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# Molar Excess Volumes and Excess Isentropic Compressibilities of Ternary Mixtures Containing 2-Pyrrolidinone

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***Abstract*—**Molar excess Volumes, $V^E_{ijk}$ and speeds of sound , $u_{ijk}$ of 2-pyrrolidinone (i) + benzene or toluene (j) + ethanol (k) ternary mixture have been measured as a function of composition at 308.15 K. The observed speeds of sound data have been utilized to determine excess isentropic compressiblities, $(\kappa_S^E)_{ijk}$ of ternary (i + j + k) mixtures. Molar excess volumes, $V^E_{ijk}$ and excess isentropic compressibilities, $(\kappa_S^E)_{ijk}$ data have fitted to the Redlich-Kister equation to calculate ternary adjustable parameters and standard deviations. The Moelywn-Huggins concept (Huggins in Polymer 12: 389-399, 1971) of connectivity between the surfaces of the constituents of binary mixtures has been extended to ternary mixtures (using the concept of a connectivity parameter of third degree of molecules, $^3\xi$ , which inturn depends on its topology) to obtain an expression that describes well the measured $V^E_{ijk}$ and $(\kappa_S^E)_{ijk}$ data.

***Keywords*—**Connectivity parameter of third degree, $^3\xi$, Excess isentropic compressibilities,$(\kappa_S^E)_{ijk}$, Interaction energy parameter, $\chi$, Molar excess volumes, $V^E_{ijk}$, Speeds of sound, $u_{ijk}$.

## I. Introduction

EVER since the suggestion that constitutional formula of a molecule is a special kind of graph [1] called molecular graph and a very good correlation have been observed [2-6] between topological index [7] of a molecule and is physico-chemical properties. The characterization of the mixtures through their topological investigations [8-10] has proved to be a reliable way to extract information about the structure of components of mixtures in pure and mixed state and molecular interactions operating among the constituents of mixtures. Further topological investigations have been successfully employed to determine molar excess volumes, molar excess enthalpies, excess isentropic compressibilities of binary[11-14] and ternary [15-17] mixtures. Cyclic amides are of great interest because the nitrogen and carbon atoms of peptide bond are linked by a ring composed of methyl groups. These compounds have generated special interest because the amide group is a structural part of peptides, polypeptides and proteins. IR spectroscopic and thermodynamic studies of 2-pyrrolidinone + benzene or toluene or o- or p- or m-xylene (j) binary mixtures have revealed [18-20] that 2-pyrrolidinone is a self associated molecular entity (mixture of cyclic and open dimer). As a continuation and extension of our studies on the thermodynamic properties of 2-pyrrolidinone (i) + benzene or toluene or o- or p- or m-xylene (j) mixture, we report here molar volumes, $V^E_{ijk}$ , speeds of sound, $u_{ijk}$ data for 2-pyrrolidinone (i) + benzene or toluene (j) + ethanol (k) ternary mixtures at 308.15 K. An attempt has also been made to develop an expression by employing topology of the constituents of mixtures that describes well molar excess volumes, $V^E_{ijk}$ and excess isentropic compressibility, $(\kappa_S^E)_{ijk}$ of these ternary mixtures.

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## II. Experimental

### A. Materials

2-Pyrrolidinone (**2-Py)** (Fluka), benzene, toluene and absolute ethanol (AR Grade) were purified by standard methods [21].

### B. Methods

The purities of the purified liquids were checked by measuring their densities with a pycknometer at 298.15 ± 0.01 K and the resulting densities (reported in Table I) agreed to within ± 0.05 $kgm^{-3}$ of their corresponding literature values [21].

Molar excess volumes, $V^E_{ijk}$ for ternary mixtures were measured in a dilatometer in the manner described elsewhere [22]. The dilatometer had three limbs for three components. The change in liquid level of dialatometer capillary was measured with a cathetometer that could read to ± 0.001 cm. The temperature of the water thermostat was controlled to better than ± 0.01 K by means of toluene regulator. The uncertainty in the measured $V^E_{ijk}$ values is ± 0.5 percent.

The speed of sound at frequency 2MHz was determined using a quartz crystal interferometer (Model-M 80, Mittal Enterprises, New Delhi, India). The measuring cell was a specially designed double walled cell in which water was circulated to maintain the temperature at 308.15 ± 0.0 1K. The speed of sound values for the purified liquids at 298.15 ±

0.01K (recorded in Table I) compare well with their corresponding experimental values [23-27]. The uncertainty in the measured speed of sound measurements is ± 1 m/sec.

