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# Topological investigations of thermodynamic properties of binary mixtures containing 2-pyrrolidinone

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ABSTRACT

Excess molar volumes, $V_m^E$, excess molar enthalpies, $H_m^E$, and speeds of sound data, $u$, of 2-pyrrolidinone ($i$) + benzene or toluene or o- or p- or m-xylene ($j$) binary mixtures have been measured as a function of composition at 308.15 K. Isentropic compressibility changes of mixing, $\kappa_S^E$ have been determined by employing speeds of sound data. The observed data have been estimated by employing Graph theory (which involves topology of the constituents of the mixtures). It has been observed that $V_m^E$, $H_m^E$ and $\kappa_S^E$ values predicted by Graph theory compare well with their corresponding experimental values. IR studies lend further credence to the nature and extent of interaction of the proposed structures of molecular species in these mixtures.



## 1. Introduction

The amide structure is of great interest since it is related to numerous structural problems of molecular biology. Cyclic amides (lactams) are of great interest because nitrogen and carbon of a peptide bond in them are linked by a ring composed of methylene groups. 2-Pyrrolidinone is a cyclic amide (lactam) and on the basis of ab initio studies [1], an enveloped confirmation is assigned to 2-pyrrolidinone. Further 2-pyrrolidinone is known to be associated through intermolecular hydrogen bonding [2–4]. The addition of compound like benzene or toluene or o- or p- or m-xylene may tender either to rupture or enhance the self association of 2-pyrrolidinone which in turn would reflect change in topology of the constituents of mixtures. In recent studies [5–8], we have employed topology of the components of the mixtures in terms of Graph theory, (i) to extract information about the state of their existence in pure as well as mixed state, and (ii) to evaluate excess molar volumes, excess molar enthalpies of binary mixtures. Thus it would be of interest to measure thermodynamic properties excess molar volumes, $V_m^E$, excess molar enthalpies, $H_m^E$, and speeds of sound data, $u$, of 2-pyrrolidinone + aromatic hydrocarbons binary mixtures and to analyze the observed data in terms of Graph theory to gain insight about the state of aggregation of components of mixtures in pure and mixed state.

## 2. Experimental

2-Pyrrolidinone (**2-Py**) [Fluka], benzene, toluene and o-, p-, m-xylene (AR Grade) were purified by standard methods [9]. The purities of the samples were checked by measuring their densities (recorded in Table 1) at 298.15 ± 0.01 K and these agreed within ±0.05 kg m$^{-3}$ with their corresponding literature values [9,10].

Excess molar volumes, $V_m^E$ 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 [11]. The uncertainties in the measured $V_m^E$ values are ±0.5%.

Excess molar enthalpies, $H_m^E$ 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 [7] and the uncertainties in the measured $H_m^E$ 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 [12–17]. The uncertainties in the measured speed of sound values are ±1 ms$^{-1}$.

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

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

| Liquid | $\rho$ (kg m$^{-3}$) | | $u$ (m s$^{-1}$) | |
|---|---|---|---|---|
| | Experimental | Literature | Experimental | Literature |
| 2-Pyrrolidinone | 1107.26 | 1107.22 [11] | 1603[a] | 1603.1[a] [12] |
| Benzene | 873.62 | 873.60 [9] | 1298 | 1298.9 [13] |
| Toluene | 862.23 | 862.19 [9] | 1305 | 1304.0 [14] |
| o-Xylene | 875.91 | 875.94 [9] | 1344 | 1345.0 [15] |
| p-Xylene | 858.68 | 856.61 [9] | 1310 | 1309.6 [16] |
| m-Xylene | 860.17 | 860.02 [9] | 1282 | 1282.2 [17] |

[a] Value at 308.15 K.

## 3. Results

Excess molar volumes, $V_m^E$, excess molar enthalpies, $H_m^E$ and speed of sound, $u$, data of **2-Py** ($i$) + benzene or toluene or o- or p- or m-xylene ($j$) binary mixtures over the entire range of composition at 308.15 K are recorded in Tables 2 and 3 respectively (plotted in Figs. 1–3). The isentropic compressibility, $\kappa_S$ for ($i+j$) mixtures were evaluated from speeds of sound data using Eq. (1)

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

**Table 2**
Measured molar excess 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$^{-1}$) |
|---|---|---|---|
| 2-Pyrrolidinone ($i$) + benzene ($j$) | | | |
| 0.0567 | −0.117 | 0.4556 | −0.551 |
| 0.1256 | −0.236 | 0.5071 | −0.557 |
| 0.1867 | −0.332 | 0.5876 | −0.539 |
| 0.2425 | −0.404 | 0.6573 | −0.496 |
| 0.2967 | −0.463 | 0.7672 | −0.388 |
| 0.3560 | −0.507 | 0.8498 | −0.278 |
| 0.4001 | −0.536 | 0.9121 | −0.173 |
| 2-Pyrrolidinone ($i$) + toluene ($j$) | | | |
| 0.0667 | −0.099 | 0.4873 | −0.585 |
| 0.1398 | −0.208 | 0.5678 | −0.602 |
| 0.1927 | −0.286 | 0.6459 | −0.577 |
| 0.2526 | −0.371 | 0.7332 | −0.508 |
| 0.3018 | −0.431 | 0.8076 | −0.410 |
| 0.3467 | −0.482 | 0.8561 | −0.325 |
| 0.4117 | −.0539 | 0.9213 | −0.196 |
| 2-Pyrrolidinone ($i$) + o-xylene ($j$) | | | |
| 0.0673 | −0.101 | 0.4964 | −0.527 |
| 0.1469 | −0.215 | 0.5804 | −0.539 |
| 0.1973 | −0.283 | 0.6673 | −0.503 |
| 0.2560 | −0.348 | 0.7569 | −0.434 |
| 0.3139 | −0.410 | 0.8065 | −0.371 |
| 0.3742 | −0.461 | 0.8789 | −0.257 |
| 0.4342 | −0.504 | 0.9314 | −0.160 |
| 2-Pyrrolidinone ($i$) + p-xylene ($j$) | | | |
| 0.0456 | −0.065 | 0.5268 | −0.587 |
| 0.1096 | −0.163 | 0.6013 | −0.573 |
| 0.1773 | −0.262 | 0.6973 | −0.507 |
| 0.2567 | −0.381 | 0.7453 | −0.455 |
| 0.3327 | −0.474 | 0.8124 | −0.364 |
| 0.3864 | −0.522 | 0.8581 | −0.288 |
| 0.4597 | −0.568 | 0.9001 | −0.210 |
| 2-Pyrrolidinone ($i$) + m-xylene ($j$) | | | |
| 0.0894 | −0.172 | 0.5819 | −0.455 |
| 0.1951 | −0.307 | 0.6491 | −0.442 |
| 0.2483 | −0.352 | 0.7233 | −0.409 |
| 0.3265 | −0.399 | 0.7958 | −0.353 |
| 0.3965 | −0.428 | 0.8359 | −0.310 |
| 0.4659 | −0.447 | 0.8533 | −0.286 |
| 0.5140 | −0.456 | 0.9287 | −0.166 |

