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Topological investigations of the molecular species and molecular interactions that characterize pyrrolidin-2-one + lower alkanol mixtures

J.S. Yadav, Dimple Sharma, V.K. Sharma*

Department of Chemistry, Maharshi Dayanand University, Rohtak 124001, India

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ABSTRACT

Molar excess volumes, V^E, molar excess enthalpies, H^E, and speeds of sound data, u, of pyrrolidin-2-one (i) + ethanol or propan-1-ol or propan-2-ol or butan-1-ol (j) binary mixtures have been determined over entire composition range at 308.15 K. The observed speeds of sound data have been utilized to predict excess isentropic compressibilities, κ_S^E of the investigated binary mixtures. The observed excess thermodynamic properties V^E, H^E and κ_S^E have been analyzed in terms of Graph theory. The analysis of V^E data by the Graph theory suggests that pyrrolidin-2-one exists mainly as a mixture of cyclic and open dimer; ethanol as a mixture of dimer and trimer; butan-1-ol and propan-2-ol as mixture of monomer and dimer and propan-1-ol as a dimer in the pure state, and their mixtures contain 1:1 molecular complex. The IR studies lend additional credence to the nature and extent of interactions for the proposed molecular entities in the mixtures. Also, it has been observed that V^E, H^E and κ_S^E values predicted by the Graph theory compare well to with their corresponding experimental values.

1. Introduction

Ab initio studies [1] on the different associated structures of pyrrolidin-2-one with water have revealed that pyrrolidin-2-one exists as a dimer in pure state and two pyrrolidin-2-one molecules are held together by intermolecular hydrogen bond [2–7]. Further, self-association in lower alkanols have been interpreted in terms of monomer-dimer equilibria by several workers [8–10]. Thus, the addition of lower alkanols (j) like ethanol or propan-1-ol or propan-2-ol or butan-1-ol to pyrrolidin-2-one (i) may enhance or rupture self-association of pyrrolidin-2-one or alkanols. Since molar excess volumes, V^E, molar excess enthalpies, H^E, and excess isentropic compressibilities, κ_S^E, reflects interaction, packing and compressibility effect, it would therefore be of interest to extract information about the nature of association of pyrrolidin-2-one and lower alkanols (from their V^E, H^E, and κ_S^E data by employing topology of the constituents of mixtures) in pure and mixed state and also about the nature of various molecular entities present in these mixtures. In recent studies [11,12], we have employed topology of the constituents of the mixtures to evaluate molar excess volumes, molar excess enthalpies and excess isentropic compressibilities. These considerations prompted us to measure molar excess volumes, molar excess enthalpies and speeds of sound data of pyrrolidin-2-one + ethanol or propan-1-ol or propan-2-ol or butan-1-ol binary mixtures.

2. Experimental

Pyrrolidin-2-one (**2-Py**) [Fluka], ethanol, propan-1-ol, propan-2-ol, butan-1-ol (AR Grade) were purified by standard methods [13]. The purities of the samples were checked by measuring their densities using pycnometer with an accuracy of 2 parts in 10^5 (recorded in Table 1) at 298.15 ± 0.01 K and these agreed to within ±0.05 kg m^{-3} with their corresponding literature values [13,14].

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 [15]. The uncertainties in the measures V^E values are ±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 [16] and the uncertainties in the measured H^E values are ±1%.

Speeds of sound, u, 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 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 [6,17–19]. The uncertainties in the measured speed of sound values are ±1 ms^{-1}.

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* Corresponding author. Tel.: +91 1262295012.
E-mail address: v_sharmachem58@rediffmail.com (V.K. Sharma).

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Table 1
Comparison of densities, ρ, and speeds of sound, u, of pure liquids with their literature values at 308.15 K respectively.

Liquid	ρ (kg m^{-3})		u (ms^{-1})	
	Experimental	Literature	Experimental	Literature
Pyrrolidin-2-one	1107.26	1107.22 [16]	1603.0	1603.1 [6]
Ethanol	785.08	785.93 [13]	1112.0	1109.05 [17]
Propan-1-ol	799.28	799.60 [13]	1188.2	1188.8 [18]
Propan-2-ol	780.98	781.26 [13]	1135.9[a]	1136.3[a] [19]
Butan-1-ol	809.50	809.75 [13]	1232.2	1232.0 [18]

[a] Value at 298.15 K.

IR spectra for **2-Py**, propan-2-ol and their equimolar mixture were recorded on a Perkin Elmer RX-1 FTIR spectrophotometer.

