (i) in their binary mixtures. Isentropic compressibilities changes of mixing, κ_S^E for binary mixtures were determined using Eq. (3):

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

κ_S^{id} values were obtained in the manner as suggested by Benson and Kiyohara [16].

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

where ϕ_i is the volume fraction of component (i) in the mixed state; $\kappa_{s,i}, v_i, \alpha_i$ 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 and C_p were taken from literature [17]. α Value for THP was determined in the same manner as described elsewhere [18]. Such κ_S^E values for the studied mixtures are recorded in Table 4. Further V^E, H^E and κ_S^E values for the investigated $(i+j)$ mixtures are plotted in Figs. 1–3. All measured thermodynamic properties (V^E, H^E and κ_S^E) have been fitted
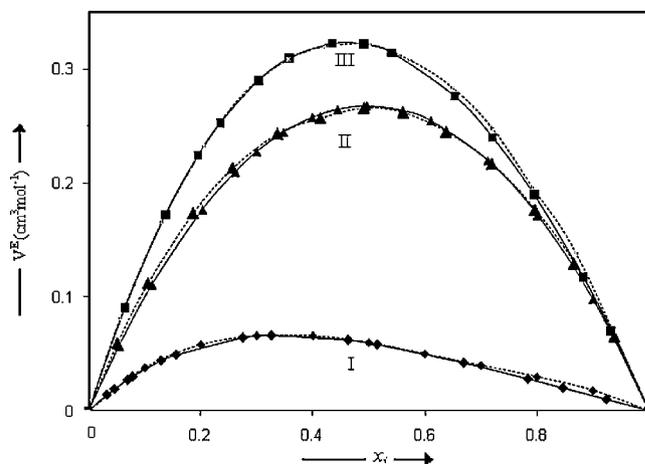
Fig. 1. Comparison of excess molar volumes, V^E of (I) tetrahydropyran (i) + n-hexane (j) ($\blacklozenge$) ($-$) experimental at 308.15 K; (.. ...) Guillen and Losa [22] at 303.15 K;(II) tetrahydropyran (i) + n-heptane (j) ($\blacktriangle$) ($-$) experimental at 308.15 K; (.. ...) Bravo et al. [24] at 308.15 K;(III) tetrahydropyran (i) + cyclohexane (j) ($\blacksquare$) ($-$) experimental at 308.15 K; (.. ...) Brocos et al. [24] at 308.15 K.
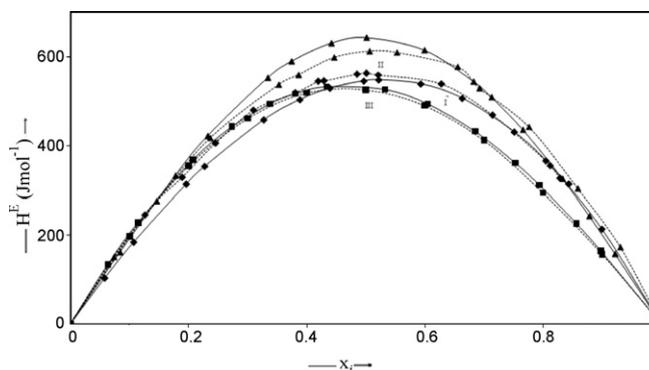
Fig. 2. Comparison of excess molar enthalpies, H^E of (I) tetrahydropyran (i) + n-hexane (j) ($\blacklozenge$) ($-$) experimental at 308.15 K; (.. ...) Castro et al. [21] at 298.15 K; (II) tetrahydropyran (i) + n-heptane (j) ($\blacktriangle$) ($-$) experimental at 308.15 K; (.. ...) Castro et al. [21] at 298.15 K; (III) tetrahydropyran (i) + cyclohexane (j) ($\blacksquare$) ($-$) experimental at 308.15 K; (.. ...) Boukais-Belaribi et al. [20] at 308.15 K.