**Table 3**
Measured molar excess 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$^{-1}$) |
|---|---|---|---|
| 2-Pyrrolidinone ($i$) + benzene ($j$) | | | |
| 0.0642 | −28.0 | 0.5390 | −165.0 |
| 0.1193 | −56.7 | 0.5681 | −163.9 |
| 0.1893 | −88.3 | 0.6369 | −148.5 |
| 0.2289 | −107.9 | 0.7004 | −125.1 |
| 0.2721 | −126.6 | 0.7850 | −91.0 |
| 0.3688 | −153.8 | 0.8539 | −59.9 |
| 0.4379 | −167.7 | 0.9346 | −23.5 |
| 2-Pyrrolidinone ($i$) + toluene ($j$) | | | |
| 0.0584 | −2.2 | 0.4874 | −30.9 |
| 0.1056 | −5.9 | 0.5824 | −25.0 |
| 0.1614 | −11.1 | 0.6258 | −21.3 |
| 0.2181 | −17.4 | 0.6725 | −16.4 |
| 0.3086 | −25.8 | 0.7361 | −8.3 |
| 0.4010 | −30.9 | 0.8134 | −0.4 |
| 0.4315 | −30.7 | 0.8746 | +4.2 |
| 2-Pyrrolidinone ($i$) + o-xylene ($j$) | | | |
| 0.0379 | 7.4 | 0.5424 | 121.0 |
| 0.0915 | 21.9 | 0.6124 | 124.4 |
| 0.1643 | 42.3 | 0.6782 | 117.7 |
| 0.2400 | 63.7 | 0.7597 | 104.9 |
| 0.3337 | 87.2 | 0.8384 | 80.8 |
| 0.3872 | 99.6 | 0.8928 | 57.1 |
| 0.5075 | 119.9 | 0.9686 | 19.9 |
| 2-Pyrrolidinone ($i$) + p-xylene ($j$) | | | |
| 0.0662 | 10.8 | 0.5418 | 85.5 |
| 0.1454 | 25.1 | 0.6177 | 83.7 |
| 0.2230 | 42.2 | 0.6665 | 78.8 |
| 0.3159 | 61.4 | 0.7037 | 74.5 |
| 0.3408 | 64.1 | 0.7637 | 65.9 |
| 0.3926 | 73.4 | 0.8016 | 57.0 |
| 0.4923 | 83.1 | 0.8831 | 35.7 |
| 2-Pyrrolidinone ($i$) + m-xylene ($j$) | | | |
| 0.0746 | 51.7 | 0.5470 | 164.8 |
| 0.1388 | 84.9 | 0.6169 | 162.7 |
| 0.2047 | 112.4 | 0.6823 | 152.0 |
| 0.2436 | 125.1 | 0.7253 | 142.8 |
| 0.3400 | 146.5 | 0.8010 | 121.4 |
| 0.3918 | 155.3 | 0.8563 | 96.4 |
| 0.4918 | 166.9 | 0.9126 | 67.1 |

The densities, $\rho_{ij}$ of binary mixtures were evaluated from their excess molar volumes data using the reaction:

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

where $x_i$, $M_i$ and $\rho_{ij}$ are the mole fraction, molar mass and density of component ($i$) of binary mixture. Isentropic compressibility changes of mixing, $\kappa_S^E$ for binary mixtures were determined using Eq. (3)

$$\kappa_S^E = \kappa_S - \kappa_S^{id} \quad (3)$$

$\kappa_S^{id}$ was obtained according to Benson and Kiyohara [18]

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

where $\phi_i$ is the volume fraction of component ($i$) in the mixture referred to as the unmixed state, $x_i$ is the corresponding mole fraction, $T$ is the absolute temperature, and $\kappa_{S,i}$, $V_i$, $\alpha_i$ and $C_{p,i}$ are the isentropic compressibility, molar volume, thermal expansion coefficient, and molar heat capacity of the pure component ($i$), respectively. The values of $\alpha$ and $C_{p,i}$ were taken from literature [19]. $\alpha$ value for **2-Py** was evaluated in the same manner as suggested by

