



TOPOLOGICAL INVESTIGATIONS OF EXCESS HEAT CAPACITIES OF TERNARY MIXTURES CONTAINING CHLOROTOLUENES AND CYCLIC AMIDES

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ABSTRACT

Excess heat capacities, $(C_p^E)_{123}$ of 1-methylpyrrolidin-2-one (1) + pyrrolidin-2-one (2) + *o*- or *m*- or *p*-chlorotoluene (3) ternary and C_p^E of 1-methylpyrrolidin-2-one (1) + pyrrolidin-2-one (2) binary mixtures have been determined at 293.15, 298.15, 303.15 K and 0.1 MPa using micro differential scanning calorimeter. The results were discussed in terms of Graph (which deals with the topology of the constituent molecules) and Flory's theories. The results suggested that C_p^E and $(C_p^E)_{123}$ values determined by Graph theory compared well with experimental values. Thermodynamics is the cornerstone for many scientific and engineering disciplines including physics, chemistry, chemical engineering, petroleum engineering and material science. It provides the basis for the design and optimization of new sustainable processes and the development of advance materials and products.

KEYWORDS: Excess heat capacity, C_p^E ; connectivity parameter, ξ ; interaction energy parameter, χ , 1-methyl pyrrolidin-2-one.



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INTRODUCTION

Heat capacity of liquids or excess heat capacities of liquid mixtures is one of the most important thermodynamic properties required in the design of acid gas adsorption system (CO₂ treatment process especially to the part that involves heat transfer¹) the determination of structural characteristics related to mixture formation and the development of solution models/theories.² In order to manage the complexity of liquid mixtures involved in chemical industrial applications (from petroleum to pharmaceuticals) models/theories are more and more often considered.^{3,4} A survey of literature on heat capacity of liquid mixtures indicates limited data on ternary liquid mixtures. In continuation of our earlier studies on thermodynamic properties like excess molar volumes, V^E , excess isentropic compressibilities, κ_S^E and excess heat capacities, C_p^E data of 1-methylpyrrolidin-2-one or pyrrolidin-2-one (1) + *o*- or *m*- or *p*-chlorotoluene (2) binary mixtures^{5,6}, we report here excess heat capacities, $(C_p^E)_{123}$ of 1-methylpyrrolidin-2-one (1) + pyrrolidin-2-one (2) + *o*- or *m*- or *p*-chlorotoluene (3) ternary mixtures. An attempt has been made to determine $(C_p^E)_{123}$ of ternary mixtures using topology of the constituent molecules (Graph theory).

Experimental

1-methylpyrrolidin-2-one (NMP) (mass fraction: 0.991), Pyrrolidin-2-one (2-Py) (mass fraction: 0.992), *o*-chlorotoluene (mass fraction: 0.989), *m*-chlorotoluene (mass fraction: 0.987), *p*-chlorotoluene (mass fraction: 0.995) were purified by standard methods.^{7,9} The source of liquids, their purification methods and final purity were reported in Table 1. The densities, ρ and speeds of sound, u values of the pure liquids were measured using a density and sound analyzer apparatus (Anton Paar DSA 5000) in the manner as described elsewhere.¹⁰⁻¹¹ The uncertainties in the density and

speed of sound measurements are $\pm 0.5 \text{ kg m}^{-3}$ and 0.1 m s^{-1} respectively. Further, uncertainty in the temperature measurement (DSA-5000) is $\pm 0.01 \text{ K}$. The molar heat capacities of the studied pure liquids and their mixtures were measured by high sensitivity differential scanning calorimeter Micro DSC (Model – $\mu\text{DSC 7 Evo}$) manufactured by SETARAM instrumentation, France in the manner described elsewhere.¹² The calibration of equipment was checked by measuring heat of fusion of naphthalene (148.21 J g^{-1}) comparable to 148.7 J g^{-1} .¹³ For a scanning sequence initial (15°C) and final temperature (45°C) were supplied along with heating rate of 0.4 K min^{-1} . The liquid or liquid mixture under investigation was taken in standard batch cell (made up of Hastelloy C276) of capacity 1 ml. An equivalent mass of water was taken in "Reference cell" to keep the calorimeter balanced, in particular in temperature scanning. The mole fraction of each liquid mixture was made by measuring masses of the components of mixtures in air tight glass bottles using an electric balance Mettler AX-205 Delta Range with an uncertainty of $\pm 10^{-5} \text{ g}$. The uncertainty in mole fraction is 1×10^{-4} . The uncertainty in measuring heat capacity is $\pm 0.3 \%$. The uncertainty in the temperature measurement (DSC) is $\pm 0.02 \text{ K}$. The densities, speeds of sound and molar heat capacities for the purified liquids at 293.15, 298.15, and 303.15 K along with their literature values¹⁴⁻¹⁸ are presented in Table 2.

RESULTS

The measured molar heat capacities, C_p and $(C_p)_{123}$ for NMP (1) + 2-Py (2) binary and NMP (1) + 2-Py (2) + *o*- or *m*- or *p*-chlorotoluene (3) ternary mixtures at 293.15, 298.15, 303.15 K and atmospheric pressure are listed in Tables 3-4 respectively. Excess heat capacities, C_p^E and $(C_p^E)_{123}$ were determined using Eqs.

$$C_p^E = C_p - x_1(C_p)_2 - x_2(C_p)_2 \quad (1)$$

$$(C_p^E)_{123} = (C_p)_{123} - x_1(C_p)_1 - x_2(C_p)_2 - x_3(C_p)_3 \quad (2)$$

Where x_1 , x_2 , x_3 are the mole fraction 1, 2 and 3 components of mixtures. Such C_p^E and $(C_p^E)_{123}$ are presented in Tables 3-4 respectively.

The C_p^E and $(C_p^E)_{123}$ were correlated by Redlich-Kister equations¹⁹ to show their composition dependence

$$C_p = x_1x_2[C_p^{(0)} + C_p^{(1)}(2x_1 - 1) + C_p^{(2)}(2x_1 - 1)^2] \quad (3)$$

$$(C_p^E)_{123} = x_1x_2 \left[\sum_{n=0}^2 (C_p)_{12}^{(n)} (x_1 - x_2)^n \right] + x_2x_3 \left[\sum_{n=0}^2 (C_p)_{23}^{(n)} (x_2 - x_3)^n \right] + x_3x_1 \left[\sum_{n=0}^2 (C_p)_{13}^{(n)} (x_3 - x_1)^n \right] + x_1x_2x_3 \left[\sum_{n=0}^2 (C_p)_{123}^{(n)} (x_2 - x_3)^n x_1^n \right] \quad (4)$$

Where $(C_P)_{12}^{(n)}$ ($n = 0-2$) etc. are parameters characteristics of binaries (1+2), (2+3), (1+3). The $(C_P)_{12}^{(n)}$ are listed in Table 5 and $(C_P)_{12}^{(n)}$ (at 298.15 K), $(C_P)_{23}^{(n)}$, $(C_P)_{13}^{(n)}$ parameters were taken from literature^{5,20}. The $(C_P)_{123}^{(n)}$ ($n = 0-2$) are parameters of (1+2+3) mixtures and were determined by least-squares optimization. Such parameters along with standard deviations, $\sigma(C_P^E)$ and $\sigma((C_P^E)_{123})$ of the present binary and ternary mixtures determined from

$$\sigma(C_P^E) = \left[\sum_1^m ((C_P^E)_{\{exptl\}} - (C_P^E)_{\{calc.equation(3)\}})^2 / (m-n) \right]^{0.5} \quad (5)$$

$$\sigma((C_P^E)_{123}) = \left[\sum_1^m ((C_P^E)_{123\{exptl\}} - (C_P^E)_{123\{calc.equation(4)\}})^2 / (m-n) \right]^{0.5} \quad (6)$$

{where m is the number of data points and n is the number of adjustable parameters of Eqs. (3) and (4)} and are given in Tables 5 and 6 respectively. Fig. 1 represent the surface area generated by $(C_P^E)_{123}$ values at 298.15 K calculated via Eq. (4).

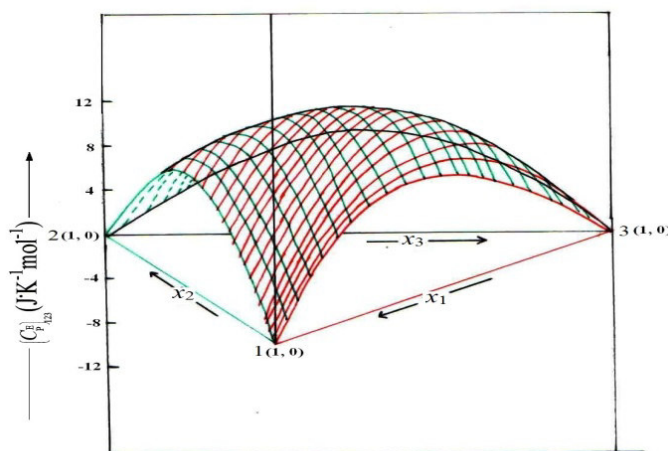


Figure 1

Excess heat capacities, $(C_P^E)_{123}$ for 1-methyl pyrrolidin-2-one (1) + pyrrolidin-2-one (2) + o-chlorotoluene (3) ternary mixture at 298.15 K, the experimental data in front of the plane (——); the experimental data behind the plane (-----).