to Redlich–Kister equation [19]:

$$X^E(X = V \text{ or } H \text{ or } \kappa_S) = x_i x_j [X^{(0)} + X^{(1)}(2x_i - 1) + X^{(2)}(2x_i - 1)^2] \tag{5}$$

where $X^{(n)}$ ($n = 0$–2) are the fitting parameters characteristic of $(i+j)$ mixtures. These parameters were determined by fitting $X^E(X = V$ or H or $\kappa_s)$ data to Eq. (5) by the least squares methods. The parame-
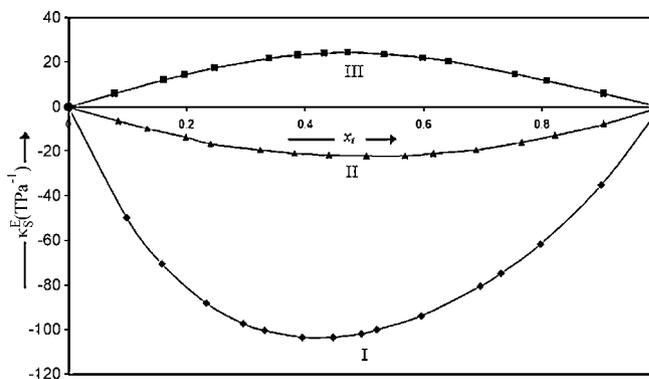
Fig. 3. Isentropic compressibilities changes of mixing (I) tetrahydropyran (i) + n-hexane (j) ($\blacklozenge$); (II) tetrahydropyran (i) + n-heptane (j) ($\blacktriangle$); (III) tetrahydropyran (i) + cyclohexane (j) ($\blacksquare$).

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. Also included are the densities of binary mixtures predicted from Eq. (2).

x_i	V^E(cm^3 mol^{-1})	ρ_{ij} (kg m^{-3})	x_i	V^E(cm^3 mol^{-1})	ρ_{ij} kg m^{-3}
	Tetrahydropyran (i) + n-hexane (j)				
0.0328	0.014	651.0	0.3262	0.066	704.3
0.0459	0.019	653.2	0.4629	0.062	732.3
0.0694	0.027	657.2	0.5150	0.058	743.7
0.0785	0.030	658.7	0.6692	0.042	779.3
0.1294	0.044	667.6	0.7837	0.028	808.1
0.1561	0.049	672.3	0.8461	0.020	824.8
0.2753	0.064	694.4	0.9239	0.010	846.5
	$V^{(0)} = 0.2377$, $V^{(1)} = -0.1625$, $V^{(2)} = 0.0531$; $\sigma(V^E) = 0.003$ cm^3 mol^{-1}				
	Tetrahydropyran (i) + n-heptane(j)				
0.0543	0.057	677.9	0.4441	0.265	738.0
0.1130	0.111	685.8	0.4964	0.268	747.6
0.2031	0.177	698.7	0.5601	0.264	759.9
0.2613	0.210	707.5	0.6107	0.255	770.2
0.2998	0.228	713.5	0.7123	0.220	792.4
0.3475	0.245	721.3	0.8011	0.172	813.7
0.3991	0.258	730.0	0.8999	0.098	839.6
	$V^{(0)} = 1.0722$, $V^{(1)} = -0.0131$, $V^{(2)} = 0.0407$; $\sigma(V^E) = 0.001$ cm^3 mol^{-1}				
	Tetrahydropyran (i) + cyclohexane (j)				
0.0648	0.091	770.2	0.4911	0.322	810.6
0.1372	0.172	776.5	0.5412	0.314	815.9
0.1954	0.224	781.8	0.6536	0.276	828.0
0.2351	0.253	785.5	0.7210	0.240	835.6
0.3030	0.290	791.9	0.7952	0.190	844.1
0.3575	0.310	797.2	0.8827	0.117	854.4
0.4351	0.323	804.9	0.9325	0.070	860.1
	$V^{(0)} = 1.284$, $V^{(1)} = -0.2179$, $V^{(2)} = 0.0266$; $\sigma(V^E) = 0.002$ cm^3 mol^{-1}				

ters that best fit the experimental data are summarized in Table 5, together with standard deviations, $\sigma(X^E)$ $(X = V$ or H or $\kappa_s)$ defined as:

$$\sigma(X^E) = \sum \frac{\left(X^E_{\text{exptl}} - X^E_{\text{calc. Eq. (5)}}\right)^2}{(m-n)^{0.5}} \qquad (6)$$

where m and n are the number of experimental points and parameters respectively.