3. Results

Molar excess volumes, V^E, molar excess enthalpies, H^E and speed of sound, u, of **2-Py** (i) + ethanol or propan-1-ol or propan-2-ol or butan-1-ol (j) binary mixtures over the entire range of composition at 308.15 K are recorded in Tables 2–4 respectively. The isentropic compressibility, κ_S for ($i+j$) mixtures were evaluated from speed of sound data using Eq. (1)

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

Table 2
Measured molar excess volumes, V^E data for the various ($i+j$) mixtures as a function of mole fraction, $\boldsymbol{x_i}$, of component (i) at 308.15 K.

x_i	V^E (cm^3 mol^{-1})	x_i	V^E (cm^3 mol^{-1})
Pyrrolidin-2-one (i) + ethanol (j)			
0.0767	−0.092	0.5479	−0.413
0.1393	−0.172	0.6015	−0.394
0.1763	−0.215	0.6573	−0.366
0.2676	−0.307	0.7145	−0.321
0.3493	−0.368	0.7982	−0.240
0.4016	−0.394	0.8560	−0.175
0.4865	−0.416	0.9200	−0.097
$V^{(0)} = -1.665$, $V^{(1)} = -0.001$, $V^{(2)} = 0.463$, $\sigma(V^E) = 0.002$ cm^3 mol^{-1}			
Pyrrolidin-2-one (i) + propan-1-ol (j)			
0.0349	−0.023	0.4495	−0.244
0.0973	−0.067	0.5246	−0.248
0.1436	−0.100	0.5749	−0.246
0.2052	−0.138	0.6516	−0.227
0.2654	−0.175	0.7453	−0.185
0.3299	−0.208	0.8357	−0.129
0.3881	−0.227	0.9206	−0.065
$V^{(0)} = -0.994$, $V^{(1)} = -0.085$, $V^{(2)} = 0.257$, $\sigma(V^E) = 0.001$ cm^3 mol^{-1}			
Pyrrolidin-2-one (i) + propan-2-ol (j)			
0.0825	−0.098	0.4756	−0.381
0.1311	−0.154	0.5684	−0.374
0.1719	−0.197	0.6315	−0.351
0.2365	−0.259	0.6921	−0.317
0.2949	−0.307	0.7193	−0.298
0.3480	−0.336	0.8048	−0.229
0.4267	−0.369	0.8941	−0.133
$V^{(0)} = -1.522$, $V^{(1)} = -0.030$, $V^{(2)} = 0.2616$, $\sigma(V^E) = 0.001$ cm^3 mol^{-1}			
Pyrrolidin-2-one (i) + butan-1-ol (j)			
0.0883	−0.065	0.5269	−0.188
0.1021	−0.076	0.5855	−0.183
0.2423	−0.147	0.6229	−0.176
0.3298	−0.172	0.7154	−0.153
0.4003	−0.187	0.7617	−0.136
0.4536	−0.190	0.8382	−0.102
0.4970	−0.192	0.8826	−0.077
$V^{(0)} = -0.763$, $V^{(1)} = 0.049$, $V^{(2)} = -0.029$, $\sigma(V^E) = 0.001$ cm^3 mol^{-1}			

Table 3
Measured molar excess enthalpies, H^E values for the various ($i+j$) mixtures as a function of mole fraction, $\boldsymbol{x_i}$, of component (i) at 308.15 K.

x_i	H^E (J mol^{-1})	x_i	H^E (J mol^{-1})
Pyrrolidin-2-one (i) + ethanol (j)			
0.0647	269.1	0.5337	494.2
0.1158	427.9	0.6050	433.5
0.2075	585.6	0.6856	349.1
0.2768	622.8	0.7539	271.4
0.3380	634.7	0.7929	230.9
0.3800	619.3	0.8436	190.3
0.4337	584.1	0.8904	130.6
$H^{(0)} = 2121.4$, $H^{(1)} = -1797.9$, $H^{(2)} = 1091.2$, $\sigma(H^E) = 6.3$ J mol^{-1}			
Pyrrolidin-2-one (i) + propan-1-ol (j)			
0.0592	248.5	0.4950	609.7
0.1085	390.4	0.5219	580.6
0.1966	566.7	0.5951	522.1
0.2273	608.3	0.6622	449.9
0.3287	671.8	0.7539	338.0
0.3782	667.1	0.8065	284.5
0.4394	648.6	0.8946	165.8
$H^{(0)} = 2416.6$, $H^{(1)} = -1506.5$, $H^{(2)} = 784.6$, $\sigma(H^E) = 6.7$ J mol^{-1}			
Pyrrolidin-2-one (i) + propan-2-ol (j)			
0.0841	460.5	0.6009	730.9
0.1776	783.1	0.6811	603.4
0.2315	877.8	0.7151	540.3
0.3340	944.6	0.7626	463.1
0.3758	949.7	0.8338	343.8
0.4453	913.5	0.8794	265.4
0.5010	860.6	0.9223	179.3
$H^{(0)} = 3415.0$, $H^{(1)} = -2190.4$, $H^{(2)} = 1172.1$, $\sigma(H^E) = 8.5$ J mol^{-1}			
Pyrrolidin-2-one (i) + butan-1-ol (j)			
0.0824	348.5	0.5451	746.4
0.1933	647.1	0.5725	712.3
0.2472	727.3	0.6427	629.9
0.3241	806.5	0.7058	532.4
0.3748	816.8	0.7499	470.1
0.4183	815.3	0.8571	275.2
0.4734	799.2	0.9247	152.7
$H^{(0)} = 3112.5$, $H^{(1)} = -1418.9$, $H^{(2)} = 363.9$, $\sigma(H^E) = 8.0$ J mol^{-1}			