Table 1
Details of chemical source, purification method, final purity and analysis method.

| Chemical name | Source | Purification method | Initial purity | Final purity | Analysis method |
|---------------------------|--------|-------------------------|----------------|--------------|-----------------|
| 1-Methyl pyrrolidin-2-one | Fluka | Vacuum Distillation | 0.98 | 0.99 | GC ^a |
| Pyrrolidin-2-one | Fluka | Vacuum Distillation | 0.98 | 0.99 | GC |
| o- Chlorotoluene | Fluka | Fractional distillation | 0.97 | 0.98 | GC |
| m- Chlorotoluene | Fluka | Fractional distillation | 0.97 | 0.98 | GC |
| p- Chlorotoluene | Fluka | Fractional distillation | 0.98 | 0.99 | GC |

^aGC = Gas chromatography

Table 2

Comparison of densities, ρ , speed of sound, u , and molar heat capacity, C_P of pure component (i) with their literature values at $T/ K = (293.15, 298.15, 303.15)$ and Pressure $p = 0.1$ MPa

| Liquids | T/K | $\rho / \text{kg m}^{-3}$ | | $u / \text{m s}^{-1}$ | | $C_P / \text{J K}^{-1} \text{mol}^{-1}$ | |
|---------------------------|--------|---------------------------|-------------------------|-----------------------|-------------------------|---|------------------------|
| | | Exptl | lit. | Exptl | lit. | Exptl | lit. |
| 1-Methyl pyrrolidin-2-one | 293.15 | 1033.28 | 1033.23 ^[14] | 1565.59 | 1565.52 ^[14] | - | 165.44 ^[14] |
| | 298.15 | 1028.26 | 1028.23 ^[14] | 1546.09 | 1546.02 ^[14] | - | 166.22 ^[14] |
| | 303.15 | 1023.49 | 1023.46 ^[14] | 1527.31 | 1527.24 ^[14] | - | 166.92 ^[14] |
| pyrrolidin-2-one | 293.15 | 1111.28 | 1111.28 ^[14] | 1651.44 | 1650.13 ^[14] | - | 168.36 ^[14] |
| | 298.15 | 1107.15 | 1107.15 ^[14] | 1635.02 | 1633.92 ^[14] | - | 169.55 ^[14] |
| | 303.15 | 1103.06 | 1103.02 ^[14] | 1618.70 | 1617.14 ^[14] | - | 171.18 ^[14] |
| o- Chlorotoluene | 293.15 | 1082.22 | - | 1316.77 | - | 176.43 | - |
| | 298.15 | 1077.34 | 1076.40 ^[15] | 1298.70 | 1301 ^[16] | 178.21 | - |

| | | | | | | | |
|-------------------------|--------|---------|-------------------------|---------|----------------------|--------|---|
| | 303.15 | 1072.46 | - | 1280.66 | - | 180.01 | - |
| | 293.15 | 1072.12 | - | 1313.63 | - | 175.21 | - |
| <i>m</i> -Chlorotoluene | 298.15 | 1067.23 | 1067.29 ^[16] | 1295.46 | 1298 ^[16] | 176.46 | - |
| | 303.15 | 1062.33 | 1062.81 ^[16] | 1277.31 | 1280 ^[16] | 177.67 | - |
| | 293.15 | 1069.27 | 1069.1 ^[17] | 1306.55 | - | 175.66 | - |
| | | | 1069.4 ^[18] | | | | |
| <i>p</i> -Chlorotoluene | 298.15 | 1064.37 | - | 1288.37 | 1289 ^[16] | 177.95 | - |
| | 303.15 | 1059.46 | - | 1270.29 | 1271 ^[16] | 180.37 | - |

The standard uncertainty in density is 0.5 kg m^{-3} ; the standard uncertainty in speed of sound is 0.1 m s^{-1} ; the standard uncertainty in heat capacity, C_p is 0.3 %.

Table 3

Measured heat capacities, C_p and excess heat capacity, C_p^E , data for the various (1 + 2) mixtures as a function of mole fraction, x_1 of component (1) at $T/\text{K} = (293.15, 298.15, 303.15)$ and Pressure $p = 0.1 \text{ MPa}$

| x_1 | $C_p / \text{J K}^{-1} \text{mol}^{-1}$ | $C_p^E / \text{J K}^{-1} \text{mol}^{-1}$ | x_1 | $C_p / \text{J K}^{-1} \text{mol}^{-1}$ | $C_p^E / \text{J K}^{-1} \text{mol}^{-1}$ |
|--|---|---|--------|---|---|
| 1-methyl pyrrolidin-2-one (1) + pyrrolidin-2-one (2) | | | | | |
| $T / \text{K} = 293.15$ | | | | | |
| 0.0834 | 168.28 | 0.16 | 0.4926 | 167.33 | 0.41 |
| 0.1281 | 168.21 | 0.23 | 0.5438 | 167.18 | 0.41 |
| 0.1534 | 168.17 | 0.25 | 0.5823 | 167.07 | 0.41 |
| 0.1822 | 168.11 | 0.28 | 0.6359 | 166.91 | 0.41 |
| 0.2278 | 168.01 | 0.32 | 0.6634 | 166.82 | 0.40 |
| 0.2548 | 167.95 | 0.34 | 0.6947 | 166.72 | 0.39 |
| 0.2843 | 167.88 | 0.35 | 0.7277 | 166.61 | 0.38 |
| 0.3258 | 167.78 | 0.37 | 0.7564 | 166.52 | 0.36 |
| 0.3567 | 167.70 | 0.38 | 0.7804 | 166.43 | 0.35 |
| 0.3934 | 167.60 | 0.39 | 0.8406 | 166.20 | 0.29 |
| 0.4395 | 167.48 | 0.40 | 0.8879 | 166.00 | 0.23 |
| 0.4652 | 167.41 | 0.40 | 0.9170 | 165.87 | 0.19 |
| $T / \text{K} = 298.15\text{K}$ | | | | | |
| 0.0834 | 169.46 | 0.19 | 0.4926 | 168.36 | 0.45 |
| 0.1281 | 169.38 | 0.25 | 0.5438 | 168.19 | 0.45 |
| 0.1534 | 169.33 | 0.29 | 0.5823 | 168.06 | 0.45 |
| 0.1822 | 169.26 | 0.32 | 0.6359 | 167.87 | 0.44 |
| 0.2278 | 169.15 | 0.36 | 0.6634 | 167.77 | 0.43 |
| 0.2548 | 169.08 | 0.38 | 0.6947 | 167.66 | 0.42 |
| 0.2843 | 169.00 | 0.39 | 0.7277 | 167.54 | 0.41 |
| 0.3258 | 168.88 | 0.41 | 0.7564 | 167.42 | 0.39 |
| 0.3567 | 168.78 | 0.42 | 0.7804 | 167.33 | 0.38 |
| 0.3934 | 168.67 | 0.43 | 0.8406 | 167.07 | 0.32 |
| 0.4395 | 168.53 | 0.44 | 0.8879 | 166.84 | 0.25 |
| 0.4652 | 168.44 | 0.44 | 0.9170 | 166.70 | 0.20 |
| $T / \text{K} = 303.15$ | | | | | |
| 0.0834 | 171.01 | 0.19 | 0.4926 | 169.57 | 0.49 |
| 0.1281 | 170.89 | 0.26 | 0.5438 | 169.35 | 0.49 |
| 0.1534 | 170.82 | 0.29 | 0.5823 | 169.19 | 0.49 |
| 0.1822 | 170.73 | 0.33 | 0.6359 | 168.95 | 0.48 |
| 0.2278 | 170.58 | 0.37 | 0.6634 | 168.82 | 0.47 |
| 0.2548 | 170.49 | 0.40 | 0.6947 | 168.68 | 0.46 |
| 0.2843 | 170.39 | 0.42 | 0.7277 | 168.52 | 0.44 |
| 0.3258 | 170.23 | 0.44 | 0.7564 | 168.38 | 0.42 |
| 0.3567 | 170.12 | 0.45 | 0.7804 | 168.25 | 0.40 |
| 0.3934 | 169.97 | 0.47 | 0.8406 | 167.93 | 0.33 |
| 0.4395 | 169.79 | 0.48 | 0.8879 | 167.66 | 0.26 |
| 0.4652 | 169.68 | 0.49 | 0.9170 | 167.48 | 0.21 |

The standard uncertainty in mole fraction value is 1.10^{-4} ; The standard uncertainty in temperature is $\pm 0.01 \text{ K}$;

Table 4

Comparison of experimental, excess heat capacities, $(C_p^E)_{123}$ data for the various (1 + 2 + 3) ternary mixtures with values evaluated from the Graph theory and Flory theory at $T/\text{K} = (293.15, 298.15 \text{ and } 303.15)$.