4. Discussion

Excess molar volumes, V^E values of THP (i) + n-hexane (j) mixtures are lesser (Fig. 1) by 0.004 cm^3 mol^{-1} from the values reported in the literature [22,26] at 303.15 K. Excess molar enthalpies, H^E data of THP (i) + cyclohexane (j) mixtures at 308.15 K agree to within ± 10 Jmol^{-1} (Fig. 2) with their literature values [20]. Further, H^E values of THP(i) + n-hexane or n-heptane (j) mixtures differ by 4–5% than the values reported for these mixtures at 298.15 K [21–23]. Our V^E values for THP (i) + cyclohexane or n-heptane (j)

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(Jmol^{-1})	x_i	H^E(Jmol^{-1})
Tetrahydropyran (i) + n-hexane (j)			
0.0581	103	0.4968	545
0.1073	184	0.5220	548
0.1962	314	0.5931	539
0.2274	353	0.6634	506
0.3276	458	0.7514	431
0.3888	503	0.8124	355
0.4395	529	0.8997	213
$H^{(0)} = 2182.9$, $H^{(1)} = 278.2$, $H^{(2)} = -68.4$; $\sigma(H^E) = 1.7$ Jmol^{-1}			
Tetrahydropyran (i) + n-heptane (j)			
0.0842	162	0.5989	614
0.1777	333	0.6821	544
0.2324	422	0.7124	509
0.3339	552	0.7654	436
0.3741	589	0.8325	326
0.4413	630	0.8778	243
0.5008	642	0.9213	158
$H^{(0)} = 2568.5$, $H^{(1)} = 56.3$, $H^{(2)} = -607.9$; $\sigma(H^E) = 2.2$ Jmol^{-1}			
Tetrahydropyran (i) + cyclohexane (j)			
0.0634	134	0.5322	526
0.1146	228	0.6045	494
0.2073	368	0.6848	432
0.2734	442	0.7529	361
0.3379	494	0.7939	311
0.3805	517	0.8564	226
0.4339	532	0.8976	165
$H^{(0)} = 2132.7$, $H^{(1)} = -287.7$, $H^{(2)} = -176.4$; $\sigma(H^E) = 0.6$ Jmol^{-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})
			Tetrahydropyran(i) + n − hexane(j)
0.0981	1054	1358.8	−49.5
0.1578	1067	1305.3	−70.2
0.1965	1075	1273.3	−80.4
0.2955	1093	1198.6	−97.2
0.3313	1099	1173.7	−100.4
0.3955	1110	1130.7	−103.3
0.4469	1118	1097.7	−103.2
0.4947	1126	1067.5	−101.6
0.5211	1130	1051.2	−100.0
0.5955	1143	1005.7	−93.6
0.6955	1161	945.2	−80.4
0.7311	1168	923.9	−74.4
0.7965	1181	885.1	−61.5
0.8992	1203	825.4	−35.1
$\kappa_S^{(0)} = -405.2, \kappa_S^{(1)} = 106.9, \kappa_S^{(2)} = -106.5; \sigma(\kappa_S^E) = 0.1$ TPa^{-1}			
			Tetrahydropyran(i) + n − heptane(j)
0.0833	1100	950.6	−6.3
0.1323	1107	938.5	−9.6
0.1977	1117	922.7	−13.5
0.2396	1127	908.2	−16.5
0.3245	1137	893.4	−19.1
0.3812	1145	880.9	−20.7
0.4396	1154	868.5	−21.7
0.5033	1163	855.5	−22.1
0.5684	1172	842.6	−21.8
0.6161	1178	833.6	−21.0
0.6880	1187	820.5	−19.1
0.7646	1197	807.2	−16.0
0.8223	1204	797.6	−12.9
0.9044	1213	784.7	−7.6
$\kappa_S^{(0)} = -88.5, \kappa_S^{(1)} = -4.6; \sigma(\kappa_S^E) = 0.1$ TPa^{-1}			
			Tetrahydropyran(i) + cyclohexane(j)
0.0785	1209	887.7	6.0
0.1610	1205	884.6	12.1
0.1965	1204	883.0	14.5
0.2477	1202	880.3	17.6
0.3378	1200	874.2	21.8
0.3879	1199	869.8	23.2
0.4330	1199	865.3	24.0
0.4712	1199	861.0	24.3
0.5344	1200	853.0	23.8
0.5988	1202	843.7	22.3
0.6421	1203	836.8	20.7
0.7533	1209	817.2	15.0
0.8066	1212	807.2	11.7
$\kappa_S^{(0)} = 96.7, \kappa_S^{(1)} = -13.3, \kappa_S^{(2)} = -35.7; \sigma(\kappa_S^E) = 0.1$ TPa^{-1}			