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

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

where x_i, M_i and ρ_{ij} are the mole fraction, molar mass and density of component (i) of binary mixture. Excess isentropic compressibility, κ_S^E for binary mixtures were predicted using Eq. (3)

$$\kappa_S^E = \kappa_S - \sum_{i=i}^{j} x_i (\kappa_S)_i \tag{3}$$

where $(\kappa_S)_i$ is the isentropic compressibility of the ith component of binary mixtures. Such κ_S^E values for the studied mixtures are recorded in Table 4.

Molar excess volumes, V^E, Molar excess enthalpies, H^E and excess isentropic compressibility, κ_S^E of various binary mixtures were fitted to Redlich–Kister equation [20], Eq. (4)

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

where $X^{(n)}(n = 0\text{–}2)$, etc. are the parameters characteristic of ($i+j$) mixture and have been determined using the least squares method and are recorded in Tables 2–4 along with standard deviation, σ $(X^E)(X = V$ or H or $\kappa_S)$ defined by

$$\sigma(X)^E = \left[\frac{\sum (X^E_{\text{expt}} - X^E_{\text{cal.Eq.(4)}})^2}{m - n} \right]^{0.5} \tag{5}$$

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

x_i	u (ms^{-1})	κ_S (TPa^{-1})	κ_S^E (TPa^{-1})
Pyrrolidin-2-one (i) + ethanol (j)			
0.0784	1172.9	897.5	−75.4
0.1607	1230.8	782.5	−121.6
0.1963	1252.8	742.9	−132.5
0.2471	1282.9	692.7	−142.7
0.338	1327.2	623.5	−143.1
0.3876	1349.4	591.9	−138.6
0.4337	1366.5	567.7	−130.2
0.4713	1381.0	548.6	−123.7
0.5347	1404.3	519.7	−109.4
0.5985	1427.8	492.9	−94.5
0.6412	1444.8	475.5	−84.9
0.7539	1492.3	432.4	−59.2
0.8064	1518.1	412.4	−48.5
0.8887	1559.4	383.4	−30.9
$\kappa_S^{(0)} = -468.201$, $\kappa_S^{(1)} = 437.037$, $\kappa_S^{(2)} = -294.726$, $\sigma(\kappa_S^E) = 0.7$			
Pyrrolidin-2-one (i) + propan-1-ol (j)			
0.0982	1219.3	817.2	−23.5
0.158	1240.8	771.2	−36.7
0.1968	1255.0	742.9	−43.7
0.2958	1294.4	673.7	−58.9
0.3309	1308.9	650.6	−62.8
0.3952	1336.5	610.3	−68.2
0.4485	1359.7	579.2	−70.4
0.4949	1391.8	553.2	−71.3
0.521	1380.7	539.8	−70.6
0.5951	1425.6	502.6	−67.8
0.6957	1470.7	458.0	−58.3
0.7314	1485.7	444.1	−53.1
0.7968	1515.4	418.9	−43.3
0.8982	1558.4	385.0	−23.1
$\kappa_S^{(0)} = -283.861$, $\kappa_S^{(1)} = 9.744$, $\kappa_S^{(2)} = 34.944$, $\sigma(\kappa_S^E) = 0.3$			
Pyrrolidin-2-one (i) + propan-2-ol (j)			
0.0835	1144.9	952.4	−43.3
0.1329	1166.9	898.0	−63.2
0.1976	1196.8	831.5	−84.5
0.2597	1225.6	773.8	−98.9
0.3244	1256.0	718.7	−108.8
0.3815	1283.5	673.6	−113.9
0.4394	1311.6	631.6	−115.4
0.5031	1343.3	588.8	−113.7
0.5682	1376.4	548.4	−108.5
0.6159	1401.1	520.9	−102.6
0.6879	1439.2	482.2	−90.8
0.765	1479.9	445.2	−73.8
0.8223	1511.6	419.3	−59.5
0.9042	1553.8	387.3	−34.0
$\kappa_S^{(0)} = -453.688$, $\kappa_S^{(1)} = 104.268$, $\kappa_S^{(2)} = -41.716$, $\sigma(\kappa_S^E) = 0.6$			
Pyrrolidin-2-one (i) + butan-1-ol (j)			
0.0632	1237.1	802.3	1.7
0.1176	1245.9	777.2	−1.3
0.186	1262.9	740.0	−10.2
0.2306	1276.6	713.9	−17.5
0.3394	1315.9	648.8	−35.4
0.3954	1338.2	616.3	−43.0
0.4442	1359.0	588.3	−48.8
0.4825	1374.9	567.8	−51.6
0.5453	1402.0	535.2	−54.7
0.5702	1412.4	523.2	−54.8
0.6427	1441.1	491.0	−51.7
0.7367	1478.0	453.1	−42.5
0.8275	1512.6	420.2	−28.2
0.9152	1551.0	388.6	−12.6
$\kappa_S^{(0)} = -211.742$, $\kappa_S^{(1)} = -106.451$, $\kappa_S^{(2)} = 198.148$, $\sigma(\kappa_S^E) = 0.3$			