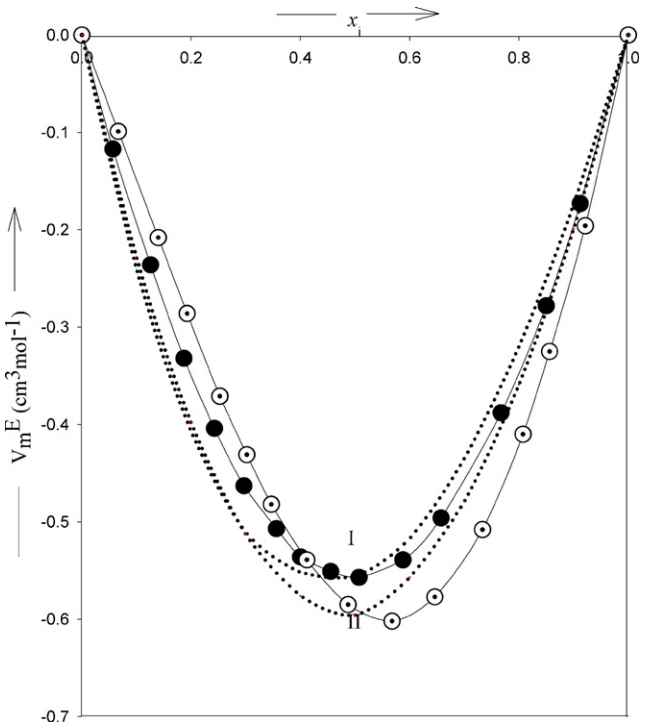



**Fig. 1.** Excess molar volumes, $V_m^E$ at 308.15 K of (I) 2-pyrrolidinone ($i$) + benzene ($j$) (●); (II) 2-pyrrolidinone ($i$) + toluene ($j$) (○) mixtures. — $V_m^E$ (exptl); - - - $V_m^E$ (Graph theory).

Hilderbrand et al. [20]. Such $\kappa_S^E$ values for the studied mixtures are recorded in Table 4 and plotted in Fig. 4.

Excess molar volumes, $V_m^E$, excess molar enthalpies, $H_m^E$ and isentropic compressibility changes of mixing, $\kappa_S^E$ of various binary mixtures were fitted to Eq. (5)

$$X^E\,(X = V_m \text{ or } H_m \text{ or } \kappa_S) = x_i x_j[X^{(0)} + X^{(1)}(2x_i - 1) + X^{(2)}(2x_i - 1)^2] \quad (5)$$

where $X^{(n)}$ ($n$ = 0–2), etc. are the parameters characteristic of ($i$ + $j$) mixtures and have been determined using the least square method and are recorded along with standard deviation, $\sigma(X^E)$ ($X = V_m$ or $H_m$ or $\kappa_S$) defined by

$$\sigma(X)^E = \left[\frac{\sum (X^E_{expt} - X^E_{cal.\,Eq.\,(5)})^2}{m - n}\right]^{0.5} \quad (6)$$

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

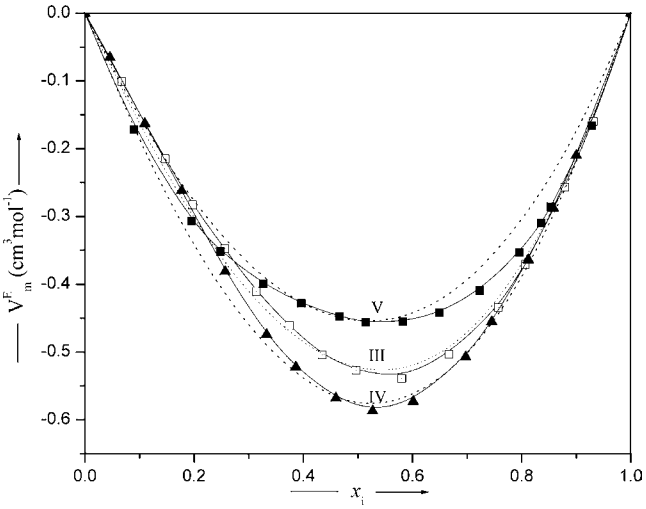



**Fig. 2.** Excess molar volumes, $V_m^E$ at 308.15 K for (III) 2-pyrrolidinone ($i$) + o-xylene ($j$) (□); (IV) 2-pyrrolidinone ($i$) + p-xylene ($j$) (▲); (V) 2-pyrrolidinone ($i$) + m-xylene ($j$) (■). — $V_m^E$ (exptl); - - - $V_m^E$ (Graph).

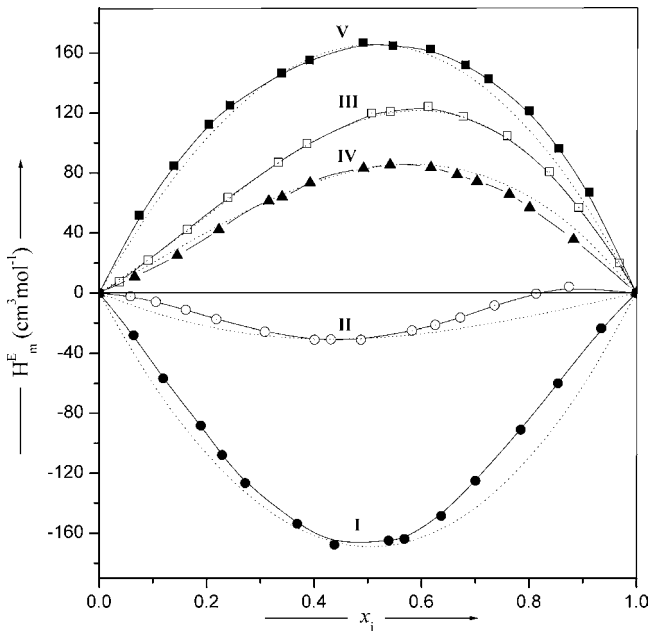



**Fig. 3.** Excess molar enthalpies, $H_m^E$ at 308.15 K for (I) 2-pyrrolidinone ($i$) + benzene ($j$) (●); (II) 2-pyrrolidinone ($i$) + toluene ($j$) (○); (III) 2-pyrrolidinone ($i$) + o-xylene ($j$) (□); (IV) 2-pyrrolidinone ($i$) + p-xylene ($j$) (▲); (V) 2-pyrrolidinone ($i$) + m-xylene ($j$) (■) — $H_m^E$ (exptl); - - - $H_m^E$ (Graph).