| x_1 | x_2 | $(C_p^E)_{123} / \text{J K}^{-1} \text{mol}^{-1}$ | $(C_p^E)_{123} / \text{J K}^{-1} \text{mol}^{-1}$ | | |
|--|--------|---|---|-------|-------|
| | | | Exptl. | Graph | Flory |
| 1-methyl pyrrolidin-2-one (1) + pyrrolidin-2-one (2) + <i>o</i> -Chlorotoluene (3) | | | | | |
| $T / \text{K} = 293.15$ | | | | | |
| 0.0925 | 0.6987 | 176.73 | 6.96 | 7.19 | 0.88 |
| 0.1021 | 0.6345 | 178.92 | 8.74 | 8.74 | 0.93 |
| 0.1145 | 0.5786 | 180.60 | 10.10 | 10.45 | 0.95 |
| 0.1326 | 0.1387 | 180.69 | 6.83 | 7.02 | 0.46 |
| 0.1768 | 0.1532 | 180.42 | 7.17 | 7.10 | 0.46 |
| 0.1976 | 0.1636 | 180.33 | 7.39 | 7.61 | 0.48 |
| 0.2245 | 0.1765 | 180.25 | 7.71 | 8.33 | 0.49 |
| 0.2476 | 0.1802 | 179.99 | 7.73 | 8.52 | 0.49 |
| 0.2757 | 0.1564 | 178.49 | 6.36 | 6.80 | 0.42 |
| 0.2835 | 0.1365 | 177.53 | 5.31 | 5.14 | 0.37 |

| | | | | | |
|----------------|--------|--------|-------|-------|------|
| 0.2935 | 0.3211 | 184.07 | 13.46 | 14.27 | 0.75 |
| 0.3023 | 0.1325 | 176.97 | 4.94 | 4.94 | 0.35 |
| 0.3328 | 0.2978 | 183.68 | 13.31 | 13.82 | 0.71 |
| 0.3425 | 0.1132 | 175.49 | 3.74 | 3.66 | 0.29 |
| 0.3534 | 0.2998 | 183.51 | 13.39 | 13.83 | 0.72 |
| 0.3638 | 0.1023 | 174.81 | 3.21 | 2.97 | 0.25 |
| 0.3729 | 0.2872 | 183.26 | 13.25 | 13.53 | 0.70 |
| 0.3829 | 0.2976 | 183.11 | 13.28 | 13.68 | 0.72 |
| 0.3932 | 0.2749 | 182.97 | 13.08 | 13.21 | 0.67 |
| 0.4123 | 0.2635 | 182.67 | 12.89 | 12.89 | 0.65 |
| 0.4312 | 0.2524 | 182.34 | 12.69 | 12.56 | 0.63 |
| 0.4537 | 0.2396 | 181.92 | 12.41 | 12.17 | 0.61 |
| 0.4738 | 0.2283 | 181.53 | 12.15 | 11.82 | 0.59 |
| 0.4928 | 0.2178 | 181.14 | 11.88 | 11.48 | 0.57 |
| 0.5121 | 0.2069 | 180.72 | 11.59 | 11.13 | 0.55 |
| 0.5347 | 0.1945 | 180.22 | 11.24 | 10.72 | 0.53 |
| 0.5512 | 0.1854 | 179.84 | 10.97 | 10.42 | 0.51 |
| 0.5738 | 0.1729 | 179.31 | 10.58 | 10.02 | 0.49 |
| 0.5947 | 0.1615 | 178.81 | 10.22 | 9.65 | 0.47 |
| 0.6137 | 0.1509 | 178.35 | 9.88 | 9.32 | 0.44 |
| 0.6356 | 0.1383 | 177.80 | 9.48 | 8.95 | 0.42 |
| 0.6576 | 0.1262 | 177.27 | 9.08 | 8.59 | 0.39 |
| 0.6754 | 0.0978 | 176.38 | 8.16 | 8.16 | 0.31 |
| 0.6935 | 0.1053 | 176.38 | 8.42 | 8.03 | 0.35 |
| 0.7123 | 0.1121 | 176.05 | 8.35 | 7.61 | 0.39 |
| T / K = 298.15 | | | | | |
| 0.0925 | 0.6987 | 179.46 | 8.41 | 8.68 | 0.88 |
| 0.1021 | 0.6345 | 181.95 | 10.46 | 10.46 | 0.91 |
| 0.1145 | 0.5786 | 183.84 | 12.01 | 12.42 | 0.96 |
| 0.1326 | 0.1387 | 183.23 | 7.81 | 8.14 | 0.98 |
| 0.1768 | 0.1532 | 183.00 | 8.24 | 8.23 | 0.48 |
| 0.1976 | 0.1636 | 182.94 | 8.52 | 8.82 | 0.49 |
| 0.2245 | 0.1765 | 182.91 | 8.92 | 9.65 | 0.50 |
| 0.2476 | 0.1802 | 182.64 | 8.96 | 9.87 | 0.52 |
| 0.2757 | 0.1564 | 180.88 | 7.33 | 7.84 | 0.52 |
| 0.2835 | 0.1365 | 179.72 | 6.09 | 5.90 | 0.45 |
| 0.2935 | 0.3211 | 187.70 | 15.79 | 16.70 | 0.39 |
| 0.3023 | 0.1325 | 179.08 | 5.64 | 5.64 | 0.78 |
| 0.3328 | 0.2978 | 187.23 | 15.59 | 16.15 | 0.38 |
| 0.3425 | 0.1132 | 177.32 | 4.20 | 4.10 | 0.73 |
| 0.3534 | 0.2998 | 187.06 | 15.68 | 16.18 | 0.31 |
| 0.3638 | 0.1023 | 176.50 | 3.54 | 3.27 | 0.74 |
| 0.3729 | 0.2872 | 186.75 | 15.50 | 15.82 | 0.28 |
| 0.3829 | 0.2976 | 186.60 | 15.56 | 16.02 | 0.72 |
| 0.3932 | 0.2749 | 186.40 | 15.28 | 15.43 | 0.74 |
| 0.4123 | 0.2635 | 186.03 | 15.04 | 15.04 | 0.70 |
| 0.4312 | 0.2524 | 185.63 | 14.78 | 14.65 | 0.68 |
| 0.4537 | 0.2396 | 185.13 | 14.43 | 14.17 | 0.66 |
| 0.4738 | 0.2283 | 184.65 | 14.10 | 13.74 | 0.63 |
| 0.4928 | 0.2178 | 184.19 | 13.77 | 13.32 | 0.61 |
| 0.5121 | 0.2069 | 183.68 | 13.41 | 12.90 | 0.59 |
| 0.5347 | 0.1945 | 183.08 | 12.97 | 12.40 | 0.57 |
| 0.5512 | 0.1854 | 182.63 | 12.64 | 12.04 | 0.55 |
| 0.5738 | 0.1729 | 182.00 | 12.16 | 11.55 | 0.53 |
| 0.5947 | 0.1615 | 181.40 | 11.72 | 11.10 | 0.51 |
| 0.6137 | 0.1509 | 180.85 | 11.31 | 10.69 | 0.49 |
| 0.6356 | 0.1383 | 180.20 | 10.81 | 10.24 | 0.47 |
| 0.6576 | 0.1262 | 179.57 | 10.33 | 9.79 | 0.44 |
| 0.6754 | 0.0978 | 178.45 | 9.19 | 9.19 | 0.42 |
| 0.6935 | 0.1053 | 178.51 | 9.53 | 9.10 | 0.33 |
| 0.7123 | 0.1121 | 178.18 | 9.49 | 8.68 | 0.37 |
| T / K = 303.15 | | | | | |
| 0.0925 | 0.6987 | 182.50 | 9.87 | 9.88 | 0.91 |
| 0.1021 | 0.6345 | 185.18 | 12.11 | 11.71 | 0.96 |
| 0.1145 | 0.5786 | 187.20 | 13.80 | 13.78 | 0.98 |
| 0.1326 | 0.1387 | 186.06 | 9.01 | 8.69 | 0.49 |
| 0.1768 | 0.1532 | 185.76 | 9.42 | 8.88 | 0.50 |
| 0.1976 | 0.1636 | 185.68 | 9.70 | 9.56 | 0.52 |
| 0.2245 | 0.1765 | 185.62 | 10.11 | 10.52 | 0.53 |
| 0.2476 | 0.1802 | 185.29 | 10.12 | 10.80 | 0.53 |
| 0.2757 | 0.1564 | 183.24 | 8.22 | 8.62 | 0.46 |
| 0.2835 | 0.1365 | 181.87 | 6.78 | 6.50 | 0.41 |
| 0.2935 | 0.3211 | 191.26 | 17.92 | 18.69 | 0.77 |
| 0.3023 | 0.1325 | 181.12 | 6.23 | 6.23 | 0.39 |
| 0.3328 | 0.2978 | 190.69 | 17.67 | 18.14 | 0.73 |
| 0.3425 | 0.1132 | 179.03 | 4.50 | 4.55 | 0.33 |
| 0.3534 | 0.2998 | 190.51 | 17.78 | 18.24 | 0.73 |
| 0.3638 | 0.1023 | 178.04 | 3.69 | 3.65 | 0.29 |
| 0.3729 | 0.2872 | 190.15 | 17.56 | 17.85 | 0.71 |
| 0.3829 | 0.2976 | 190.02 | 17.65 | 18.15 | 0.73 |
| 0.3932 | 0.2749 | 189.73 | 17.29 | 17.42 | 0.69 |
| 0.4123 | 0.2635 | 189.29 | 17.00 | 17.00 | 0.67 |