where m, n are the number of data points and adjustable parameters in Eq. (5).

4. Discussion

V^E data for **2-Py** (i) + ethanol or 1-propanol or 2-propanol or 1-butanol at 303.15 K and 313.15 K have been reported in literature [21,22]. Our V^E values at 308.15 K lie within the values reported at 303.15 K and 313.15 K. We are unaware of any H^E and κ_S^E values of the investigated mixtures with which to compare our results. V^E data for the studied $(i+j)$ mixtures are negative; H^E data are positive over entire composition range. While V^E data for an equimolar composition vary as butan-1-ol > propan-1-ol > propan-2-ol > ethanol; H^E data vary in the order: propan-2-ol > butan-1-ol > propan-1-ol > ethanol. Further κ_S^E values of **2-Py** (i) + ethanol or propan-1-ol or propan-2-ol (j) binary mixtures are negative over the entire composition range. The sign of κ_S^E for **2-Py** (i) + butan-1-ol (j) mixtures are dictated by the relative proportion of 2-Py (i) and for an equimolar mixture vary as: butan-1-ol > propan-1-ol > propan-2-ol > ethanol.

The observed H^E data for $(i+j)$ binary mixtures can be explained qualitatively, if it be assumed; (1) **2-Py** and alkanols are associated molecular entities; (2) there is interaction between **2-Py** and alkanols; (3) interactions between (i) and (j) then weakens i_n and j_n interactions which in turn lead to their depolymerization; (4) monomers of (i) and (j) then undergo interactions to form $i{:}j$ molecular complex; (5) there is a steric repulsion between **2-Py** (i) and propan-2-ol molecules due to the presence of bulky —CH_3 group. H^E data for **2-Py** (i) + ethanol (j) mixtures suggest that contribution due to factor (3) far outweighs the contribution due to factors (2) and (4), so that overall H^E values of this mixture are positive. Consequently, H^E data for **2-Py** (i) + propan-1-ol or butan-1-ol mixtures are higher than that for **2-Py** (i) + ethanol (j) mixtures. This may be due to the presence of long carbon chain in alkanols which leads to decrease in alkanol–alkanol interactions. V^E and κ_S^E data for the studied mixtures suggest that ethanol gives more packed arrangement while butan-1-ol gives relatively less packed arrangement in **2-Py** (i).

5. Graph theory and results

The addition of **2-Py** (i) to alkanols (j) may result in change in topology of (i) or (j) in $(i+j)$ mixtures. Since molar excess volume, V^E, is a packing effect which in turn reflects change in topology of (i) or (j), so it was worthwhile to analyse the observed V^E data of various $(i+j)$ mixtures in terms of Graph theory [23] that employs the concept of connectivity parameter of third degree $^3\xi$ of a molecule. V^E according to the theory is given by

$$V^E = \alpha_{ij}\Big[\Big[\sum x_i ({}^3\xi_i)_m\Big]^{-1} - \Big[\sum x_i ({}^3\xi_i)\Big]^{-1}\Big] \tag{6}$$

where $({}^3\xi_i)$ ($i = i$ or j) and $({}^3\xi_i)_m$ ($i = i$ or j) are connectivity parameters of the third degree of (i) and (j) components of $(i+j)$ mixtures in pure and mixed state; x_i is the mole fraction of component (i) and α_{ij} is a constant characteristic of $(i+j)$ mixture. Singh and Kier [24,25] defined $^3\xi$ by

$$^3\xi = \sum_{\ell<m<n<o} (\delta_\ell^v \delta_m^v \delta_n^v \delta_o^v)^{-0.5} \tag{7}$$

where δ_m^v, etc. reflect explicitly for forming bonding of the mth vertex in molecular graph of a molecule, and is related to the maximum valency, z_m, and the number of hydrogen atoms attached to the mth vertex, by the relation $\delta_m^v = z_m - h_m$ [25].