mixtures differ by ±0.005 cm^3 mol^{-1} from the V^E values reported for these mixtures in the literature [24,25]. We are unaware of any V^E, H^E and κ_S^E data of the remaining mixtures at 308.15 K with which to compare our results. Excess molar enthalpies, H^E data for the studied mixtures are positive over the entire mole fraction range and for an equimolar composition vary in the order: n-heptane > n-hexane > cyclohexane. V^E values are positive for THP (i) + cyclohexane or n-heptane or n-hexane (j) binary mixtures over entire composition. Further κ_S^E values for THP (i) + n-hexane or n-heptane (j) are negative and positive for THP (i) + cyclohexane (j) binary mixtures over whole mole fraction range. V^E and κ_S^E data for an equimolar composition vary in the order: cyclohexane > n-heptane > n-hexane.

5. Graph theory and results

The addition of THP (i) to cyclohexane or n-heptane or n-hexane (j) may change the topology of (i) or (j) in the mixed state. Excess molar volumes, V^E reflects change in topology of the constituents of the mixtures, so it was worthwhile to analyze the observed V^E data in terms of Graph theory. According to Graph theory [27], V^E is given by:

$$V^E = \alpha_{ij} \left\{ \left[\sum x_i (^3\zeta_i)_m \right]^{-1} - \left[\sum x_i (^3\zeta_i) \right]^{-1} \right\} \quad (7)$$

where α_{ij} is a constant characteristic of $(i+j)$ mixture and x_i is the mole fraction of component (i). $(^3\xi_i)$ $(i = i$ or $j)$ and $(^3\xi_i)_m$ $(i = i$ or $j)$ are connectivity parameters of the third degree of (i) and (j) in their pure and mixed state $^3\xi$ are defined [28] by Eq. (8):

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

where δ_m^v has the same significance described elsewhere [29].

As the degree of association of (i) or (j) is not known with certainty, we regarded these parameters as adjustable parameters and determined them by fitting experimental V^E data of the $(i+j)$ mixtures to Eq. (7). Only those $(^3\xi_i)$ and $(^3\xi_i)_m$ $(i = i$ or $j)$ values were retained that best reproduced the experimental V^E data. Such V^E values along with $(^3\xi_i)$ and $(^3\xi_i)_m$ $(i = i$ or $j)$ for the investigated mixtures at various x_i are recorded in Table 5 and V^E values are compared with their corresponding experimental values. Exami-