| | | | | | |
|--|--------|--------|-------|-------|------|
| 0.4312 | 0.2524 | 188.82 | 16.68 | 16.56 | 0.65 |
| 0.4537 | 0.2396 | 188.23 | 16.28 | 16.03 | 0.63 |
| 0.4738 | 0.2283 | 187.67 | 15.88 | 15.55 | 0.60 |
| 0.4928 | 0.2178 | 187.13 | 15.49 | 15.08 | 0.59 |
| 0.5121 | 0.2069 | 186.54 | 15.07 | 14.59 | 0.57 |
| 0.5347 | 0.1945 | 185.85 | 14.56 | 14.03 | 0.54 |
| 0.5512 | 0.1854 | 185.33 | 14.17 | 13.61 | 0.53 |
| 0.5738 | 0.1729 | 184.60 | 13.62 | 13.04 | 0.50 |
| 0.5947 | 0.1615 | 183.92 | 13.12 | 12.52 | 0.48 |
| 0.6137 | 0.1509 | 183.28 | 12.64 | 12.04 | 0.46 |
| 0.6356 | 0.1383 | 182.54 | 12.07 | 11.50 | 0.43 |
| 0.6576 | 0.1262 | 181.81 | 11.53 | 10.98 | 0.41 |
| 0.6754 | 0.0978 | 180.47 | 10.17 | 10.17 | 0.33 |
| 0.6935 | 0.1053 | 180.61 | 10.61 | 10.13 | 0.37 |
| 0.7123 | 0.1121 | 180.32 | 10.62 | 9.76 | 0.40 |
| 1-methyl pyrrolidin-2-one (1) + pyrrolidin-2-one (2) + <i>m</i> -Chlorotoluene (3) | | | | | |
| T/ K = 293.15 | | | | | |
| 0.0928 | 0.1867 | 179.41 | 6.39 | 6.45 | 0.49 |
| 0.1023 | 0.2093 | 179.73 | 6.96 | 7.02 | 0.52 |
| 0.1127 | 0.2342 | 180.07 | 7.57 | 7.62 | 0.56 |
| 0.1222 | 0.2576 | 180.39 | 8.13 | 8.13 | 0.59 |
| 0.1345 | 0.2875 | 180.78 | 8.85 | 8.73 | 0.63 |
| 0.1419 | 0.3045 | 181.01 | 9.27 | 9.06 | 0.64 |
| 0.1546 | 0.3234 | 181.30 | 9.82 | 9.63 | 0.66 |
| 0.1657 | 0.3376 | 181.54 | 10.26 | 10.08 | 0.67 |
| 0.1928 | 0.3495 | 181.94 | 11.00 | 11.15 | 0.66 |
| 0.2021 | 0.3654 | 182.15 | 11.42 | 11.32 | 0.67 |
| 0.1987 | 0.6904 | 173.76 | 5.22 | 5.22 | 0.74 |
| 0.2197 | 0.6543 | 174.64 | 6.06 | 5.94 | 0.76 |
| 0.2231 | 0.3876 | 182.44 | 12.07 | 11.67 | 0.69 |
| 0.2487 | 0.6281 | 174.61 | 6.13 | 6.13 | 0.78 |
| 0.2567 | 0.3897 | 182.68 | 12.65 | 12.34 | 0.68 |
| 0.2689 | 0.6235 | 173.72 | 5.41 | 5.68 | 0.80 |
| 0.3768 | 0.3458 | 182.62 | 13.46 | 13.60 | 0.62 |
| 0.3978 | 0.3512 | 182.17 | 13.25 | 13.02 | 0.63 |
| 0.4056 | 0.4534 | 176.52 | 8.37 | 8.12 | 0.78 |
| 0.4123 | 0.4721 | 174.61 | 6.66 | 6.80 | 0.81 |
| 0.4216 | 0.4557 | 175.22 | 7.25 | 7.24 | 0.80 |
| 0.4357 | 0.3261 | 181.89 | 13.17 | 13.17 | 0.60 |
| 0.4478 | 0.3987 | 177.77 | 9.67 | 9.12 | 0.74 |
| 0.4765 | 0.4082 | 175.01 | 7.25 | 7.09 | 0.78 |
| 0.4876 | 0.3989 | 174.94 | 7.23 | 7.03 | 0.77 |
| 0.4967 | 0.3213 | 179.85 | 11.69 | 11.21 | 0.63 |
| 0.5123 | 0.3654 | 175.87 | 8.17 | 7.73 | 0.74 |
| 0.5237 | 0.3423 | 176.89 | 9.14 | 8.56 | 0.70 |
| 0.5437 | 0.3245 | 176.85 | 9.17 | 8.57 | 0.68 |
| 0.6754 | 0.2024 | 176.29 | 9.06 | 9.05 | 0.49 |
| 0.6875 | 0.1953 | 175.93 | 8.77 | 8.76 | 0.49 |
| 0.6978 | 0.1891 | 175.63 | 8.53 | 8.53 | 0.48 |
| 0.7133 | 0.1799 | 175.16 | 8.15 | 8.15 | 0.47 |
| 0.7356 | 0.1662 | 174.48 | 7.60 | 7.62 | 0.45 |
| 0.7421 | 0.1624 | 174.27 | 7.42 | 7.44 | 0.44 |
| T/ K = 298.15 | | | | | |
| 0.0928 | 0.1867 | 181.07 | 6.85 | 6.86 | 0.51 |
| 0.1023 | 0.2093 | 181.39 | 7.43 | 7.46 | 0.54 |
| 0.1127 | 0.2342 | 181.74 | 8.05 | 8.09 | 0.58 |
| 0.1222 | 0.2576 | 182.05 | 8.62 | 8.62 | 0.61 |
| 0.1345 | 0.2875 | 182.45 | 9.35 | 9.24 | 0.64 |
| 0.1419 | 0.3045 | 182.67 | 9.77 | 9.59 | 0.66 |
| 0.1546 | 0.3234 | 182.97 | 10.33 | 10.17 | 0.67 |
| 0.1657 | 0.3376 | 183.20 | 10.77 | 10.63 | 0.68 |
| 0.1928 | 0.3495 | 183.59 | 11.52 | 11.73 | 0.68 |
| 0.2021 | 0.3654 | 183.80 | 11.93 | 11.89 | 0.69 |
| 0.1987 | 0.6904 | 175.14 | 5.48 | 5.45 | 0.75 |
| 0.2197 | 0.6543 | 176.05 | 6.36 | 6.21 | 0.77 |
| 0.2231 | 0.3876 | 184.09 | 12.59 | 12.23 | 0.70 |
| 0.2487 | 0.6281 | 176.00 | 6.43 | 6.43 | 0.79 |
| 0.2567 | 0.3897 | 184.32 | 13.18 | 12.89 | 0.69 |
| 0.2689 | 0.6235 | 175.08 | 5.69 | 5.99 | 0.80 |
| 0.3768 | 0.3458 | 184.21 | 14.00 | 14.15 | 0.63 |
| 0.3978 | 0.3512 | 183.76 | 13.80 | 13.58 | 0.64 |
| 0.4056 | 0.4534 | 177.94 | 8.77 | 8.65 | 0.78 |
| 0.4123 | 0.4721 | 175.97 | 7.00 | 7.34 | 0.81 |
| 0.4216 | 0.4557 | 176.61 | 7.61 | 7.79 | 0.80 |
| 0.4357 | 0.3261 | 183.47 | 13.73 | 13.73 | 0.61 |
| 0.4478 | 0.3987 | 179.23 | 10.11 | 9.69 | 0.74 |
| 0.4765 | 0.4082 | 176.39 | 7.63 | 7.70 | 0.78 |
| 0.4876 | 0.3989 | 176.32 | 7.61 | 7.66 | 0.77 |
| 0.4967 | 0.3213 | 181.38 | 12.23 | 11.79 | 0.64 |
| 0.5123 | 0.3654 | 177.28 | 8.59 | 8.36 | 0.74 |
| 0.5237 | 0.3423 | 178.33 | 9.60 | 9.19 | 0.70 |
| 0.5437 | 0.3245 | 178.30 | 9.65 | 9.21 | 0.68 |