As the degree of association of i or j is not known in pure and mixed state we presumed $^3\xi_i$ ($i = i$ or j) and $({}^3\xi_i)_m$ ($i = i$ or j) as adjustable parameters. These parameters were determined by

Table 5

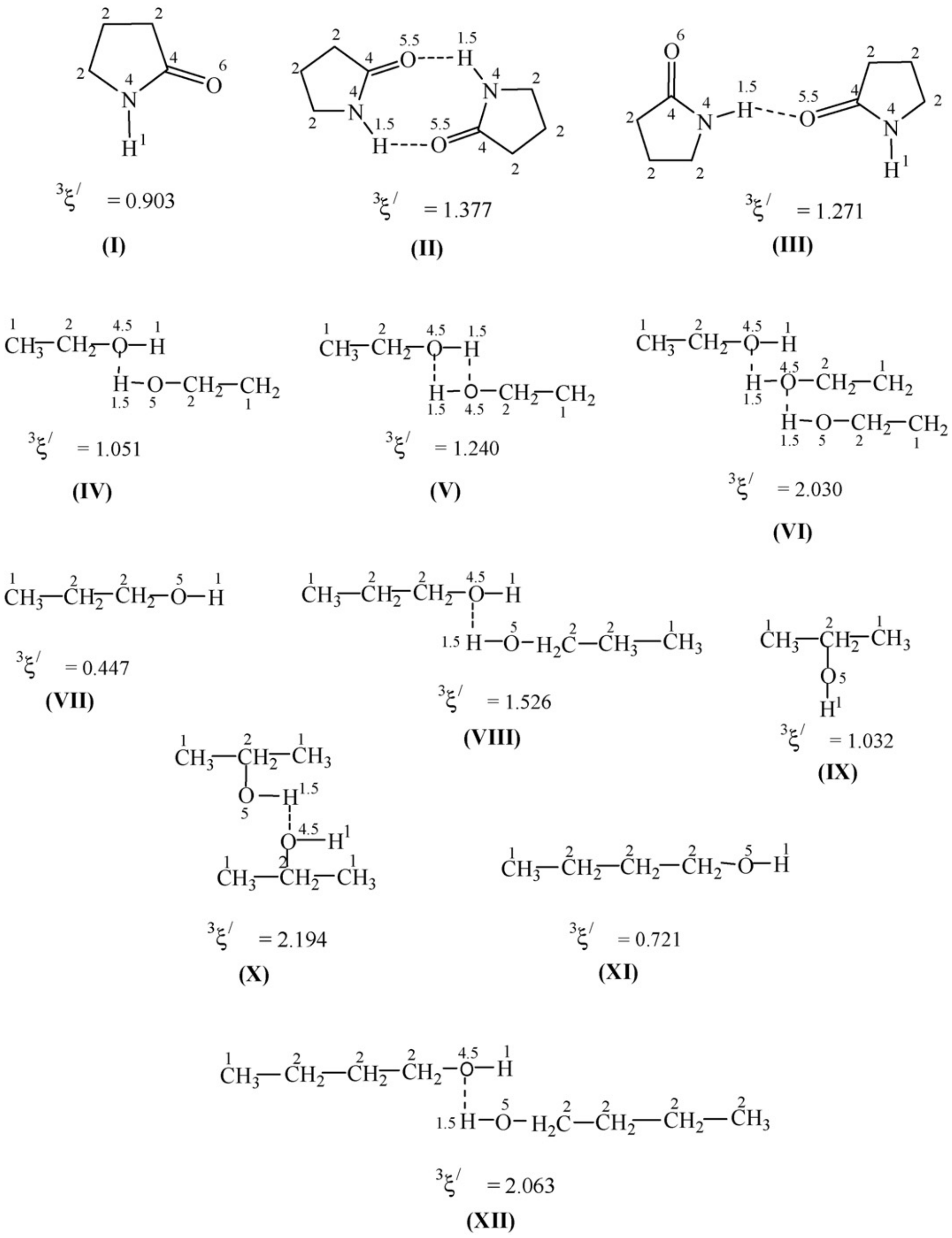
Comparison of V^E, H^E and κ_S^E values calculated from Eqs. (6) and (14) with their corresponding experimental values at 308.15 K along with various $(^3\xi_i)$ and $(^3\xi_i)_m$ ($i = i$ or j); α_{ij} parameters for the various $(i + j)$ mixtures as a function of, x_i, mole fraction of component (i).