Table 5
Comparison of V^E, H^E and κ_S^E values calculated from Eqs. (7) and (15) with their corresponding experimental values at 308.15 K along with their $(^3\xi_i)$ and $(^3\xi_i)_m$ $(i = i$ or $j)$; α_{ij} and χ'_{ij} parameters 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
Tetrahydropyran (i) + n-hexane (j)									
V^E (exptl)	0.036	0.057	0.065	0.065	0.059	0.050	0.038	0.026	0.013
V^E (graph)	0.024	0.042	0.053	0.058	–	0.055	0.047	0.035	0.019
H^E (exptl)	173	319	433	510	546	537	480	372	213
H^E (graph)	179	324	437	512	–	–	481	375	215
κ_S^E (exptl)	−50.3	−81.2	−97.6	−103.4	−101.3	−93.1	−79.7	−60.7	−34.9
κ_S^E (graph)	−43.8	−75.0	−94.6	–	−102.5	–	−76.5	−54.3	−28.7
$(^3\xi_i) = (^3\xi_i)_m = 1.301$; $(^3\xi_j) = (^3\xi_j)_m = 0.957$; $\alpha_{ij} = -2.803\,\mathrm{cm^3\,mol^{-1}}$									
$\chi'_{ij} = 979.9$; $\chi_{ii} = 424.4\,\mathrm{J\,mol^{-1}}$									
$\chi'_{ij} = -481.1$; $\chi_{12} = 252.4\,\mathrm{TPa^{-1}}$									
Tetrahydropyran (i) + n-heptane (j)									
V^E (exptl)	0.100	0.175	0.228	0.258	0.268	0.257	0.225	0.173	0.098
V^E (graph)	0.103	0.181	0.233	0.262	–	0.253	0.218	0.163	0.090
H^E (exptl)	191	370	514	608	642	613	524	382	200
H^E (graph)	235	417	544	619	–	–	534	405	227
κ_S^E (exptl)	−7.5	−13.6	−18.2	−21.0	−22.1	−21.4	−18.7	−14.2	−7.9
κ_S^E (graph)	−7.7	−13.8	−18.2	–	22.1	–	−18.9	−14.6	−8.3
$(^3\xi_i) = (^3\xi_i)_m = 1.302$; $(^3\xi_j) = (^3\xi_j)_m = 1.100$; $\alpha_{ij} = -45.586\,\mathrm{cm^3\,mol^{-1}}$									
$\chi'_{ij} = 2624.2$; $\chi_{ii} = -505.2\,\mathrm{J\,mol^{-1}}$									
$\chi'_{ij} = -83.7$ $\chi_{ii} = 4.0\,\mathrm{TPa^{-1}}$									
Tetrahydropyran (i) + cyclohexane (j)									
V^E (exptl)	0.133	0.228	0.289	0.319	0.321	0.298	0.252	0.186	0.101
V^E (graph)	0.1093	0.197	0.262	0.304	–	0.313	0.278	0.215	0.123
H^E (exptl)	203	359	466	524	533	496	418	304	161
H^E (graph)	217	374	476	528	–	–	421	311	170
κ_S^E (exptl)	7.6	14.7	20.2	23.5	24.2	22.2	18.0	12.1	5.7
κ_S^E (graph)	9.6	16.6	21.2	–	23.8	–	18.9	14.0	7.7
$(^3\xi_i) = (^3\xi_i)_m = 1.303$; $(^3\xi_j) = (^3\xi_j)_m = 1.500$; $\alpha_{ij} = -88.616\,\mathrm{cm^3\,mol^{-1}}$									
$\chi'_{ij} = 2486.9$; $\chi_{ii} = -382.0\,\mathrm{J\,mol^{-1}}$									
$\chi'_{ij} = 109.7$; $\chi_{ii} = -14.5\,\mathrm{TPa^{-1}}$									

nation of Table 5 reveals that predicted V^E values compare well with their experimental values. $(^3\xi_i)$ and $(^3\xi_i)_m$ $(i = i$ or $j)$ values thus can be relied upon to extract information about the state of components $(i)/(j)$ in pure and mixed state. Structures were then assumed for THP and their $^3\xi_i{}^/$ values were predicted by employing structural considerations [via Eq. (8)]. Any structure or combination of structures that provided $^3\xi^/$ value which compare well with $^3\xi$ value (determined by Eq. (7)) was taken to be representative structure of THP. We assumed that THP exists as molecular entities I–II (Scheme 1). $^3\xi^/$ values for these molecular entities were then calculated to be 1.078 and 1.349. $^3\xi$ values 1.301, 1.302 and 1.303 [Table 5] suggest that THP exists as associated molecular entity II. Further $^3\xi^/$ values of 1.500, 0.957 and 1.100 for cyclohexane, n-hexane and n-heptane [molecular entities (III–V)] suggest that they exist as monomers.