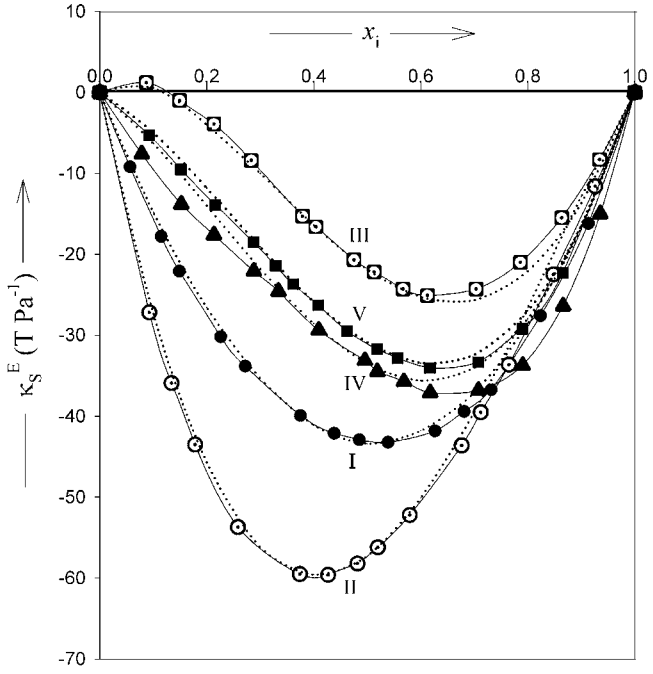



**Fig. 4.** Isentropie compressibilities changes of mixing, $\kappa_S^E$ at 308.15 K for (I) 2-pyrrolidinone ($i$) + benzene ($j$) (●); (II) 2-pyrrolidinone ($i$) + toluene ($j$) (○); (III) 2-pyrrolidinone ($i$) + o-xylene ($j$) (□); (IV) 2-pyrrolidinone ($i$) + p-xylene ($j$) (▲); (V) 2-pyrrolidinone ($i$) + m-xylene ($j$) (■) — $\kappa_S^E$ (exptl); - - - $\kappa_S^E$ (Graph).

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

| $x_i$ | $u$ (m s$^{-1}$) | $\kappa_S$ (T Pa$^{-1}$) | $\kappa_S^E$ (T Pa$^{-1}$) |
|---|---|---|---|
| 2-Pyrrolidinone $(i)$ + benzene $(j)$ | | | |
| 0.0564 | 1274 | 703.2 | −9.1 |
| 0.1149 | 1291 | 675.2 | −17.7 |
| 0.1488 | 1300 | 659.6 | −22.1 |
| 0.2261 | 1322 | 625.4 | −30.2 |
| 0.2718 | 1336 | 606.0 | −33.8 |
| 0.3752 | 1368 | 563.3 | −39.9 |
| 0.4379 | 1389 | 537.9 | −42.1 |
| 0.4851 | 1405 | 520.0 | −42.9 |
| 0.5389 | 1424 | 499.4 | −43.2 |
| 0.6267 | 1457 | 467.1 | −41.8 |
| 0.6811 | 1478 | 448.1 | −39.4 |
| 0.7316 | 1499 | 430.7 | −36.7 |
| 0.8238 | 1536 | 401.6 | −27.6 |
| 0.9132 | 1572 | 375.5 | −16.2 |
| 2-Pyrrolidinone $(i)$ + toluene $(j)$ | | | |
| 0.0926 | 1295 | 684.9 | −27.2 |
| 0.1342 | 1309 | 664.0 | −35.9 |
| 0.1784 | 1323 | 643.0 | −43.5 |
| 0.2585 | 1348 | 607.6 | −53.7 |
| 0.3741 | 1380 | 563.7 | −59.5 |
| 0.4268 | 1394 | 544.9 | −59.6 |
| 0.4818 | 1409 | 526.5 | −58.2 |
| 0.5199 | 1418 | 514.3 | −56.2 |
| 0.5796 | 1434 | 495.2 | −52.2 |
| 0.6766 | 1463 | 464.0 | −43.6 |
| 0.7123 | 1474 | 453.0 | −39.5 |
| 0.7649 | 1492 | 435.6 | −33.6 |
| 0.848 | 1524 | 408.3 | −22.5 |
| 0.9262 | 1562 | 380.6 | −11.6 |
| 2-Pyrrolidinone $(i)$ + o-xylene $(j)$ | | | |
| 0.0869 | 1331 | 640.6 | 1.2 |
| 0.1493 | 1336 | 627.7 | −1.0 |
| 0.2136 | 1346 | 610.4 | −3.9 |
| 0.2832 | 1360 | 589.4 | −8.4 |
| 0.379 | 1383 | 558.8 | −15.3 |
| 0.4037 | 1389 | 550.9 | −16.6 |
| 0.4754 | 1408 | 527.0 | −20.7 |
| 0.5129 | 1419 | 514.7 | −22.2 |
| 0.5667 | 1435 | 496.7 | −24.3 |
| 0.6125 | 1450 | 481.3 | −25.1 |
| 0.7033 | 1479 | 451.8 | −24.3 |
| 0.7865 | 1509 | 424.7 | −21.0 |
| 0.8634 | 1539 | 399.7 | −15.5 |
| 0.9343 | 1570 | 376.4 | −8.3 |
| 2-Pyrrolidinone $(i)$ + p-xylene $(j)$ | | | |
| 0.0785 | 1290 | 698.1 | −7.6 |
| 0.1523 | 1303 | 673.8 | −13.8 |
| 0.2133 | 1314 | 653.7 | −17.6 |
| 0.2878 | 1329 | 628.0 | −22.1 |
| 0.3341 | 1339 | 611.9 | −24.6 |
| 0.4093 | 1358 | 583.9 | −29.4 |
| 0.4956 | 1383 | 551.2 | −33.1 |
| 0.5187 | 1391 | 541.8 | −34.5 |
| 0.5685 | 1407 | 522.4 | −35.7 |
| 0.6176 | 1426 | 502.1 | −37.1 |
| 0.7079 | 1463 | 465.2 | −36.8 |
| 0.7904 | 1501 | 431.6 | −33.7 |
| 0.866 | 1538 | 401.7 | −26.4 |
| 0.9357 | 1573 | 375.9 | −15.0 |
| 2-Pyrrolidinone $(i)$ + m-xylene $(j)$ | | | |
| 0.0925 | 1295 | 687.8 | −5.3 |
| 0.1518 | 1305 | 669.1 | −9.5 |
| 0.2162 | 1317 | 648.1 | −13.9 |
| 0.287 | 1332 | 623.7 | −18.5 |
| 0.3284 | 1341 | 609.3 | −21.4 |
| 0.3613 | 1350 | 597.1 | −23.7 |
| 0.4083 | 1362 | 580.1 | −26.3 |
| 0.4622 | 1378 | 559.6 | −29.5 |
| 0.5177 | 1394 | 538.8 | −31.7 |
| 0.5567 | 1407 | 523.8 | −32.8 |
| 0.6169 | 1428 | 500.3 | −34.0 |