TABLE I
COMPARISON OF DENSITIES, ρ, AND SPEEDS OF SOUND, U, OF PURE LIQUIDS WITH THEIR LITERATURE VALUES AT 298.15 K.

| Liquid | ρ (kg. m$^{-3}$) | | u (ms$^{-1}$) | |
|---|---|---|---|---|
| | Exptl. | Lit. | Exptl | Lit. |
| 2-pyrrolidinone | 1107.26 | 1107.22[23] | 1603.0 [a] | 1603.1[a24] |
| Benzene | 873.62 | 873.60[21] | 1298.2 | 1298.9[25] |
| Toluene | 862.23 | 862.19[21] | 1304.6 | 1304.0[26] |
| Ethanol | 785.08 | 785.93[21] | 1112.0 | 1109.05[27] |

[A] VALUE AT 308.15 K

## III. RESULTS

Molar excess volumes, $V^E_{ijk}$, and speeds of sound, $u_{ijk}$, data of **2-Py** (i) + benzene or toluene (j) + ethanol (k) ternary mixtures as a function of composition at 308.15 K are recorded in Tables II and III respectively. The isentropic compressibilities, $(\kappa_S)_{ijk}$ for ternary mixtures were determined using the expression:

$$(\kappa_S)_{ijk} = (\rho_{ijk}\, u^2_{ijk})^{-1} \quad (1)$$

The densities, $\rho_{ijk}$ of ternary mixtures were calculated from their experimental molar excess volumes data using the Equation (2)

$$V^E_{ijk} = \sum_{i=i}^{k} x_i M_i (\rho_{ijk})^{-1} - \sum_{i=i}^{k} x_i M_i (\rho_i)^{-1} \quad (2)$$

where $x_i$, $M_i$ and $\rho_i$ are the mole fraction, molar mass and density respectively of component (i) in (i +j + k) ternary mixtures.

Excess isentropic compressibilities, $(\kappa^E_S)_{ijk}$ were evaluated using Equation (3)

$$(\kappa^E_S)_{ijk} = (\kappa_S)_{ijk} - \kappa^{id}_S \quad (3)$$

$\kappa^{id}_S$ was obtained according to Benson and Kiyohara [28]

$$\kappa^{id}_S = \sum_{i}^{j\,or\,k} \phi_i \left[ \kappa_{S,i} + \frac{T V_i \alpha_i^2}{C_{p,i}} \right] - T \left( \sum_{i}^{j\,or\,k} x_i V_i \right) \frac{\left( \sum_{i}^{j\,or\,k} \phi_i \alpha_i \right)^2}{\left( \sum_{i}^{j\,or\,k} x_i C_{p,i} \right)} \quad (4)$$

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 [29]. $\alpha$ value for **2-Py** was evaluated in the same manner as suggested by Hilderbrand [30]. The resulting $(\kappa_S)_{ijk}$ and $(\kappa^E_S)_{ijk}$ values for the studied (i + j + k) ternary mixtures are recorded in Table III and $V^E_{ijk}$, $(\kappa^E_S)_{ijk}$ values are plotted in Figs. 1, 2, 3 and 4 respectively.

$V^E_{ijk}$ and $(\kappa^E_S)_{ijk}$ values for ternary mixtures were fitted to Redlich-Kister Equation (5)

$$X^E_{ijk}(X = V \text{or } \kappa_S) = x_i x_j [\sum_{n=0}^{2} X^{(n)}_{ij} (x_i - x_j)^n] + x_j x_k [\sum_{n=0}^{2} X^{(n)}_{jk} (x_j - x_k)^n] + x_i x_k [\sum_{n=0}^{2} X^{(n)}_{ik} (x_k - x_i)^n] + x_i x_j x_k [\sum_{n=0}^{2} X^{(n)}_{ijk} (x_j - x_k)^n x_i^n] \quad (5)$$

where $x_i$ and $x_j$ are the mole fractions of i$^{th}$ and j$^{th}$ components of (i + j + k) ternary mixture; $X^{(n)}_{ij}$ (n=0-2) etc. (X=V or $\kappa_S$) are the parameters characteristic of (i+j), (j+k) and (i+k) binary mixtures and have been taken from literature [20,31,32]. $X^{(n)}_{ijk}$ (X= V or $\kappa_S$) parameters were determined by fitting $X^E_{ijk}$ data to Equation (6) by the least-squares method and