Mole fraction, $\boldsymbol{x_i}$									
Property	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Pyrrolidin-2-one (i) + ethanol (j)									
V^E (Exptl)	−0.226	−0.401	−0.515	−0.568	−0.560	−0.499	−0.395	−0.263	−0.123
V^E (Graph)	−0.172	−0.317	−0.431	−0.511	–	−0.554	−0.506	−0.403	−0.237
H^E (Exptl)	383.1	574.6	633.4	605.0	530.0	433.1	331.8	229.7	124.3
H^E (Graph)	355.7	549.1	620.9	–	–	420.0	295.6	174.3	71.4
κ_S^E (Exptl)	−90.6	−133.8	−144.9	−136.2	−117.1	−94.2	−71.5	−49.9	−27.6
κ_S^E (Graph)	−82.9	−126.8	−141.8	–	–	−90.5	−61.4	−34.2	−12.6
$(^3\xi_i) = (^3\xi_i)_m = 1.001$; $(^3\xi_j) = (^3\xi_j)_m = 1.503$; $\alpha_{ij} = 16.620\ \text{cm}^3\ \text{mol}^{-1}$									
$\chi_{ij}' = 387.6\ \text{J mol}^{-1}$; $\chi^* = 4137.5\ \text{J mol}^{-1}$									
$\chi_{ij}' = -54.0\ \text{T Pa}^{-1}$; $\chi^* = -1009.0\ \text{T Pa}^{-1}$									
Pyrrolidin-2-one (i) + propan-1-ol (j)									
V^E (Exptl)	−0.136	−0.242	−0.316	−0.357	−0.366	−0.344	−0.292	−0.215	−0.116
V^E (Graph)	−0.115	−0.211	−0.286	−0.339	–	−0.365	−0.332	−0.263	−0.154
H^E (Exptl)	371.2	576.6	660.1	659.8	604.0	515.3	407.4	287.3	154.5
H^E (Graph)	352.9	559.7	652.8	–	–	505.5	381.8	247.8	116.7
κ_S^E (Exptl)	−24.2	−44.3	−59.3	−68.3	−71.0	−67.3	−57.6	−42.5	−22.8
κ_S^E (Graph)	−25.8	−45.7	−59.9	–	–	−68.0	−59.4	−45.2	−25.4
$(^3\xi_i) = (^3\xi_i)_m = 1.001$; $(^3\xi_j) = (^3\xi_j)_m = 1.451$; $\alpha_{ij} = 12.842\ \text{cm}^3\ \text{mol}^{-1}$									
$\chi_{ij}' = 768.8\ \text{J mol}^{-1}$; $\chi^* = 3612.9\ \text{J mol}^{-1}$									
$\chi_{ij}' = -204.2\ \text{T Pa}^{-1}$; $\chi^* = -83.3\ \text{T Pa}^{-1}$									
Pyrrolidin-2-one (i) + propan-2-ol (j)									
V^E (Exptl)	−0.120	−0.226	−.308	−0.361	−0.381	−0.364	−0.313	−0.231	−0.124
V^E (Graph)	−0.124	−0.226	−0.304	−0.356	–	−0.375	−0.338	−0.264	−0.153
H^E (Exptl)	532.4	824.5	940.1	936.5	853.7	725.7	572.5	403.6	217.0
H^E (Graph)	497.3	792.4	926.5	–	–	709.0	528.5	336.0	153.3
κ_S^E (Exptl)	−50.7	−85.0	−105.4	−114.3	−113.4	−104.3	−87.9	−64.9	−35.7
κ_S^E (Graph)	−49.7	−84.1	−105.0	–	–	−103.7	−86.4	−62.4	−33.6
$(^3\xi_i) = (^3\xi_i)_m = 1.001$; $(^3\xi_j) = (^3\xi_j)_m = 1.300$; $\alpha_{ij} = 25.315\ \text{cm}^3\ \text{mol}^{-1}$									
$\chi_{ij}' = 861.1\ \text{J mol}^{-1}$; $\chi^* = 5270.9\ \text{J mol}^{-1}$									
$\chi_{ij}' = -231.4\ \text{T Pa}^{-1}$; $\chi^* = -349.0\ \text{T Pa}^{-1}$									
Pyrrolidin-2-one (i) + butan-1-ol (j)									
V^E (Exptl)	−0.076	−0.148	−0.206	−0.244	−0.257	−0.245	−0.208	−0.150	−0.078
V^E (Graph)	−0.079	−0.146	−0.199	−0.236	–	−0.258	−0.236	−0.189	−0.079
H^E (Exptl)	403.2	655.2	785.0	818.6	778.1	682.4	546.7	382.8	198.9
H^E (Graph)	404.3	655.4	784.9	–	–	681.3	543.2	376.6	192.4
κ_S^E (Exptl)	1.2	−10.1	−26.2	−41.0	−50.3	−51.8	−45.1	−31.7	−15.0
κ_S^E (Graph)	−5.5	−16.2	−28.9	–	–	−55.0	−53.5	−44.5	−27.0
$(^3\xi_i) = (^3\xi_i)_m = 1.001$; $(^3\xi_j) = (^3\xi_j)_m = 1.552$; $\alpha_{ij} = 6.716\ \text{cm}^3\ \text{mol}^{-1}$									
$\chi_{ij}' = 1501.9\ \text{J mol}^{-1}$; $\chi^* = 3430.9\ \text{J mol}^{-1}$									
$\chi_{ij}' = -248.5\ \text{T Pa}^{-1}$; $\chi^* = 232.6\ \text{T Pa}^{-1}$									