| | | | | | |
|--|--------|--------|-------|-------|------|
| 0.6754 | 0.2024 | 177.77 | 9.62 | 9.61 | 0.50 |
| 0.6875 | 0.1953 | 177.40 | 9.33 | 9.32 | 0.49 |
| 0.6978 | 0.1891 | 177.09 | 9.09 | 9.08 | 0.48 |
| 0.7133 | 0.1799 | 176.61 | 8.69 | 8.69 | 0.47 |
| 0.7356 | 0.1662 | 175.91 | 8.13 | 8.14 | 0.45 |
| 0.7421 | 0.1624 | 175.69 | 7.96 | 7.96 | 0.44 |
| T/ K = 303.15 | | | | | |
| 0.0928 | 0.1867 | 182.93 | 7.47 | 7.34 | 0.52 |
| 0.1023 | 0.2093 | 183.25 | 8.04 | 7.97 | 0.56 |
| 0.1127 | 0.2342 | 183.57 | 8.63 | 8.63 | 0.59 |
| 0.1222 | 0.2576 | 183.86 | 9.18 | 9.18 | 0.62 |
| 0.1345 | 0.2875 | 184.23 | 9.88 | 9.83 | 0.66 |
| 0.1419 | 0.3045 | 184.45 | 10.28 | 10.18 | 0.67 |
| 0.1546 | 0.3234 | 184.86 | 10.95 | 10.71 | 0.69 |
| 0.1657 | 0.3376 | 185.18 | 11.48 | 11.11 | 0.69 |
| 0.1928 | 0.3495 | 185.27 | 11.94 | 12.44 | 0.68 |
| 0.2021 | 0.3654 | 185.54 | 12.42 | 12.54 | 0.69 |
| 0.1987 | 0.6904 | 176.69 | 5.63 | 5.53 | 0.73 |
| 0.2197 | 0.6543 | 177.59 | 6.53 | 6.35 | 0.75 |
| 0.2231 | 0.3876 | 185.84 | 13.08 | 12.85 | 0.70 |
| 0.2487 | 0.6281 | 177.52 | 6.60 | 6.60 | 0.77 |
| 0.2567 | 0.3897 | 186.07 | 13.69 | 13.50 | 0.69 |
| 0.2689 | 0.6235 | 176.55 | 5.82 | 6.15 | 0.77 |
| 0.3768 | 0.3458 | 185.99 | 14.61 | 14.79 | 0.61 |
| 0.3978 | 0.3512 | 185.79 | 14.67 | 15.30 | 0.62 |
| 0.4056 | 0.4534 | 180.94 | 10.57 | 10.24 | 0.75 |
| 0.4123 | 0.4721 | 177.90 | 7.72 | 8.20 | 0.78 |
| 0.4216 | 0.4557 | 178.05 | 7.87 | 8.31 | 0.77 |
| 0.4357 | 0.3261 | 185.24 | 14.37 | 14.37 | 0.59 |
| 0.4478 | 0.3987 | 180.81 | 10.54 | 10.28 | 0.71 |
| 0.4765 | 0.4082 | 177.83 | 7.93 | 8.34 | 0.75 |
| 0.4876 | 0.3989 | 177.76 | 7.92 | 8.31 | 0.74 |
| 0.4967 | 0.3213 | 183.09 | 12.85 | 12.45 | 0.61 |
| 0.5123 | 0.3654 | 178.78 | 8.99 | 9.06 | 0.71 |
| 0.5237 | 0.3423 | 179.90 | 10.08 | 9.89 | 0.67 |
| 0.5437 | 0.3245 | 179.87 | 10.15 | 9.93 | 0.65 |
| 0.6754 | 0.2024 | 179.41 | 10.32 | 10.31 | 0.48 |
| 0.6875 | 0.1953 | 179.03 | 10.02 | 10.01 | 0.47 |
| 0.6978 | 0.1891 | 178.71 | 9.77 | 9.77 | 0.46 |
| 0.7133 | 0.1799 | 178.21 | 9.37 | 9.37 | 0.45 |
| 0.7356 | 0.1662 | 177.48 | 8.80 | 8.81 | 0.43 |
| 0.7421 | 0.1624 | 177.25 | 8.61 | 8.62 | 0.42 |
| 1-methyl pyrrolidin-2-one (1) + pyrrolidin-2-one (2) + <i>p</i> -Chlorotoluene (3) | | | | | |
| T/ K = 293.15 | | | | | |
| 0.0989 | 0.2292 | 178.65 | 5.67 | 5.93 | 0.82 |
| 0.1023 | 0.2367 | 178.73 | 5.84 | 6.09 | 0.84 |
| 0.1136 | 0.2651 | 179.01 | 6.44 | 6.60 | 0.89 |
| 0.1222 | 0.2960 | 179.23 | 6.98 | 6.98 | 0.94 |
| 0.1312 | 0.3362 | 179.44 | 7.57 | 7.34 | 1.00 |
| 0.1476 | 0.3543 | 179.64 | 8.08 | 7.89 | 1.01 |
| 0.1584 | 0.3624 | 179.76 | 8.37 | 8.22 | 1.01 |
| 0.1765 | 0.6011 | 177.25 | 7.78 | 7.79 | 1.05 |
| 0.1897 | 0.5758 | 177.81 | 8.29 | 8.22 | 1.06 |
| 0.2013 | 0.5564 | 178.21 | 8.67 | 8.56 | 1.06 |
| 0.2234 | 0.5213 | 178.87 | 9.30 | 9.16 | 1.05 |
| 0.2436 | 0.4784 | 179.58 | 9.90 | 9.74 | 1.04 |
| 0.2645 | 0.4618 | 179.77 | 10.19 | 10.08 | 1.02 |
| 0.2876 | 0.4454 | 179.91 | 10.44 | 10.38 | 1.00 |
| 0.3064 | 0.4322 | 179.99 | 10.61 | 10.58 | 0.99 |
| 0.3236 | 0.4208 | 180.02 | 10.73 | 10.72 | 0.97 |
| 0.3424 | 0.4079 | 180.02 | 10.84 | 10.84 | 0.96 |
| 0.3657 | 0.3315 | 180.54 | 11.04 | 11.57 | 0.86 |
| 0.3875 | 0.3778 | 179.90 | 10.96 | 10.98 | 0.92 |
| 0.4055 | 0.3662 | 179.80 | 10.95 | 10.97 | 0.90 |
| 0.4236 | 0.3435 | 179.84 | 11.02 | 11.11 | 0.87 |
| 0.4437 | 0.3265 | 179.73 | 10.99 | 11.12 | 0.85 |
| 0.3021 | 0.3580 | 180.61 | 10.65 | 11.11 | 0.91 |
| 0.4898 | 0.3404 | 178.26 | 10.09 | 10.00 | 0.87 |
| 0.5124 | 0.3153 | 178.21 | 10.09 | 10.02 | 0.84 |
| 0.5346 | 0.3305 | 176.82 | 9.04 | 9.00 | 0.87 |
| 0.5505 | 0.3261 | 176.25 | 8.60 | 8.60 | 0.87 |
| 0.5787 | 0.2589 | 177.43 | 9.58 | 9.58 | 0.74 |
| 0.6108 | 0.2290 | 177.06 | 9.32 | 9.40 | 0.69 |
| 0.6387 | 0.2223 | 176.14 | 8.63 | 8.64 | 0.68 |
| 0.6547 | 0.2188 | 175.53 | 8.16 | 8.14 | 0.68 |
| 0.6758 | 0.2035 | 175.10 | 7.83 | 7.82 | 0.65 |
| 0.6938 | 0.1915 | 174.68 | 7.50 | 7.50 | 0.63 |
| 0.7133 | 0.1799 | 174.15 | 7.09 | 7.09 | 0.61 |
| 0.7345 | 0.1665 | 173.59 | 6.65 | 6.65 | 0.59 |
| T/ K = 298.15 | | | | | |
| 0.0989 | 0.2292 | 181.08 | 6.22 | 6.69 | 0.84 |
| 0.1023 | 0.2367 | 181.18 | 6.42 | 6.85 | 0.85 |

| | | | | | |
|---------------|--------|--------|-------|-------|------|
| 0.1136 | 0.2651 | 181.52 | 7.13 | 7.38 | 0.90 |
| 0.1222 | 0.2960 | 181.82 | 7.79 | 7.79 | 0.95 |
| 0.1312 | 0.3362 | 182.11 | 8.52 | 8.17 | 1.01 |
| 0.1476 | 0.3543 | 182.34 | 9.10 | 8.73 | 1.02 |
| 0.1584 | 0.3624 | 182.47 | 9.42 | 9.07 | 1.02 |
| 0.1765 | 0.6011 | 179.97 | 9.14 | 9.01 | 1.05 |
| 0.1897 | 0.5758 | 180.58 | 9.69 | 9.48 | 1.06 |
| 0.2013 | 0.5564 | 181.00 | 10.09 | 9.85 | 1.06 |
| 0.2234 | 0.5213 | 181.69 | 10.74 | 10.49 | 1.06 |
| 0.2436 | 0.4784 | 182.40 | 11.32 | 11.03 | 1.04 |
| 0.2645 | 0.4618 | 182.57 | 11.60 | 11.41 | 1.02 |
| 0.2876 | 0.4454 | 182.67 | 11.84 | 11.73 | 1.01 |
| 0.3064 | 0.4322 | 182.71 | 11.99 | 11.92 | 0.99 |
| 0.3236 | 0.4208 | 182.71 | 12.09 | 12.06 | 0.98 |
| 0.3424 | 0.4079 | 182.67 | 12.16 | 12.16 | 0.96 |
| 0.3657 | 0.3315 | 182.95 | 12.08 | 12.57 | 0.87 |
| 0.3875 | 0.3778 | 182.42 | 12.19 | 12.22 | 0.92 |
| 0.4055 | 0.3662 | 182.26 | 12.14 | 12.18 | 0.91 |
| 0.4236 | 0.3435 | 182.21 | 12.11 | 12.22 | 0.87 |
| 0.4437 | 0.3265 | 182.01 | 12.01 | 12.16 | 0.85 |
| 0.3021 | 0.3580 | 183.18 | 11.78 | 12.13 | 0.92 |
| 0.4898 | 0.3404 | 180.48 | 11.14 | 11.08 | 0.87 |
| 0.5124 | 0.3153 | 180.32 | 11.03 | 10.97 | 0.84 |
| 0.5346 | 0.3305 | 178.89 | 9.99 | 9.96 | 0.87 |
| 0.5505 | 0.3261 | 178.25 | 9.50 | 9.50 | 0.86 |
| 0.5787 | 0.2589 | 179.22 | 10.23 | 10.25 | 0.75 |
| 0.6108 | 0.2290 | 178.67 | 9.81 | 9.94 | 0.69 |
| 0.6387 | 0.2223 | 177.66 | 9.07 | 9.10 | 0.68 |
| 0.6547 | 0.2188 | 177.01 | 8.58 | 8.55 | 0.68 |
| 0.6758 | 0.2035 | 176.48 | 8.17 | 8.16 | 0.66 |
| 0.6938 | 0.1915 | 175.98 | 7.78 | 7.78 | 0.63 |
| 0.7133 | 0.1799 | 175.38 | 7.31 | 7.31 | 0.61 |
| 0.7345 | 0.1665 | 174.74 | 6.81 | 6.81 | 0.59 |
| T/ K = 303.15 | | | | | |
| 0.0989 | 0.2292 | 183.29 | 6.36 | 6.89 | 0.86 |
| 0.1023 | 0.2367 | 183.40 | 6.58 | 7.06 | 0.88 |
| 0.1136 | 0.2651 | 183.77 | 7.36 | 7.62 | 0.93 |
| 0.1222 | 0.2960 | 184.09 | 8.08 | 8.08 | 0.98 |
| 0.1312 | 0.3362 | 184.42 | 8.90 | 8.53 | 1.04 |
| 0.1476 | 0.3543 | 184.74 | 9.61 | 9.16 | 1.04 |
| 0.1584 | 0.3624 | 184.92 | 10.01 | 9.57 | 1.04 |
| 0.1765 | 0.6011 | 182.55 | 10.07 | 10.46 | 1.06 |
| 0.1897 | 0.5758 | 183.28 | 10.75 | 10.98 | 1.06 |
| 0.2013 | 0.5564 | 183.80 | 11.25 | 11.39 | 1.07 |
| 0.2234 | 0.5213 | 184.64 | 12.06 | 12.08 | 1.06 |
| 0.2436 | 0.4784 | 185.44 | 12.74 | 12.58 | 1.05 |
| 0.2645 | 0.4618 | 185.69 | 13.12 | 13.03 | 1.03 |
| 0.2876 | 0.4454 | 185.86 | 13.46 | 13.42 | 1.01 |
| 0.3064 | 0.4322 | 185.94 | 13.67 | 13.65 | 0.99 |
| 0.3236 | 0.4208 | 185.96 | 13.81 | 13.81 | 0.98 |
| 0.3424 | 0.4079 | 185.94 | 13.92 | 13.92 | 0.96 |
| 0.3657 | 0.3315 | 185.97 | 13.56 | 13.88 | 0.87 |
| 0.3875 | 0.3778 | 185.66 | 13.98 | 13.96 | 0.92 |
| 0.4055 | 0.3662 | 185.47 | 13.92 | 13.89 | 0.90 |
| 0.4236 | 0.3435 | 185.33 | 13.82 | 13.82 | 0.87 |
| 0.4437 | 0.3265 | 185.05 | 13.65 | 13.68 | 0.85 |
| 0.3021 | 0.3580 | 186.17 | 13.15 | 13.34 | 0.93 |
| 0.4898 | 0.3404 | 183.52 | 12.87 | 12.75 | 0.86 |
| 0.5124 | 0.3153 | 183.22 | 12.64 | 12.50 | 0.83 |
| 0.5346 | 0.3305 | 181.75 | 11.60 | 11.56 | 0.85 |
| 0.5505 | 0.3261 | 181.02 | 11.05 | 11.05 | 0.84 |
| 0.5787 | 0.2589 | 181.70 | 11.49 | 11.42 | 0.74 |
| 0.6108 | 0.2290 | 180.91 | 10.86 | 10.94 | 0.68 |
| 0.6387 | 0.2223 | 179.78 | 10.04 | 10.02 | 0.67 |
| 0.6547 | 0.2188 | 179.05 | 9.50 | 9.42 | 0.67 |
| 0.6758 | 0.2035 | 178.38 | 8.97 | 8.93 | 0.64 |
| 0.6938 | 0.1915 | 177.76 | 8.49 | 8.48 | 0.62 |
| 0.7133 | 0.1799 | 177.04 | 7.92 | 7.92 | 0.60 |
| 0.7345 | 0.1665 | 176.27 | 7.31 | 7.34 | 0.58 |