$$\begin{bmatrix} X^E_{ijk} - x_i x_j [\sum_{n=0}^{2} X^{(n)}_{ij} (x_i - x_j)^n] \\ - x_j x_k [\sum_{n=0}^{2} X^{(n)}_{jk} (x_j - x_k)^n] \\ - x_k x_i [\sum_{n=0}^{2} X^{(n)}_{jk} (x_k - x_i)^n] \end{bmatrix} \begin{bmatrix} \\ x_i x_j x_k \\ \\ \end{bmatrix}^{-1} = [\sum_{n=0}^{2} X^n_{ijk} (x_j - x_k)^n x_i^n] \quad (6)$$

are recorded along with their standard deviations, $\sigma\,(X^E)_{ijk}$ (X=V or $\kappa_S$) defined by

$$\sigma(X^E_{ijk}) = [\Sigma (X^E_{ijk(exptl)} - X^E_{ijk(Calc.Equation(4))})^2 / (m-p)]^{0.5}$$

{where m, n are the number of data points and adjustable parameters in Equation (5)} in Tables II and III respectively.

TABLE II
COMPARISON OF MEASURED, $V^E_{ijk}$ VALUES FOR THE VARIOUS (i+j+k) TERNARY MIXTURES EVALUATED FROM GRAPH THEORY WITH THEIR CORRESPONDING EXPERIMENTAL VALUES; ALSO INCLUDED ARE THE VARIOUS PARAMETERS $V^{(n)}_{ijk}$ (n = 0-2) ALONG WITH THEIR STANDARD DEVIATION, $\sigma\,(V^E_{ijk})$, INTERACTION PARAMETERS $\chi^*$, $\chi'_{ij}$ ETC. AND CONNECTIVITY PARAMETERS OF THIRD DEGREE, $^3\xi_i$ (i= i - k)

| $x_i$ | $x_j$ | $V^E_{ijk}$ (cm$^3$mol$^{-1}$) | |
|---|---|---|---|
| | | Exptl | Graph |
| 2-pyrrolidinone (i) +benzene (j) + ethanol (k) | | | |
| 0.1058 | 0.7933 | - 0.121 | - 0.100 |
| 0.1214 | 0.6976 | - 0.100 | - 0.115 |
| 0.2083 | 0.3519 | - 0.243 | - 0.242 |
| 0.2455 | 0.4351 | - 0.269 | - 0.277 |
| 0.2806 | 0.1970 | - 0.390 | - 0.388 |

| | | | |
|---|---|---|---|
| 0.3477 | 0.3556 | - 0.392 | - 0.380 |
| 0.4078 | 0.3679 | - 0.398 | - 0.397 |
| 0.4624 | 0.2948 | - 0.455 | - 0.438 |
| 0.5326 | 0.1630 | - 0.497 | - 0.497 |
| 0.5872 | 0.1713 | - 0.474 | - 0.470 |
| 0.6615 | 0.2302 | - 0.394 | - 0.391 |
| 0.7106 | 0.1382 | - 0.388 | - 0.394 |
| 0.7500 | 0.0703 | - 0.339 | - 0.382 |
| 0.8405 | 0.0721 | - 0.237 | - 0.261 |
| 0.8801 | 0.0656 | - 0.188 | - 0.204 |

$V_{ijk}^{(0)}$ = - 0.513; $V_{ijk}^{(1)}$ = 19.431; $V_{ijk}^{(2)}$ = 181.875;
$\sigma(V_{ijk}^{E})$ = 0.003
$({}^3\xi_i)$= 1.001 ; $({}^3\xi_j)$= 0.666; $({}^3\xi_k)$= 1.503
$\chi^*$ = - 1.100; $\chi'_{ij}$ = - 0.317; $\chi'_{jk}$ = 0.979; $\chi'_{ik}$ = - 1.058

**2-pyrrolidinone (i) +toluene (j) + ethanol (k)**

| | | | |
|---|---|---|---|
| 0.0514 | 0.9290 | -0.066 | -0.159 |
| 0.1159 | 0.7845 | -0.163 | -0.276 |
| 0.2421 | 0.4736 | -0.356 | -0.355 |
| 0.3283 | .02435 | -0.333 | -0.336 |
| 0.3892 | 0.3584 | -0.514 | -0.515 |
| 0.4268 | 0.4038 | -0.609 | -0.624 |
| 0.5178 | 0.2826 | -0.554 | -0.557 |
| 0.5799 | 0.1663 | -0.428 | -0.427 |
| 0.6243 | 0.2258 | -0.530 | -0.533 |
| 0.6976 | 0.0816 | -0.340 | -0.308 |
| 0.7655 | 0.1069 | -0.343 | -0.331 |
| 0.8588 | 0.452 | -0.203 | -0.180 |
| 0.8898 | 0.0629 | -0.198 | -0.164 |
| 0.9426 | 0.0311 | -0.105 | -0.108 |