α_{ij} is in $\text{cm}^3\ \text{mol}^{-1}$.

employing V^E data to Eq. (6). Only those $(^3\xi_i)$ ($i = i$ or j) and $(^3\xi_i)_m$ ($i = i$ or j) were taken that best reproduced the experimental V^E values. Such $^3\xi_i$($i = i$ or j) and $(^3\xi_i)_m$ ($i = i$ or j) values along with V^E values {calculated via Eq. (6)} are recorded in Table 5 and V^E values are also compared with their corresponding experimental values. Since the agreement between the experimental and the calculated V^E values is reasonably good, $(^3\xi_i)$ and $(^3\xi_i)_m$ ($i = i$ or j) values thus obtained can be relied upon to understand the state of i or j in pure and mixed state. A number of structures were then assumed for **2-Py**, ethanol or propan-1-ol or propan-2-ol or butan-1-ol in their pure and mixed state and their $^3\xi'$ values calculated from structural considerations {via Eq. (7)}. Only those structure or combination of structures that yielded $^3\xi'$ values (calculated by Eq. (6)) which compare well with $^3\xi$ values predicted from the analysis of V^E data were taken to be representative structure of that component. For this purpose, it was assumed that **2-Py**, ethanol, propan-1-ol propan-2-ol and butan-1-ol exist as molecular entities **I–III**, **IV–VI**, **VII–VIII**, **IX–X** and **XI–XII** respectively. $^3\xi'$ values for these molecular entities were then calculated to be 0.903, 1.377, 1.271, 1.051, 1.240, 2.031, 0.447, 1.526, 1.032, 2.194 and 0.721, 2.063 respectively. $^3\xi$ values of 1.001, 1.002, 1.003, 1.004 for **2-Py** (Table 5) suggest that **2-Py** mainly exist a mixture of cyclic and open dimer ($^3\xi' = 1.324$); a small amount of monomer may also be present, or alternatively it may exist as an equilibrium mixture of all three molecular entities ($^3\xi' = 1.183$). These observations are consistent with observation obtained from ab initio calculations [1] on the different associated structures of **2-Py** and association of **2-Py** in cyclohexane and CCl_4 [5], which infers that **2-Py** exist as an associated molecular entity. Further $^3\xi'$ values of 1.503, 1.451, 1.301 and 1.552 for ethanol, propan-1-ol, propan-2-ol and butan-1-ol suggest that while ethanol exists as a mixture of dimer and trimer ($^3\xi' = 1.635$); propan-2-ol, butan-1-ol exist as a mixture of monomer and dimer ($^3\xi' = 1.613$, 1.552) and propan-1-ol exists as a dimer ($^3\xi' = 1.526$).

$(^3\xi_j')_m$ values were then determined and utilized to extract information about the state of alkanols in **2-Py**. For this purpose, we assumed that **2-Py** (i) + alkanols (j) mixtures exist as molecular entities **XIII–XVI** and $(^3\xi_j')_m$ value calculated for these molecular entities was 1.711. In evaluating $(^3\xi_j')_m$ value, it was assumed that these molecular entities are characterized by interaction between hydrogen and nitrogen atoms of **2-Py** with oxygen and hydrogen atoms of alkanol respectively. The $(^3\xi_j')_m$ value of 1.503, 1.451, 1.301 and 1.552 for alkanols in **2-Py** (Table 5) suggest that **2-Py** (i) + alkanols (j) mixtures are characterized by the presence of molecular entities **XIII–XVI**. The postulation of the molecular entities **XIII–XVI** in these mixtures suggests that the addition of alkanol to **2-Py** changes the N-H stretching of **2-Py** and