Table 5

Binary adjustable parameters, C_p^n ($n = 0$ to 2) of Eq. 3 along with standard deviations,

$\sigma(C_p^E)$ at $T/ K = (293.15, 298.15, 303.15)$.

| Parameters | T/K | | |
|--|--------|--------|--------|
| | 293.15 | 298.15 | 303.15 |
| 1-methyl pyrrolidin-2-one (1) + pyrrolidin-2-one (2) | | | |
| $C_p^{(0)}$ | 1.63 | 1.79 | 1.96 |

| | | | |
|---|------|------|------|
| $C_p^{(1)}$ | 0.19 | 0.12 | 0.17 |
| $C_p^{(2)}$ | 0.95 | 1.06 | 0.88 |
| $\sigma(C_p^E)/\text{J}\cdot\text{K}^{-1}\text{mol}^{-1}$ | 0.00 | 0.00 | 0.00 |

Table 6

Ternary adjustable parameters $(C_p^E)_{123}^{(n)}$ ($n = 0 - 2$) of Eq. (4) along with standard deviation $\sigma(C_p^E)_{123}$

| Parameters | T/K | | |
|--|-----------|-----------|-----------|
| | 293.15 | 298.15 | 303.15 |
| 1-methyl pyrrolidin-2-one (1) + pyrrolidin-2-one (2) + o-chlorotoluene (3) | | | |
| $(C_p^E)_{123}^{(0)}$ | 123.65 | 165.45 | 204.87 |
| $(C_p^E)_{123}^{(1)}$ | 127.76 | 147.34 | 185.65 |
| $(C_p^E)_{123}^{(2)}$ | -16767.40 | -18857.20 | -21083.22 |
| $\sigma(C_p^E)_{123}$ /($\text{J}\cdot\text{K}^{-1}\text{mol}^{-1}$) | 0.03 | 0.04 | 0.05 |
| 1-methyl pyrrolidin-2-one (1) + pyrrolidin-2-one (2) + m-Chlorotoluene (3) | | | |
| $(C_p^E)_{123}^{(0)}$ | 98.34 | 99.22 | 91.06 |
| $(C_p^E)_{123}^{(1)}$ | 1145.37 | 1178.90 | 1283.56 |
| $(C_p^E)_{123}^{(2)}$ | -8553.92 | -8756.26 | -9538.09 |
| $\sigma(C_p^E)_{123}$ /($\text{J}\cdot\text{K}^{-1}\text{mol}^{-1}$) | 0.04 | 0.04 | 0.05 |
| 1-methyl pyrrolidin-2-one (1) + pyrrolidin-2-one (2) + p-chlorotoluene (3) | | | |
| $(C_p^E)_{123}^{(0)}$ | 92.35 | 111.25 | 164.34 |
| $(C_p^E)_{123}^{(1)}$ | 733.97 | 871.02 | 1092.01 |
| $(C_p^E)_{123}^{(2)}$ | -777.41 | -414.22 | 90.08 |
| $\sigma(C_p^E)_{123}$ /($\text{J}\cdot\text{K}^{-1}\text{mol}^{-1}$) | 0.03 | 0.04 | 0.04 |

Table 7

Comparison of calculated excess heat capacity, C_p^E values from appropriate equations with their corresponding experimental values at $T/K = 293.15, 298.15, 303.15$

| Property / $\text{J}\cdot\text{K}^{-1}\text{mol}^{-1}$ | Mole fraction of component | | | | | | | | |
|---|----------------------------|------|------|------|------|------|------|------|------|
| | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
| 1-methylpyrrolidin-2-one (1) + pyrrolidin-2-one (2) | | | | | | | | | |
| $T = 293.15\text{ K}$ | | | | | | | | | |
| C_p^E (exptl.) | 0.19 | 0.30 | 0.36 | 0.39 | 0.41 | 0.41 | 0.39 | 0.33 | 0.21 |
| C_p^E (Graph) | 0.14 | 0.25 | 0.33 | 0.39 | 0.42 | 0.41 | 0.37 | 0.28 | 0.16 |
| C_p^E (Flory) | 0.42 | 0.67 | 0.84 | 0.94 | 0.97 | 0.93 | 0.82 | 0.64 | 0.40 |
| $T = 298.15\text{ K}$ | | | | | | | | | |
| C_p^E (exptl.) | 0.21 | 0.34 | 0.40 | 0.43 | 0.45 | 0.45 | 0.42 | 0.36 | 0.23 |
| C_p^E (Graph) | 0.16 | 0.28 | 0.37 | 0.43 | 0.46 | 0.45 | 0.39 | 0.30 | 0.17 |
| C_p^E (Flory) | 0.43 | 0.66 | 0.83 | 0.93 | 0.95 | 0.92 | 0.81 | 0.64 | 0.40 |
| $T = 303.15\text{ K}$ | | | | | | | | | |

| | | | | | | | | | |
|------------------|------|------|------|------|------|------|------|------|------|
| C_P^E (exptl.) | 0.22 | 0.35 | 0.43 | 0.47 | 0.49 | 0.49 | 0.45 | 0.38 | 0.24 |
| C_P^E (Graph) | 0.17 | 0.30 | 0.40 | 0.47 | 0.50 | 0.49 | 0.43 | 0.33 | 0.19 |
| C_P^E (Flory) | 0.42 | 0.63 | 0.79 | 0.88 | 0.90 | 0.87 | 0.77 | 0.61 | 0.38 |

Table 8

Interaction energy χ_{12}'' and χ^* parameters along with connectivity parameter of third degree (${}^3\xi_i$) ($i = 1$ or 2) for the various (1 + 2) mixtures as a function of x_1 , mole fraction of component (1) at $T/K = 293.15, 298.15, 303.15$

| Parameters | T/K | | |
|--|--------|--------|--------|
| | 293.15 | 298.15 | 303.15 |
| 1-methyl pyrrolidin-2-one (1) + pyrrolidin-2-one (2) | | | |
| ${}^3\xi_1$ | 1.012 | 1.012 | 1.012 |
| ${}^3\xi_2$ | 1.203 | 1.203 | 1.203 |
| $\chi_{12}'' / \text{J.K}^{-1} \text{mol}^{-1}$ | 0.73 | 0.85 | 0.91 |
| $\chi^* / \text{J.K}^{-1} \text{mol}^{-1}$ | 0.72 | 0.73 | 0.82 |
| $\sigma(C_P^E)_{\text{Graph}}$ | 0.03 | 0.04 | 0.03 |
| $\chi_{12}^{**} / \text{J.K}^{-1} \text{mol}^{-1}$ | -1.32 | -1.29 | -1.32 |
| $\sigma(C_P^E)_{\text{Flory}}$ | 0.45 | 0.40 | 0.33 |