$V_{ijk}^{(0)}$ = 1.320; $V_{ijk}^{(1)}$ = - 46.051; $V_{ijk}^{(2)}$ = 22.942;
$\sigma(V_{ijk}^{E})$ = 0.004
$({}^3\xi_i)$= 1.001 ; $({}^3\xi_j)$= 0.840; $({}^3\xi_k)$= 1.503
$\chi^*$ = - 1.137; $\chi'_{ij}$ = - 1.778; $\chi'_{jk}$ = 1.796; $\chi'_{ik}$ = - 0.449

$V_{ijk}^{(n)}$ (n = 0-2) and $\sigma$ ($V_{ijk}^{(E)}$) are in $cm^3\ mol^{-1}$
$\chi^*$ and $\chi'_{ij}$ etc. are in $cm^3\ mol^{-1}$

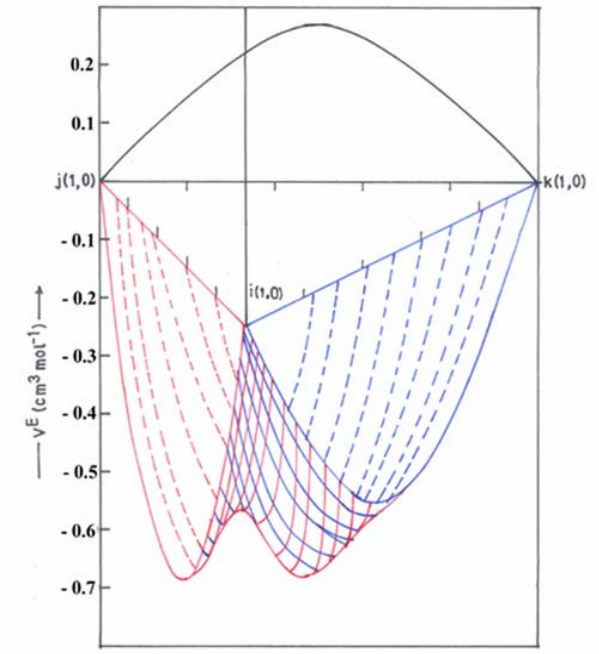


Fig. 1 Molar excess volumes, $V^E$ for 2-pyrrolidinone (i) + benzene (j) + ethanol (k) ternary mixture at 308.15 K

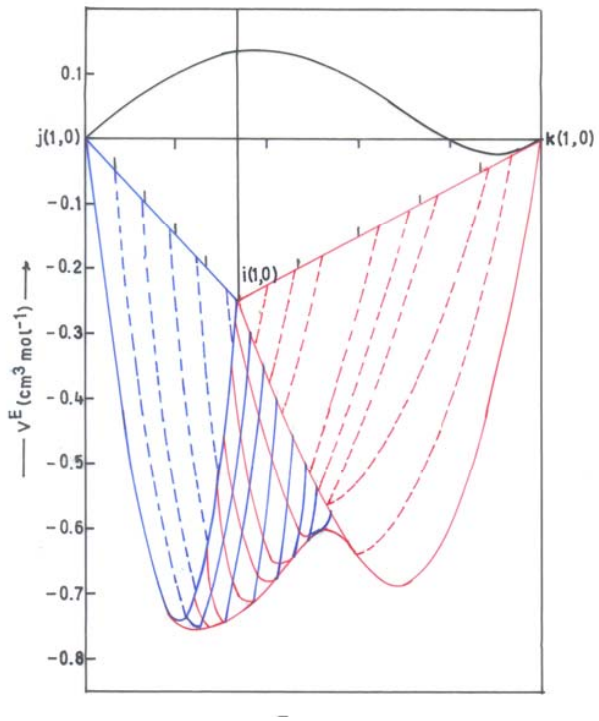


Fig. 2 Molar excess volumes, $V^E$ for 2-pyrrolidinone (i) + toluene (j) + ethanol (k) ternary mixture at 308.15 K