In order to extract information about the state of THP (i) in THP(i) + cyclohexane or n-hexane or n-heptane (j) mixtures, it was assumed that studied mixtures may contain molecular entities VI–VIII and their $^3\xi^/$ were calculated to be 1.364, 1.552 and 1.552. In evaluating $^3\xi^/$ values for molecular entities VI–VIII it was assumed that molecular entity VI is characterized by interactions between oxygen atoms of THP and three axial hydrogen atoms of cyclohexane. Further molecular entities VII–VIII are characterized by interactions between dipole of THP and induced dipole of n-hexane or n-heptane. $(^3\xi_i)_m$ values of 1.301, 1.302 and 1.303 for THP(i) [Table 5] suggest the presence of molecular entities VI–VIII in the investigated mixtures. The postulation of molecular entities VI–VIII reveals that the addition (j) to (i) must change in C–O–C stretching vibrations of THP. In view of this, we analyzed IR spectral data of pure THP(i) and THP(i) + cyclohexane or n-hexane(j) equimolar mixtures. It was observed that characteristic stretching vibrations (C–O–C) at 1090 cm^{-1} in pure THP [30] shifted to 1106 cm^{-1} and 1110 cm^{-1} respectively in THP (i) + cyclohexane or n-hexane (j)

mixtures. The IR spectra data of THP (i) + cyclohexane or n-hexane (j) mixtures thus reveals that addition of (j) to (i) does influence the C–O–C stretching vibrations of THP and also lends additional support to the existence of molecular entities VI–VIII in various $(i+j)$ mixtures.

The energetics and the isentropic compressibilities changes of mixing of the studied mixtures can be studied if it be assumed that THP (i) + cyclohexane or n-hexane or n-heptane (j) mixtures formation involve processes: (1) THP exist an associated molecular entity (i_n); (2) formation of unlike contacts between (i_n) and (j) then weakens $i_n - j$ interactions which leads to depolymerization of (i_n) to give monomers of (i); (3) monomers of (i) and (j) then undergo dipole–induced dipole interactions to form i:j molecular complex. If χ'_{ij}, χ_{ii} and χ_{12} are molecular interaction energies and molar compressibilities parameters of i–j, i–i contacts and dipole–induced dipole interactions respectively, then change in molar thermodynamic properties, $\Delta X (X = H$ or $\kappa_S)$ due to processes (1–3) would be given by [31–33] by:

$$\Delta X_1 (X = H \text{ or } \kappa_S) = x_i \chi_{ij} S_j \tag{9}$$

where S_j, the surface fraction of j, involved in $(i$–$j)$ contacts is defined [32] by:

$$S_j = \frac{x_j v_j}{\displaystyle\sum_{i=i}^{j} x_i v_i}$$

so that

$$\Delta X_1 (X = H \text{ or } \kappa_S) = \frac{x_i x_j v_j \chi_{ij}}{\sum x_i v_i} \tag{10}$$

$$\,^3\xi' = 1.078$$

(I)

$$\,^3\xi' = 1.349$$

(II)

$$\,^3\xi' = 1.500$$

(III)

$$\,^3\xi' = 0.957$$

(IV)

$$\,^3\xi' = 1.100$$

(V)

$$\,^3\xi' = 1.364$$

(VI)

$$\,^3\xi' = 1.552$$

(VII)

$$\,^3\xi' = 1.552$$

(VIII)