Table 9

Interaction energies $\chi_{12}^*, \chi_{23}^*, \chi_{13}^*, \chi^*$ and $\chi_{12}^{**}, \chi_{23}^{**}, \chi_{13}^{**}$ parameters along with connectivity parameters of third degree of a molecule, (${}^3\xi_i$) or (${}^3\xi_i)_m$ ($i = 1$ or 2 or 3) utilized in Graph and Flory theories for the determination of $(C_P^E)_{123}$ at $T/K = 293.15, 298.15, 303.15$. Also included are the deviations, $\sigma(C_P^E)_{123\text{Graph}}$ and $\sigma(C_P^E)_{123\text{Flory}}$ between experimental values of $(C_P^E)_{123}$ and values obtained from Graph and Flory theories.

| Parameters | T/K | | |
|--|---------|---------|---------|
| | 293.15 | 298.15 | 303.15 |
| 1-methyl pyrrolidin-2-one (1) + pyrrolidin-2-one (2) + o-chlorotoluene (3) | | | |
| $({}^3\xi_1) = ({}^3\xi_1)_m$ | 1.023 | 1.023 | 1.023 |
| $({}^3\xi_2) = ({}^3\xi_2)_m$ | 1.211 | 1.211 | 1.211 |
| $({}^3\xi_3) = ({}^3\xi_3)_m$ | 1.311 | 1.311 | 1.311 |
| $\chi_{12}^* / \text{J.K}^{-1} \text{mol}^{-1}$ | -48.35 | 80.53 | 94.59 |
| $\chi_{23}^* / \text{J.K}^{-1} \text{mol}^{-1}$ | -128.21 | 81.05 | 84.03 |
| $\chi_{13}^* / \text{J.K}^{-1} \text{mol}^{-1}$ | -62.35 | 37.29 | 39.56 |
| $\chi^* / \text{J.K}^{-1} \text{mol}^{-1}$ | 257.82 | -156.45 | -167.61 |
| $\sigma(C_P^E)_{123\text{Graph}}$ | 0.44 | 0.50 | 0.29 |
| $\chi_{12}^{**} / \text{J.K}^{-1} \text{mol}^{-1}$ | -1.32 | -1.29 | -1.32 |
| $\chi_{23}^{**} / \text{J.K}^{-1} \text{mol}^{-1}$ | -0.20 | -0.19 | -0.18 |
| $\chi_{13}^{**} / \text{J.K}^{-1} \text{mol}^{-1}$ | 3.87 | 3.79 | 3.77 |
| $\sigma(C_P^E)_{123\text{Flory}}$ | 10.24 | 11.96 | 13.62 |
| 1-methyl pyrrolidin-2-one (1) + pyrrolidin-2-one (2) + m-chlorotoluene (3) | | | |
| $({}^3\xi_1) = ({}^3\xi_1)_m$ | 1.016 | 1.016 | 1.016 |

| | | | |
|--|--------|--------|--------|
| $({}^3\xi_2) = ({}^3\xi_2)_m$ | 1.203 | 1.203 | 1.203 |
| $({}^3\xi_3) = ({}^3\xi_3)_m$ | 1.980 | 1.980 | 1.980 |
| $\chi_{12}^* / \text{J}\cdot\text{K}^{-1} \text{mol}^{-1}$ | 3.92 | 2.97 | 0.60 |
| $\chi_{23}^* / \text{J}\cdot\text{K}^{-1} \text{mol}^{-1}$ | -0.87 | -3.50 | -7.84 |
| $\chi_{13}^* / \text{J}\cdot\text{K}^{-1} \text{mol}^{-1}$ | 58.53 | 57.35 | 56.14 |
| $\chi^* / \text{J}\cdot\text{K}^{-1} \text{mol}^{-1}$ | -21.47 | -12.06 | 1.43 |
| $\sigma(C_P^E)_{123\text{Graph}}$ | 0.28 | 0.23 | 0.29 |
| $\chi_{12}^{**} / \text{J}\cdot\text{K}^{-1} \text{mol}^{-1}$ | -1.32 | -1.29 | -1.32 |
| $\chi_{23}^{**} / \text{J}\cdot\text{K}^{-1} \text{mol}^{-1}$ | -0.48 | -0.46 | -0.45 |
| $\chi_{13}^{**} / \text{J}\cdot\text{K}^{-1} \text{mol}^{-1}$ | 6.67 | 6.54 | 6.51 |
| $\sigma(C_P^E)_{123\text{Flory}}$ | 9.75 | 9.25 | 10.34 |
| 1-methyl pyrrolidin-2-one (1) + pyrrolidin-2-one (2) + <i>p</i> -chlorotoluene (3) | | | |
| $({}^3\xi_1) = ({}^3\xi_1)_m$ | 1.016 | 1.016 | 1.016 |
| $({}^3\xi_2) = ({}^3\xi_2)_m$ | 1.203 | 1.203 | 1.203 |
| $({}^3\xi_3) = ({}^3\xi_3)_m$ | 1.397 | 1.397 | 1.397 |
| $\chi_{12}^* / \text{J}\cdot\text{K}^{-1} \text{mol}^{-1}$ | 19.59 | 31.88 | 48.34 |
| $\chi_{23}^* / \text{J}\cdot\text{K}^{-1} \text{mol}^{-1}$ | 8.31 | 16.40 | 21.69 |
| $\chi_{13}^* / \text{J}\cdot\text{K}^{-1} \text{mol}^{-1}$ | 34.10 | 36.42 | 40.18 |
| $\chi^* / \text{J}\cdot\text{K}^{-1} \text{mol}^{-1}$ | -18.01 | -40.84 | -66.16 |
| $\sigma(C_P^E)_{123\text{Graph}}$ | 0.18 | 0.24 | 0.24 |
| $\chi_{12}^{**} / \text{J}\cdot\text{K}^{-1} \text{mol}^{-1}$ | -1.32 | -1.29 | -1.32 |
| $\chi_{23}^{**} / \text{J}\cdot\text{K}^{-1} \text{mol}^{-1}$ | 0.00 | 0.00 | 0.02 |
| $\chi_{13}^{**} / \text{J}\cdot\text{K}^{-1} \text{mol}^{-1}$ | 3.43 | 3.36 | 3.34 |
| $\sigma(C_P^E)_{123\text{Flory}}$ | 8.96 | 10.06 | 11.41 |

Table 10

Parameters of the pure components i.e characteristic volume, V^* , characteristic pressure, P^* , coefficient of thermal expansion, α , molar volume, V and reduced volume, \tilde{v} used in Flory theory calculations at $T/\text{K} = (293.15, 298.15, 303.15)$

| Components | T/K | $V^* / \text{cm}^3 \text{mol}^{-1}$ | $P^* / \text{J}\cdot\text{cm}^{-3}$ | $\alpha (\times 10^{-3}) / \text{K}^{-1}$ | $V / \text{cm}^3 \text{mol}^{-1}$ | $\tilde{v} / \text{cm}^3 \text{mol}^{-1}$ |
|---------------------------|--------------|-------------------------------------|-------------------------------------|---|-----------------------------------|---|
| 1-Methyl pyrrolidin-2-one | 293.15 | 77.70 | 800.47 | 0.954 | 95.94 | 1.23 |
| | 298.15 | 77.91 | 799.25 | 0.950 | 96.41 | 1.24 |
| | 303.15 | 78.27 | 795.06 | 0.935 | 96.86 | 1.24 |
| pyrrolidin-2-one | 293.15 | 64.40 | 1282.58 | 0.741 | 76.58 | 1.19 |
| | 298.15 | 64.46 | 1284.10 | 0.743 | 76.87 | 1.19 |
| | 303.15 | 64.55 | 1284.55 | 0.743 | 77.15 | 1.20 |
| <i>o</i> -Chlorotoluene | 293.15 | 95.57 | 553.09 | 0.901 | 116.97 | 1.22 |
| | 298.15 | 95.69 | 553.71 | 0.905 | 117.50 | 1.23 |
| | 303.15 | 95.78 | 554.60 | 0.911 | 118.03 | 1.23 |
| <i>m</i> -Chlorotoluene | 293.15 | 96.28 | 575.22 | 0.913 | 118.07 | 1.23 |
| | 298.15 | 96.39 | 576.02 | 0.917 | 118.61 | 1.23 |
| | 303.15 | 96.49 | 577.01 | 0.923 | 119.16 | 1.23 |
| <i>p</i> -Chlorotoluene | 293.15 | 96.45 | 489.61 | 0.918 | 118.38 | 1.23 |
| | 298.15 | 96.57 | 490.12 | 0.922 | 118.93 | 1.23 |
| | 303.15 | 96.67 | 490.86 | 0.928 | 119.48 | 1.24 |

DISCUSSION

Excess heat capacity, C_p^E is a very sensitive indicator for the interpretation of intermolecular forces and describe the molecular orientation effect. The C_p^E values are valuable in the design and optimization of industrial processes. The $(C_p^E)_{123}$ data of the studied ternary mixtures were not available in the literature. The $(C_p^E)_{123}$ values of NMP (1) + 2-Py (2) + *o*- or *m*- or *p*-chlorotoluene (3) mixtures are positive over entire mole fractions range. The positive $(C_p^E)_{123}$ values for these mixtures suggest that interactions between NMP, 2-Py and *o*- or *m*- or *p*-chlorotoluene are more intense and provide more compact structure than pure state. The $(C_p^E)_{123}$ values of NMP (1) + 2-Py (2) + *o*-chloro toluene (3) mixture are higher than those for NMP (1) + 2-Py (2) + *m*- or *p*-chlorotoluene (3) mixtures which in turn suggest more compact structure of *o*-CT in NMP:2-Py molecular entity as compared to *m*- or *p*-chlorotoluene. The $(\partial C_p^E / \partial T)$ and $(\partial(C_p^E)_{123} / \partial T)$ for the present binary and ternary mixtures are positive. This may be due the destruction of associated molecular entities NMP, 2-Py, *o*- or *m*- or *p*-CT which makes the

interactions between like molecules more difficult than between unlike molecule and thus enhance non-randomness in mixed state.