TABLE III
SPEEDS OF SOUND, $U_{ijk}$, ISENTROPIC COMPRESSIBILITIES, $(\kappa_S)_{ijk}$, EXCESS ISENTROPIC COMPRESSIBILITIES, $(\kappa_S^E)_{ijk}$ FOR THE VARIOUS (i+j+k) TERNARY MIXTURES AS A FUNCTION OF COMPOSITION, $x_i$, MOLE FRACTION OF COMPONENT (i) AT 308.15 K WITH $(\kappa_S^E)_{ijk}$ VALUES EVALUATED FROM GRAPH THEORY ALSO INCLUDED ARE VARIOUS PARAMETERS $(\kappa_S^{(n)})_{ijk}$ (n = 0-2) ALONG WITH THEIR STANDARD DEVIATION, $\sigma(\kappa_S^E)_{ijk}$, THE INTERACTION PARAMETERS $\chi'_{ij}$, $\chi_{ij}$*ETC AND $({}^3\xi_i)$ (i = i - k)

| $x_i$ | $x_j$ | $u_{ijk}$ ($ms^{-1}$) | $(\kappa_S)_{ijk}$ ($Tpa^{-1}$) | $(\kappa_S^E)_{ijk}$ ($Tpa^{-1}$) | |
|---|---|---|---|---|---|
| | | | | Exptl. | Graph |
| **2-pyrrolidinone (i) +benzene (j) + ethanol (k)** | | | | | |
| 0.0982 | 0.1092 | 1201 | 836.2 | -75.7 | -69.4 |
| 0.1526 | 0.1529 | 1233 | 770.6 | -84.9 | -83.9 |
| 0.2465 | 0.1712 | 1274 | 692.7 | -89.3 | -.89.5 |
| 0.3018 | 0.6178 | 1327 | 613.1 | -30.6 | -30.1 |
| 0.3440 | 0.0830 | 1315 | 630.1 | -108.4 | -78.5 |
| 0.3925 | 0.5038 | 1353 | 576.7 | -37.9 | -37.7 |
| 0.4510 | 0.1324 | 1351 | 573.7 | -80.6 | -80.2 |
| 0.5022 | 0.4118 | 1395 | 527.5 | -42.3 | -35.9 |
| 0.6378 | 0.0699 | 1431 | 484.7 | -64.7 | -59.7 |
| 0.7112 | 0.1368 | 1472 | 448.9 | -46.8 | -44.9 |
| 0.7331 | 0.2113 | 1493 | 434.2 | -38.5 | -27.1 |
| 0.8316 | 0.0612 | 1530 | 403.6 | -34.7 | -30.1 |
| 0.8748 | 0.0310 | 1550 | 389.2 | -29.2 | -23.6 |
| $(\kappa_S^{(0)})_{ijk}$ = - 3.3, $(\kappa_S^{(1)})_{ijk}$ = 48.9, $(\kappa_S^{(2)})_{ijk}$ = 274.1, $\sigma(\kappa_S^E)_{ijk}$ = 0.1 $TPa^{-1}$ | | | | | |
| $({}^3\xi_i)$ =1.001 ; $({}^3\xi_j)$ = 0.666 ; $({}^3\xi_k)$ = 2.000 | | | | | |
| $\chi^*$ = -32.5 ; $\chi'_{ij}$ = - 26.7 ; $\chi'_{jk}$ = - 346.1 ; $\chi'_{ik}$ = - 89.3 | | | | | |
| **2-pyrrolidinone (i) + toluene (j) + ethanol (k)** | | | | | |
| 0.0582 | 0.9018 | 1276 | 712.4 | -14.1 | -2.9 |
| 0.0910 | 0.0605 | 1195 | 851.9 | -81.6 | -73.3 |
| 0.1282 | 0.7892 | 1288 | 689.1 | -23.8 | -11.9 |
| 0.1646 | 0.0298 | 1236 | 771.8 | -116.2 | -107.0 |
| 0.2062 | 0.0859 | 1260 | 726.4 | -109.7 | -109.9 |
| 0.3080 | 0.6142 | 1337 | 611.1 | -43.8 | -43.5 |
| 0.3557 | 0.0638 | 1321 | 624.0 | -112.2 | -112.6 |
| 0.4140 | 0.5088 | 1364 | 571.2 | -46.5 | -63.9 |
| 0.4451 | 0.0319 | 1361 | 569.8 | -111.8 | -99.9 |
| 0.5643 | 0.0674 | 1394 | 523.7 | -74.9 | -74.4 |
| 0.7605 | 0.0346 | 1485 | 436.4 | -47.5 | -32.7 |
| 0.8612 | 0.0726 | 1531 | 402.1 | -25.1 | -40.2 |
| 0.9263 | 0.0413 | 1565 | 378.3 | -15.2 | -25.0 |
| $(\kappa_S^{(0)})_{ijk}$ = - 2.0, $(\kappa_S^{(1)})_{ijk}$ = - 18.1, $(\kappa_S^{(2)})_{ijk}$ = - 33.9, $\sigma(\kappa_S^E)_{ijk}$ = 0.1 $TPa^{-1}$ | | | | | |
| $({}^3\xi_i)$ =1.101 ; $({}^3\xi_j)$ = 0.84 ; $({}^3\xi_k)$ = 2.000 | | | | | |
| $\chi^*$ = - 582.2 ; $\chi'_{ij}$ = - 9.5 ; $\chi'_{jk}$ = - 1.7; $\chi'_{ik}$ = 20.8 | | | | | |