Table 4 (*Continued*)

| $x_i$ | $u$ (m s$^{-1}$) | $\kappa_S$ (T Pa$^{-1}$) | $\kappa_S^E$ (T Pa$^{-1}$) |
|---|---|---|---|
| 0.7071 | 1463 | 465.1 | −33.3 |
| 0.7898 | 1498 | 432.9 | −29.2 |
| 0.8656 | 1533 | 403.9 | −22.3 |

**Table 5**
Parameters used in Eqs. (5), (7) and (15) for the investigated binary mixtures at 308.15 K.

| Parameters |
|---|
| 2-Pyrrolidinone ($i$) + benzene ($j$) |
| $V^{(0)} = -2.225$, $V^{(1)} = 0.011$, $V^{(2)} = 0.099$; $\sigma(V^E) = 0.003$ cm$^3$ mol$^{-1}$ |
| $H^{(0)} = -675.8$, $H^{(1)} = 51.1$, $H^{(2)} = 322.2$; $\sigma(H^E) = 1.7$ J mol$^{-1}$ |
| $\kappa_S^{(0)} = -173.8$, $\kappa_S^{(1)} = -15.8$, $\kappa_S^{(2)} = -19.7$; $\sigma(\kappa_S^E) = 0.3$ T Pa$^{-1}$ |
| $({}^3\xi_i) = ({}^3\xi_i)_m = 1.001$; $({}^3\xi_j) = ({}^3\xi_j)_m = 0.666$; $\alpha_{ij} = 11.139$ cm$^3$ mol$^{-1}$ |
| $\chi'_{ij} = -230.9$ J mol$^{-1}$; $\chi_{12} = -433.6$ J mol$^{-1}$ |
| $\chi'_{ij} = -61.6$ T Pa$^{-1}$; $\chi_{12} = -101.7$ T Pa$^{-1}$ |
| 2-Pyrrolidinone ($i$) + toluene ($j$) |
| $V^{(0)} = -2.365$, $V^{(1)} = -0.648$, $V^{(2)} = 0.353$; $\sigma(V^E) = 0.003$ cm$^3$ mol$^{-1}$ |
| $H^{(0)} = -121.2$, $H^{(1)} = 73.6$, $H^{(2)} = 188.8$; $\sigma(H^E) = 0.3$ J mol$^{-1}$ |
| $\kappa_S^{(0)} = -229.1$, $\kappa_S^{(1)} = 93.5$, $\kappa_S^{(2)} = -18.4$; $\sigma(\kappa_S^E) = 0.3$ T Pa$^{-1}$ |
| $({}^3\xi_i) = ({}^3\xi_i)_m = 1.001$; $({}^3\xi_j) = ({}^3\xi_j)_m = 0.840$; $\alpha_{ij} = 71.242$ cm$^3$ mol$^{-1}$ |
| $\chi'_{ij} = -24.9$ J mol$^{-1}$; $\chi_{12} = -127.2$ J mol$^{-1}$ |
| $\chi'_{ij} = -50.5$ T Pa$^{-1}$; $\chi_{12} = -270.2$ T Pa$^{-1}$ |
| 2-Pyrrolidinone ($i$) + o-xylene ($j$) |
| $V^{(0)} = -2.119$, $V^{(1)} = -0.516$, $V^{(2)} = 0.113$; $\sigma(V^E) = 0.003$ cm$^3$ mol$^{-1}$ |
| $H^{(0)} = 472.8$, $H^{(1)} = 219.6$, $H^{(2)} = -58.2$; $\sigma(H^E) = 1.2$ J mol$^{-1}$ |
| $\kappa_S^{(0)} = -87.7$, $\kappa_S^{(1)} = -88.9$, $\kappa_S^{(2)} = 37.3$; $\sigma(\kappa_S^E) = 0.2$ T Pa$^{-1}$ |
| $({}^3\xi_i) = ({}^3\xi_i)_m = 1.002$; $({}^3\xi_j) = ({}^3\xi_j)_m = 1.426$; $\alpha_{ij} = 20.207$ cm$^3$ mol$^{-1}$ |
| $\chi'_{ij} = 472.1$ J mol$^{-1}$; $\chi_{12} = -269.3$ J mol$^{-1}$ |
| $\chi'_{ij} = -118.8$ T Pa$^{-1}$; $\chi_{12} = 144.0$ T Pa$^{-1}$ |
| 2-Pyrrolidinone ($i$) + p-xylene ($j$) |
| $V^{(0)} = -2.331$, $V^{(1)} = -0.439$, $V^{(2)} = 0.558$; $\sigma(V^E) = 0.003$ cm$^3$ mol$^{-1}$ |
| $H^{(0)} = 332.7$, $H^{(1)} = 106.3$, $H^{(2)} = -100.7$; $\sigma(H^E) = 0.8$ J mol$^{-1}$ |
| $\kappa_S^{(0)} = -134.0$, $\kappa_S^{(1)} = -84.6$, $\kappa_S^{(2)} = -54.5$; $\sigma(\kappa_S^E) = 0.2$ T Pa$^{-1}$ |
| $({}^3\xi_i) = ({}^3\xi_i)_m = 1.003$; $({}^3\xi_j) = ({}^3\xi_j)_m = 1.250$; $\alpha_{ij} = 52.200$ cm$^3$ mol$^{-1}$ |
| $\chi'_{ij} = 277.6$ J mol$^{-1}$; $\chi_{12} = -83.9$ J mol$^{-1}$ |
| $\chi'_{ij} = -124.5$ T Pa$^{-1}$; $\chi_{12} = 72.1$ T Pa$^{-1}$ |
| 2-Pyrrolidinone ($i$) + m-xylene ($j$) |
| $V^{(0)} = -1.810$, $V^{(1)} = -0.199$, $V^{(2)} = -0.684$; $\sigma(V^E) = 0.002$ cm$^3$ mol$^{-1}$ |
| $H^{(0)} = 662.3$, $H^{(1)} = 62.8$, $H^{(2)} = 166.4$; $\sigma(H^E) = 1.6$ J mol$^{-1}$ |
| $\kappa_S^{(0)} = -123.6$, $\kappa_S^{(1)} = -81.3$, $\kappa_S^{(2)} = -17.8$; $\sigma(\kappa_S^E) = 0.2$ T Pa$^{-1}$ |
| $({}^3\xi_i) = ({}^3\xi_i)_m = 1.004$; $({}^3\xi_j) = ({}^3\xi_j)_m = 1.174$; $\alpha_{ij} = 76.376$ cm$^3$ mol$^{-1}$ |
| $\chi'_{ij} = 405.3$ J mol$^{-1}$; $\chi_{12} = 224.2$ J mol$^{-1}$ |
| $\chi'_{ij} = -115.6$ T Pa$^{-1}$; $\chi_{12} = 78.1$ T Pa$^{-1}$ |