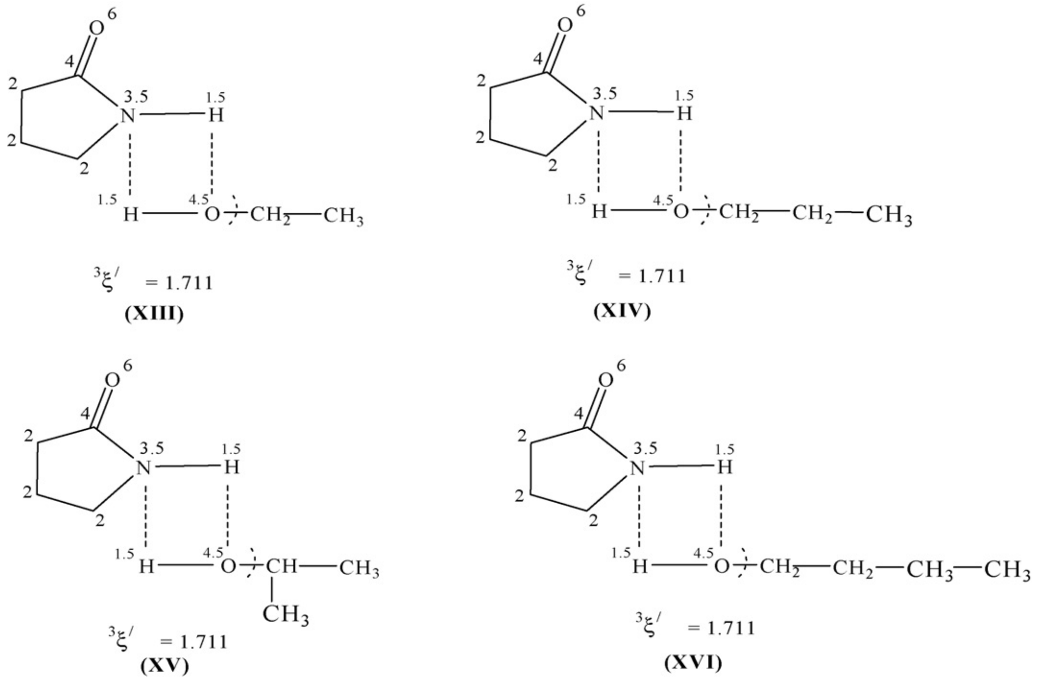
Scheme 1. Connectivity parameters of various molecular entities in pure state.

O-H stretching of alkanols. In view of this, we analyzed IR spectra of pure **2-Py**, propan-2-ol and their equimolar mixture. It was observed that **2-Py** (*i*) and propan-2-ol (*j*) in pure state show characteristic absorption at 3260 (N–H stretching) and 3370 cm^{-1}(O–H stretching)[26], respectively. The IR spectrum of equimolar mixture of **2-Py** (*i*) + propan-2-ol shows characteristic vibrations at 3285(N–H stretching) and 3360 cm^{-1} (O–H stretching). IR spectral studies thus indicate that addition of **2-Py** (*i*) to alkanols (*j*) does influence the N–H stretching vibration of **2-Py** (*i*) and O–H vibrations in alkanol (*j*) and lends an additional support to the existence of molecular entities **XIII**–**XVI** in these mixtures (Schemes 1 and 2).

H^E and κ_S^E data of studied $(i+j)$ mixtures were next analyzed in terms of Graph theory. For this purpose, it was assumed that mixture formation in **2-Py** (*i*) + ethanol or propan-1-ol or propan-2-ol or butan-1-ol mixtures involve processes: (1) formation of unlike contacts between i_n and j_n molecules; (2) unlike contact formation then weakens $i_n - j_n$ interactions in turn leads to the depolmerization of i_n and j_n; (3) 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 energy and molar compressibilities 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(a, b) and 3} would be given [27–29] by relations:

$$\Delta X_1 = \frac{x_i x_j\ \chi_{ij} \upsilon_j}{\sum x_i\, \upsilon_i} \tag{8}$$

$$\Delta X_2 = \frac{x_i^2 x_j\ \chi_{ii}\, \upsilon_j}{\sum x_1 \upsilon_i} \tag{9}$$



Scheme 2. Connectivity parameters of various molecular entities in mixed state.

$$\Delta X_3 = \frac{x_i^2 x_j\, \chi_{jj}\, v_j}{\sum x_1 v_i} \tag{10}$$

$$\Delta X_4 = \frac{x_i\, x_j^2\, \chi_{12}\, v_j}{\sum x_1 v_i} \tag{11}$$

where v_i is the molar volume of component (i). The overall excess thermodynamic property, X^E ($X = H$ or κ_S) for the investigated ($i+j$) mixtures can, therefore, be expressed by Eq. (11)

$$X^E = \sum_{i=1}^{4} \Delta X_i = \left[\frac{x_i x_j v_j}{\sum x_i v_i}\right] [\chi_{ij} + x_i\, \chi_{ii} + x_i\, \chi_{jj} + x_j\, \chi_{12}] \tag{12}$$

Singh et al. [30] have suggested that $^3\xi$ parameter of a molecule represents a measure of the probability that the surface area of a molecule interacts effectively with the surface of the other molecule and is related to its molar volume by relation $V \propto 1/{}^3\xi$. Thus $v_j/v_i = {}^3\xi_i/{}^3\xi_j$ [30]. Consequently Eq. (12) reduces to

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

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

$$X^E = \left[\frac{x_i x_j ({}^3\xi_i/{}^3\xi_j)}{x_i + x_j({}^3\xi_i/{}^3\xi_j)}\right] [(1 + x_j)\chi'_{ij} + 2x_i \chi^*] \tag{14}$$

Eq. (14) 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 ($x_i = 0.4$ and 0.5). These parameters were then employed to predict H^E and κ_S^E values at other values of x_i. Such calculated H^E and κ_S^E data along with χ'_{ij} and χ^* parameters are recorded in Table 5.

An examination of Table 5 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. (14).

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