$(\kappa_S^{(n)})_{ijk}$ (n=0-2) and $\sigma(\kappa_S^E)_{ijk}$ are in $Tpa^{-1}$
$\chi^*$, $\chi'_{ii}$ etc. are in $Tpa^{-1}$

## IV. DISCUSSION

We are unaware of any published $V^E_{ijk}$ and $(\kappa_S^E)_{ijk}$ data of the studied (i + j + k) mixtures at 308.15 K with which to compare our results. $V^E_{ijk}$ and $(\kappa_S^E)_{ijk}$ values for **2-Py** (i) + benzene or toluene (j) + ethanol (k) mixtures are negative over entire composition range.

### *A. Graph Theory and Results*

An analysis of molar excess volumes, $V^E$ and molar excess enthalpies, $H^E$ data of **2-Py** (i) + benzene or toluene or ethanol (j) binary mixtures have revealed [20,31] that **(i)** while **2-Py** (i) and ethanol exists as a mixture of open and cyclic dimer; benzene or toluene exist as a monomer. Analysis of $V^E$ and $H^E$ data of **2-Py** (i) + benzene or toluene (j) mixtures in terms of Graph theory have suggested that these binary mixtures are characterized by interactions between π-electron spilling over nitrogen and oxygen atoms of **2-Py** (i) and π-electron cloud of aromatic ring of benzene or toluene to form 1:1 molecular complex. The thermodynamic properties, $X^E$ (X = H or $\kappa_S$) for these binary mixtures were expressed by Equation (7)

$$X^E(X = V \text{ or } H) = \frac{x_i x_j \left({}^3\xi_i / {}^3\xi_j\right)}{x_i + x_j \left({}^3\xi_i / {}^3\xi_j\right)} \left[(1 + x_i)\chi'_{ij} + x_j \chi_{12}\right] \quad (7)$$

Further, thermo dynamical investigations of **2-Py** (i) + ethanol (j) mixtures in terms of Graph theory suggests that studied mixtures are characterized by interactions between hydrogen and oxygen atoms of **2-Py** (i) and oxygen, hydrogen atoms of ethanol (j). Thermodynamic properties, $X^E$ (X = H or $\kappa_S$) for **2-Py** (i) + ethanol (j) mixtures were then expressed by Equation (8)

$$X^E(X = V \text{ or } H) = \left[(1 + x_j)\chi'_{ij} + 2x_i\chi^*\right] \quad (8)$$

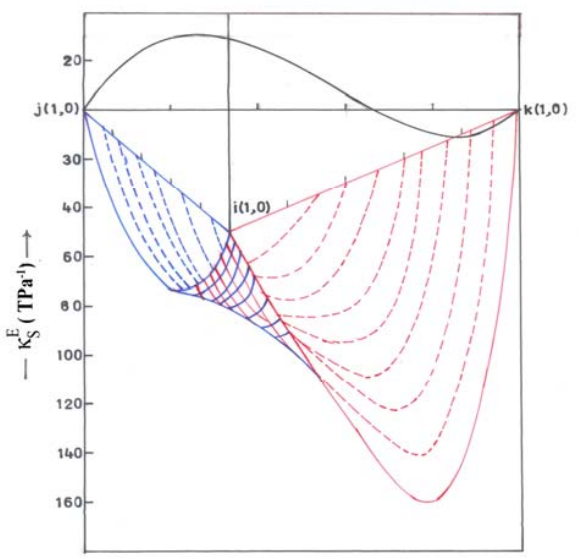


Fig. 3 Excess isentropic compressibilities, $\kappa_S^E$ for 2-pyrrolidinone (i) + benzene (j) + ethanol (k) ternary mixture at 308.15 K