## 4. Discussion

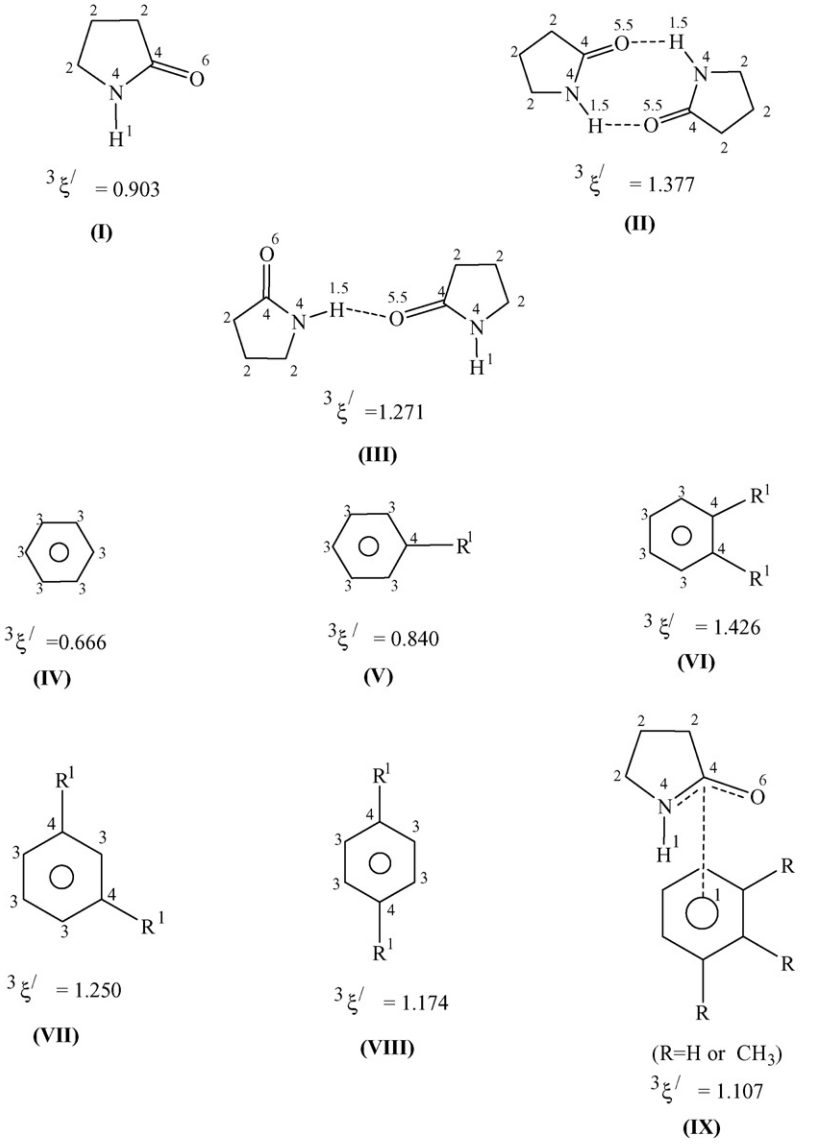
We are unaware of any $V_m^E$, $H_m^E$ and $\kappa_S^E$ data of the investigated mixtures with which to compare our result. $V_m^E$ data of **2-Py** ($i$) + benzene or toluene or o- or p- or m-xylene ($j$) binary mixtures are negative over entire composition range. $H_m^E$ data are negative for **2-Py** ($i$) + benzene ($j$) and positive for **2-Py** ($i$) + o- or p- or m-xylene ($j$) mixtures over whole composition range; however, $H_m^E$ values change sign from negative to positive for **2-Py** ($i$) + toluene ($j$) mixture at $x_i > 0.82$. While $V_m^E$ data for an equimolar mixture vary in the order: m-xylene > o-xylene > benzene > p-xylene > toluene; $H_m^E$ data vary as m-xylene > o-xylene > p-xylene > toluene > benzene. Further, $\kappa_S^E$ values for **2-Py** + benzene or toluene or p- or m-xylene mixtures are negative over the entire composition range. However for **2-Py** + o-xylene mixtures, $\kappa_S^E$ values change sign from positive to negative at $x_i \leq 0.14$. $\kappa_S^E$ values for an equimolar mixture vary as: o-xylene > m-xylene > p-xylene > benzene > toluene.