Carbon　　Oxygen　　Hydrogen
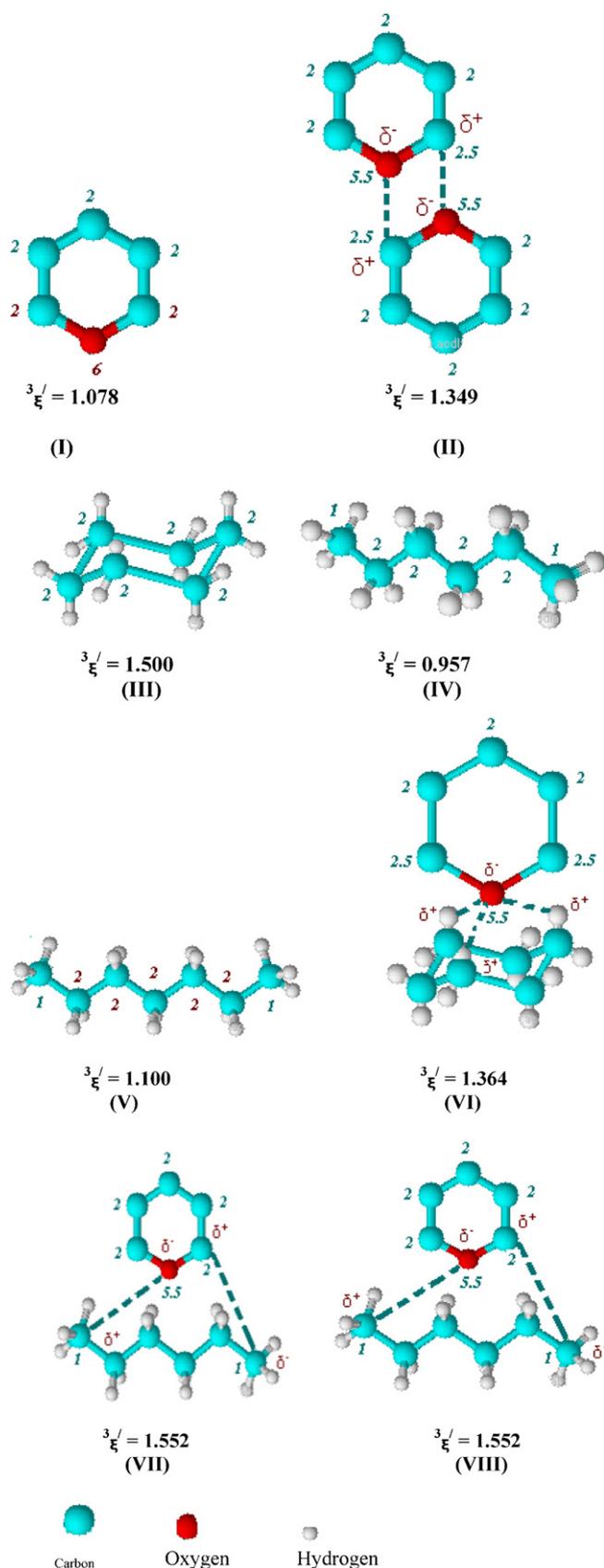
Scheme 1. Connectivity parameters of various molecular entities in pure state.

$$\Delta X_2(X = H \,\text{or}\, \kappa_S) = \frac{x_i^2 x_j v_j \chi_{ii}}{\sum x_i v_i} \tag{11}$$

$$\Delta X_3(X = H \,\text{or}\, \kappa_S) = \frac{x_i x_j^2 \chi_{12}}{\sum x_i v_i} \tag{12}$$

where v_j is the molar volume of component (j). The overall change in thermodynamic property, X^E ($X = H$ or κ_S) due to processes (1–3) then can be expressed as Eq. (13):

$$X^E = \sum_{i=1}^{4} \Delta X_i(X = H \,\text{or}\, \kappa_S) = \frac{x_i x_j v_j}{\sum [x_i v_i]} [\chi_{ij} + x_i \chi_{ij} + x_j \chi_{12}] \tag{13}$$

For the studied mixtures, if it be assumed that $\chi_{ii} \cong \chi_{ij} = \chi'_{ij}$ then Eq. (13) reduces to Eq. (14):

$$X^E = \frac{x_i x_j v_j}{\sum x_i v_i} [(1 + x_i)\chi'_{ij} + x_j \chi_{12}] \tag{14}$$

Further $v_j/v_i = \,^3\xi_i/\,^3\xi_j$ [34]; Eq. (14) can, therefore, be expressed as:

$$X^E(X = H \,\text{or}\, \kappa_S) = \left[\frac{x_i x_j (\,^3\xi_i/\,^3\xi_j)}{x_i + x_j (\,^3\xi_i/\,^3\xi_j)} \right] [(1 + x_i)\chi'_{ij} + x_j \chi_{12}] \tag{15}$$

Eq. (15) contains two unknown parameters (χ'_{ij} and χ_{ii}) and for the present investigations, we determined these parameters by employing X^E ($X = H$ or κ_S) data at two compositions. Predicted parameters were then utilized to determine X^E ($X = H$ or κ_S) data at various values of x_i. Such H^E and κ_S^E values along with χ'_{ij} and χ_{ii} parameters are recorded in Table 5 are also compared with their corresponding experimental values.

A perusal of data in Table 5 reveals that H^E and κ_S^E values compare well with their corresponding experimental values which lends additional support to the assumptions made in deriving Eq. (14).

Acknowledgements

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