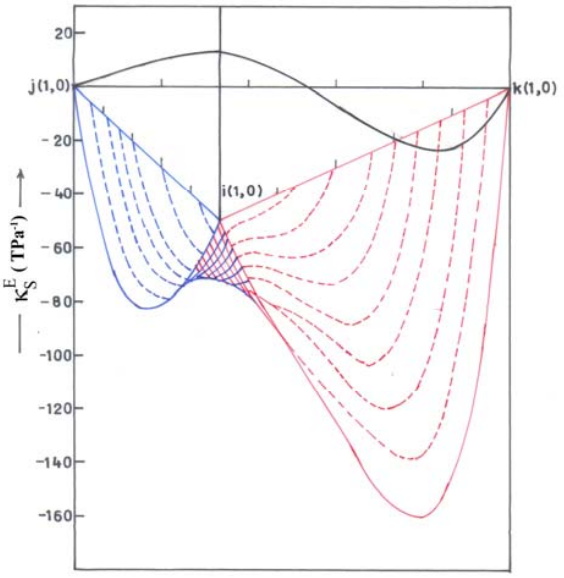


Fig. 4 Excess isentropic compressibilities, $\kappa_S^E$ for 2-pyrrolidinone (i) + toluene (j) + ethanol (k) ternary mixture at 308.15 K

where $\chi_{ij}^{/}$, $\chi_{12}$ etc. are the molar volume and enthalpy interaction parameters unlike i-j contacts and specific interaction between (i) and (j) components of (i + j) binary mixtures. $H^E$ and $V^E$ data predicted for these (i+j) binary mixtures {via Equation (7) and (8)} were in good agreement with their corresponding experimental values, which inturn lends additional support to the assumptions made in deriving Equations (7) and (8).

If a third component like ethanol is added to **2-Py** (i) + benzene or toluene (j) binary mixtures, then **2-Py** (i) + benzene or toluene (j) + ethanol (k) ternary mixtures formation may be assumed to involve processes (1) the establishment of (a) $i_n$-j , (b) j-$k_n$ and $i_n$-$k_n$ unlike contacts, (2) formation of unlike contacts would then depolymerize $i_n$ and $k_n$ to form their respective monomers, and (3) specific interaction between i, j and k contacts to form i : j, j : k molecular entities .If $\chi_{ij}^{/}$, $\chi_{jk}^{/}$ and $\chi_{ik}^{/}$ are the molar volume and molar compressibility interaction parameters of unlike (i-j), (j-k) and (i-k) contacts, then change in molar properties, $X^E$ (X = V or $\kappa_S$) due to processes 1{(a)-(c)} can be expressed by relation [33-35]:

$$\Delta X_1 = \left[\frac{x_i x_j v_j}{\sum x_i v_i}\right]\chi_{ij}^{/} + \left[\frac{x_j x_k v_k}{\sum x_j v_j}\right]\chi_{jk}^{/} + \left[\frac{x_k x_i v_i}{\sum x_k v_k}\right]\chi_{ik}^{/} \qquad (9)$$

where $v_i$ etc is the molar volume of component (i).

Further, if $\chi_{ii}^{/}, \chi_{kk}^{/}, \chi_{12}, \chi_{12}^{/}$ and $\chi_{12}^{//}$ are molar volume and compressibility interaction parameter for i-i, k-k like contacts and specific interactions (leading to the formation of i : j, j : k and i : k molecular entities), then change in molar properties, $\Delta X$ (X = V or $\kappa_S$) due to processes (2) [$\Delta X_2$, $\Delta X_3$] and (3) [$\Delta X_4$- $\Delta X_6$] would be expressed [33-35] as

$$\Delta X_2 = x_i^2 x_j v_j \chi_{ii}^{/} / \sum_{i=i}^{j} x_i v_i \qquad (10)$$

$$\Delta X_3 = x_i x_k v_k \chi_{kk}^{/} / \sum_{i=i}^{j} x_i v_i \qquad (11)$$

$$\Delta X_4 = x_i x_j^2 v_j \chi_{12} / \sum x_i v_i \qquad (12)$$

$$\Delta X_5 = x_j x_k^2 v_k \chi_{12}^{/} / \sum x_j v_j \qquad (13)$$

$$\Delta X_6 = x_k x_i^2 v_i \chi_{12}^{//} / \sum x_k v_k \qquad (14)$$

The overall changes in thermodynamic property, $X^E$ (X = V or $\kappa_S$) due to processes 1(a)-(c), 2 and 3 then can be expressed by Equation (15)