The observed $H_m^E$ data for these mixtures can be explained if it be assumed that: (i) **2-Py** is an associated molecular entity; (ii) there is interaction between π-electrons spilling over nitrogen and oxygen atom of **2-Py** and π-electron cloud of benzene or toluene or o- or p- or m-xylene to form weak p-complex [21]; (iii) interactions between ($i$) and ($j$) components of binary mixture then weakens *i–i* interactions and lead to its depolymerization, (iv) monomers of ($i$) and ($j$) then undergo specific interaction to form *i:j* molecular entity, (v) there is steric repulsion between **2-Py** and toluene or xylene molecules because of the presence of bulky $-CH_3$ groups. $H_m^E$ data for **2-Py** + benzene mixture suggest that contribution due to factors (ii) and (iv) far outweigh the contribution due to factor (iii), so that over all $H_m^E$ values for this mixture are negative. The introduction of one $-CH_3$ group into benzene (as in toluene) or two $-CH_3$ groups in benzene (as in xylenes) would increase the π-electron donating capacity of aromatic ring of toluene or xylenes and thus interactions between **2-Py** and toluene or xylene must be stronger than that in **2-Py** + benzene mixtures. However, at the same time there exists a steric hindrance between **2-Py** and toluene or xylene molecules due to the presence of $-CH_3$ groups. Higher $H_m^E$ values for **2-Py** + toluene or xylenes mixtures than those for **2-Py** + benzene mixtures suggest that contribution due to hindrance is more than that due to interactions.

Lower values of $V_m^E$ and $\kappa_S^E$ for **2-Py** + benzene or toluene mixtures than those for **2-Py** + xylene mixtures suggest that benzene or toluene gives relatively more packed structure than xylene in **2-Py**. This may be due to the presence of bulky $-CH_3$ groups in xylene which restricts the approach of xylene molecule towards **2-Py**.

### 4.1. Graph theory and results

Excess molar volumes, $V_m^E$, reflect the packing of the constituents in ($i+j$) mixtures which in turn provides information about the change in topology of $i$ or $j$ constituents on addition of $i$ to $j$ in binary ($i+j$) mixture. Thus analysis of $V_m^E$ data of binary mixtures in terms of Graph




**Scheme.** Connectivity Parameters of various molecular entities

theory that employs the graph—theoretical concept of connectivity parameter of third degree, $^3\xi$ of a molecule (which in turn depends on its topology) can provide information about the state of components in pure and mixed state. According to this approach, $V^E$ for a binary mixture is given [22] by

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

where $x_i$ is the mole fraction of component ($i$) and $\alpha_{ij}$ is a constant characteristic of binary mixture. ($^3\xi_i$, $i = i$ or $j$) and ($^3\xi_i)_m$ ($i = i$ or $j$) are the connectivity parameters of components ($i$) and ($j$) in pure and mixture state and are defined [23] by

$$^3\xi = \sum_{\ell<m<n<o} (\delta_\ell^v \delta_m^v \delta_n^v \delta_o^v)^{-0.5} \quad (8)$$

where $\delta_\ell^v$, etc. reflect degree of $m$, $n$, etc. vertices of the graph of a molecule and are related to maximum valency, $Z_m$ and number of hydrogen atoms attached to $m$th vertex by relation $\delta_m^v = Z_m - h_m$ [24].

The degree of association of ($i$) or ($j$) in pure and mixture state is not known, therefore, we regarded ($^3\xi_i$) ($i = i$ or $j$) and ($^3\xi_i)_m$ ($i = i$ or $j$) as adjustable parameters. These parameters were evaluated by fitting $V_m^E$ data of mixtures to Eq. (7). Only those values of parameters were retained that best reproduced the experimental $V_m^E$ data. Such ($^3\xi_i$) ($i = i$ or $j$) and ($^3\xi_i)_m$($i = i$ or $j$) values are recorded in Table 5. Also $V_m^E$ values {evaluated by employing Eq. (7)} at various mole fractions of ($i$), $x_i$, are plotted in Figs. 1 and 2 and are compared with their corresponding experimental values. A perusal of Figs. 1 and 2 reveals that $V_m^E$ values compare well with their corresponding experimental values. Thus ($^3\xi_i$) ($i = i$ or $j$) and ($^3\xi_i)_m$ ($i = i$ or $j$) values can be relied upon to extract information about the state of aggregation of ($i$) or ($j$) in pure and mixed state. Structures were then assumed for **2-Py**, benzene, toluene, o-, p- and m-xylene and their $^3\xi'$ values were predicted by employing topology {via Eq. (8)}. These $^3\xi'$ values were then compared with $^3\xi$ values (calculated by Eq. (7)). Any structure or combination of structures that gives $^3\xi'$ values which compare well with $^3\xi$ values was considered to be a representative structure of that component.

For the investigated ($i+j$) binary mixtures, we assumed that **2-Py** exists as molecular entities **I**, **II** and **III**. $^3\xi'$ values for these molecular entities were then calculated to be 0.903, 1.377, 1.271 respectively. $^3\xi_i$ values of 1.001, 1.001, 1.002, 1.003 and 1.004, for **2-Py** in ($i+j$)

mixtures (Table 5) suggest that **2-Py** in pure state mainly exists as a mixture of cyclic and open dimer ($^3\xi' = 1.321$); a small amount of monomer may also be present, or alternatively it may exist as an equilibrium mixture of all these molecular entities ($^3\xi' = 1.183$). These observations are consistent with observation obtained from ab initio calculations on the different associated structures of **2-Py** [25]. $^3\xi'$ values of 0.666, 0.840, 1.426, 1.250 and 1.174 for benzene, toluene, o-, p- and m-xylene [molecular entities **IV–VIII**] suggest that they exist as monomers. Connectivity parameters of third degree of components ($i$) and ($j$) in mixed state, $(^3\xi_i)_m$ ($i = i$ or $j$) were then calculated and employed to extract information about the state of **2-Py** in benzene or toluene or o- or p- or m-xylene. It was assumed that studied ($i+j$) mixtures contain molecular entity **IX**. In evaluating $^3\xi'$ values for molecular entity **IX**, it was assumed that molecular entity **IX** is characterized by interaction between π-electron cloud spilling over nitrogen and oxygen atom of **2-Py** and π-electron cloud of aromatic ring of aromatic hydrocarbon. $\delta_\ell^\nu$ values for various vertices are shown in molecular entities **I–IX** and $\delta^\nu(\pi)$ has been assigned [24] value one (where π-electron cloud of molecule is unvalued in interaction with π-electron of another molecule). $(^3\xi_i)_m$ values of 1.001, 1.001, 1.002, 1.003 and 1.004 for **2-Py** in benzene or toluene or o- or p- or m-xylene (Table 5) suggest that investigated mixtures are characterized by the presence of molecular entity **IX** ($^3\xi' = 1.107$). The existence of molecular entity **IX** suggests that addition of **2-Py** ($i$) to benzene or toluene or o- or p- or m-xylene should have influenced the C=O and N–H stretching of **2-Py** and also the ring vibrations of aromatic ring of aromatic hydrocarbon. To substantiate this, we analyzed the IR spectra data of an equimolar mixture of **2-Py** ($i$) + benzene ($j$) mixture. It was observed while benzene ($j$) in pure state showed ring vibrations at 1582, 1496, 1440 $cm^{-1}$ respectively, **2-Py** ($i$) showed vibrations at 1682 (C=O) and 3260 $cm^{-1}$ (N-H) [26]. On the other hand, IR spectra of **2-Py** ($i$) + benzene ($j$) mixtures showed characteristic vibrations at 1610, 1512, 1482 $cm^{-1}$ (ring vibrations), 1674 (C=O) and 3250 $cm^{-1}$ (N–H). The IR spectra of **2-Py** ($i$) + benzene ($j$) mixtures thus infer that addition of **2-Py** ($i$) to benzene ($j$) does influence C=O and N–H stretching of **2-Py** ($i$) and also the ring vibrations of aromatic ring of benzene. This lends additional support to the proposed molecular entity **IX** in these mixtures and also to the assumption made in evaluating its $^3\xi'$ values.

$H_m^E$ and $\kappa_S^E$ data of investigated mixtures were then analyzed in terms of Graph theory. For this purpose we assumed that ($i+j$) mixtures formation involves following processes: (1) **2-Py** ($i$) is an associated molecular entity, (2) formation of unlike contact between **2-Py** ($i$) and aromatic hydrocarbons ($j$) then influences **2-Py–2-Py** interaction which yield their monomers, (3) monomers of ($i$) and ($j$) then undergo specific interactions to form *i:j* molecular entity. Consequently, if $\chi_{ij}$, $\chi_{ii}$ and $\chi_{12}$ are molar energy and molar compressibility parameters for *i–j*, *i–i* and specific interactions respectively. Then change in molar thermodynamic property, $\Delta X$ ($X = H_m$ or $\kappa_S$) due to processes (1–3) would be given [27–29] by

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

where $S_j$ is the surface fraction of $j$, defined [27] by

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

so that

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

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

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

where $v_j$ is the molar volume of component ($j$) of ($i+j$) mixtures. The overall changes in thermodynamic property, $X^E$ ($X = H_m$ or $\kappa_S$) due to processes (1–3) then can be expressed by

$$X^E\,(X = H_m \text{ or } \kappa_S) = \sum_{i=1}^{3} \Delta H_i = \left[\frac{x_i x_j v_j}{\sum x_i v_i}\right][\chi_{ij} + x_i \chi_{ii} + x_j \chi_{12}] \tag{13}$$

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

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

Further $v_j/v_i = {}^3\xi_i/{}^3\xi_j$ [30]; Eq. (14) can, therefore, be expressed as:

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

Eq. (15) contains two unknown parameter $\chi'_{ij}$ and $\chi_{12}$. These parameters were evaluated by employing $X^E$ ($X = H_m$ or $\kappa_S$) data at two compositions ($x_i = 0.4$ and 0.5) and were then utilized (recorded in Table 5) to predict $X^E$ ($X = H_m$ or $\kappa_S$) data at various values of $x_i$. Such $H_m^E$ and $\kappa_S^E$ values are plotted in Figs. 3 and 4 and are also compared with their corresponding experimental values.

Examination of Figs. 3 and 4 reveals that $H_m^E$ and $\kappa_S^E$ values compare well with their corresponding experimental values. This lends additional support to the basic assumptions made in qualitative analysis of thermodynamic data and also to the assumptions made in deriving Eq. (15).

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