$$X^E = \sum_{1=1}^{6}\Delta X_i = \left[\frac{x_i x_j v_j}{\sum_{i=i}^{j} x_i v_i}\right]\left[\chi_{ij}^{/} + x_i\chi_{ii}^{/} + x_j\chi_{12}\right] + \left[\frac{x_j x_k v_k}{\sum_{j=j}^{k} x_j v_j}\right]\left[\chi_{jk}^{/} + x_k\chi_{12}^{/}\right] + \left[\frac{x_i x_k v_i}{\sum_{k=k}^{i} x_k v_k}\right]\left[x_k + x_i\chi_{12}^{//} + x_k\chi_{kk}^{/}\right] \qquad (15)$$

Because $v_j / v_i = {}^3\xi_i / {}^3\xi_j$ [36]; Equation (15) reduces to Equation (16)

$$X^E = \sum_{I=1}^{6} \Delta X_i = \left[\frac{x_i x_j \left({}^3\xi_i / {}^3\xi_j\right)}{x_i + x_j \left({}^3\xi_i / {}^3\xi_j\right)}\right]\left[\chi'_{ij} + x_i\chi'_{ii} + x_j\chi_{12}\right] + \left[\frac{x_j x_k \left({}^3\xi_j / {}^3\xi_k\right)}{x_j + x_k \left({}^3\xi_j / {}^3\xi_k\right)}\right]\left[\chi'_{jk} + x_k\chi'_{12}\right] + \left[\frac{x_i x_k \left({}^3\xi_i / {}^3\xi_k\right)}{x_i + x_k \left({}^3\xi_i / {}^3\xi_k\right)}\right]\left[x_k + x_i\chi''_{12} + x_k\chi'_{kk}\right] \quad (16)$$

For the investigated mixtures, if it is assumed that $\chi'_{ij} \cong \chi_{12}$ ; $\chi'_{ik} \cong \chi''_{12}$ ; $\chi'_{jk} \cong \chi'_{12}$ ; $\chi'_{ii} \cong \chi'_{kk} \cong \chi^*$, then Equation (16) can be written as

$$X^E = \sum_{I=1}^{6} \Delta X_i = \left[\frac{x_i x_j \left({}^3\xi_i / {}^3\xi_j\right)}{x_i + x_j \left({}^3\xi_i / {}^3\xi_j\right)}\right]\left[(1+x_j)\chi'_{ij} + x_i\chi^*\right] + \left[\frac{x_j x_k \left({}^3\xi_j / {}^3\xi_k\right)}{x_j + x_k \left({}^3\xi_j / {}^3\xi_k\right)}\right]\left[(1+x_k)\chi'_{jk}\right] + \left[\frac{x_i x_k \left({}^3\xi_i / {}^3\xi_k\right)}{x_i + x_k \left({}^3\xi_i / {}^3\xi_k\right)}\right]\left[(1+x_i)\chi'_{ik} + x_k\chi^*\right] \quad (17)$$

Equation (17) contains four unknown parameters, $\chi^*, \chi'_{ij}, \chi'_{jk}$ and $\chi'_{ik}$ and we evaluated these parameters by employing the $V^E_{ijk}$ and $(\kappa_S^E)_{ijk}$ data of the investigated ternary mixtures at four compositions. These parameters were then subsequently utilized to predict $X^E$ (X = V or $\kappa_S$) values at other values of $x_i$ and $x_j$ . Such predicted $V^E_{ijk}$ and $(\kappa_S^E)_{ijk}$ values along with $\chi^*, \chi'_{ij}$ etc. parameters are recorded in Tables II and III respectively.

Examination of Tables II and III reveals that predicted $V^E_{ijk}$ and $(\kappa_S^E)_{ijk}$ compare well with their experimental values. This lends additional support to the assumptions made in deriving Equation (17). Even in those cases where agreement between experimental and calculated values is not good, the predicted values are of the same sign as the experimental values. This may be due to the presence of ternary i-j-k contacts which have not been presently considered.

## V. Conclusion

In conclusion, $V^E_{ijk}$ and $(\kappa_S^E)_{ijk}$ values predicted by employing topology of the constituents of ternary mixtures have revealed that these $V^E_{ijk}$ and $(\kappa_S^E)_{ijk}$ values compare well with their corresponding experimental values; where agreement between theoretical and experimental values is not impressive, the predicted values are of same sign.

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