Graph Theory

Excess heat capacities of binary mixtures

The analyses of excess molar volumes, V^E , excess isentropic compressibilities, κ_S^E and IR spectral data of NMP (1) + 2-Py or *o*- or *m*- or *p*-chlorotoluene (2); 2-Py (1) + *o*- or *m*- or *p*-chlorotoluene (2) mixtures have shown that NMP, 2-Py, *o*- or *m*- or *p*-chlorotoluene exist as associated molecular entities⁶. Consequently, NMP (1) + 2-Py (2) mixture formation was assumed to have processes (i) unlike 1_n-2_n ($n = 2$) contact formation; (ii) establishment of these formation then weakens 1_n , 2_n association to form 1 and 2 molecules and enhances randomness; and (iii) 1 and 2 molecules undergo interactions to form 1:2 molecular complex which in turn leads to more compact structure in mixed state. If χ_{12} , χ_{11} , χ_{22} and χ'_{12} are molar interaction parameters for unlike contacts, increase in randomness due to rupture of 1_n , 2_n ; and formation of molecular complex respectively, then change in thermodynamic property, C_p^E due to processes (i) – (iii) was given²¹⁻²⁶ by

$$C_p^E = \left[\frac{x_1 x_2 \left(\frac{{}^3\xi_1}{{}^3\xi_2} \right)}{x_1 + x_2 \left(\frac{{}^3\xi_1}{{}^3\xi_2} \right)} \right] \left[\chi_{12} + x_1 \chi_{11} + x_2 \chi_{22} + x_2 \chi'_{12} \right] \quad (7)$$

Where ${}^3\xi_i$ ($i = 1$ or 2) is the connectivity parameter of third degree, ${}^3\xi$ of a molecule defined²⁷ by

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

where δ_m^v , etc. values reflects the valency of the atoms forming the bond and are expressed.^{28a, 28b} For the present (1 + 2) mixtures, if the interaction parameters for unlike contacts, and interactions between 1 and 2

components; rupture of 1_n or 2_n components are assumed to be nearly equal i.e $\chi_{12} \cong \chi'_{12} = \chi''_{12}$ and $\chi_{11} \cong \chi_{22} = \chi^*$ then Eq. (7) was reduced to

$$C_p^E = \left[\frac{x_1 x_2 \left(\frac{{}^3\xi_1}{{}^3\xi_2} \right)}{x_1 + x_2 \left(\frac{{}^3\xi_1}{{}^3\xi_2} \right)} \right] \left[(1 + x_2) \chi''_{12} + 2x_1 \chi^* \right] \quad (9)$$

Two parameters χ''_{12} and χ^* were determined by using C_p^E data at two compositions and were then used to evaluate C_p^E values of mixture at various mole fractions. The predicted C_p^E values and χ''_{12} , χ^* parameters for (1 + 2) mixture are reported in Tables 7-8 respectively. Examination of data in Table 7 suggests that C_p^E values predicted via Eq. (9) compare well with their experimental values.

Excess heat capacities of ternary mixtures

The various processes involved in the present mixtures formation were assumed to be (i) establishment of

unlike (a) 1_n-2_n , (b) 2_n-3_n , (c) 1_n-3_n contacts; (ii) unlike contact formation then rupture association of (a) 1_n ; (b) 2_n (c) 3_n to yields 1, 2 and 3 molecules and leads to randomness; and (iii) molecules of 1, 2 and 3 then undergo interactions to form (a) 1:2 (b) 2:3 and (c) 1:3 complexes enhancing non-randomness in the mixed state. If χ_{12} , χ_{23} , χ_{13} ; χ_{11} , χ_{22} , χ_{33} , χ'_{12} , χ'_{12} and χ'''_{12} are the molar interaction parameters for unlike (a) 1_n-2_n , (b) 2_n-3_n , (c) 1_n-3_n contacts, due to rupture of 1_n or 2_n or 3_n increase in randomness, and non-randomness due to formation 1:2, 2:3, 1:3 molecular complexes, then change in thermodynamic property, ΔC_p , due to processes (1) - (3) (a)-(c) were given²¹⁻²⁶ by

$$(\Delta C_p)_1 = \left[\frac{x_1 x_2 \left(\frac{{}^3\xi_1}{{}^3\xi_2} \right)}{x_1 + x_2 \left(\frac{{}^3\xi_1}{{}^3\xi_2} \right)} \right] \left[\chi_{12} + x_1 \chi_{11} + x_2 \chi'_{12} \right] \quad (10)$$

$$(\Delta C_p)_2 = \left[\frac{x_2 x_3 \left(\frac{{}^3\xi_2}{{}^3\xi_3} \right)}{x_2 + x_3 \left(\frac{{}^3\xi_2}{{}^3\xi_3} \right)} \right] \left[\chi_{23} + x_2 \chi_{22} + x_3 \chi''_{12} \right] \quad (11)$$

$$(\Delta C_p)_3 = \left[\frac{x_3 x_1 \left(\frac{{}^3\xi_3}{{}^3\xi_1} \right)}{x_3 + x_1 \left(\frac{{}^3\xi_3}{{}^3\xi_1} \right)} \right] \left[\chi_{13} + x_3 \chi_{33} + x_1 \chi'''_{12} \right] \quad (12)$$

Then total change in ΔC_p

$$\begin{aligned} (C_p^E)_{123} &= \sum_{i=1}^3 (\Delta C_p)_i = \left[\frac{x_1 x_2 \left(\frac{{}^3\xi_1}{{}^3\xi_2} \right)}{x_1 + x_2 \left(\frac{{}^3\xi_1}{{}^3\xi_2} \right)} \right] \left[\chi_{12} + x_1 \chi_{11} + x_2 \chi'_{12} \right] \\ &+ \left[\frac{x_2 x_3 \left(\frac{{}^3\xi_2}{{}^3\xi_3} \right)}{x_2 + x_3 \left(\frac{{}^3\xi_2}{{}^3\xi_3} \right)} \right] \left[\chi_{23} + x_2 \chi_{22} + x_3 \chi''_{12} \right] \\ &+ \left[\frac{x_3 x_1 \left(\frac{{}^3\xi_3}{{}^3\xi_1} \right)}{x_3 + x_1 \left(\frac{{}^3\xi_3}{{}^3\xi_1} \right)} \right] \left[\chi_{13} + x_3 \chi_{33} + x_1 \chi'''_{12} \right] \end{aligned} \quad (13)$$

For the present mixtures, we assumed that $\chi_{12} \cong \chi'_{12} = \chi_{12}^*$; $\chi_{23} \cong \chi''_{12} = \chi_{23}^*$; $\chi_{13} \cong \chi'''_{12} = \chi_{13}^*$; $\chi_{11} \cong \chi_{22} \cong \chi_{33} = \chi^*$, equation (13) was then reduced to

$$\begin{aligned} (C_p^E)_{123} &= \left[\frac{x_1 x_2 \left(\frac{{}^3\xi_1}{{}^3\xi_2} \right)}{x_1 + x_2 \left(\frac{{}^3\xi_1}{{}^3\xi_2} \right)} \right] \left[(1+x_2) \chi_{12}^* + x_1 \chi^* \right] + \left[\frac{x_2 x_3 \left(\frac{{}^3\xi_2}{{}^3\xi_3} \right)}{x_2 + x_3 \left(\frac{{}^3\xi_2}{{}^3\xi_3} \right)} \right] \left[(1+x_3) \chi_{23}^* + x_2 \chi^* \right] \\ &+ \left[\frac{x_3 x_1 \left(\frac{{}^3\xi_3}{{}^3\xi_1} \right)}{x_3 + x_1 \left(\frac{{}^3\xi_3}{{}^3\xi_1} \right)} \right] \left[(1+x_1) \chi_{13}^* + x_3 \chi^* \right] \end{aligned} \quad (14)$$

Eq. (14) involves four unknown χ_{12}^* , χ_{23}^* , χ_{13}^* , χ^* parameters and were determined by utilizing $(C_p^E)_{123}$ data at four arbitrary compositions. Such parameters were then subsequently employed to $(C_p^E)_{123}$ data at other values of x_1 and x_2 .

The $(C_p^E)_{123}$ values (calculated via Eq. 14) are listed in Table 4. The χ_{12}^* , χ_{23}^* , χ_{13}^* , χ^* parameters are reported in Table 9. Examination of data in Table 4 has indicated

that $(C_p^E)_{123}$ values determined by Graph theory agree well with experimental values.

Flory's Theory

Differentiating Flory's expression for excess molar enthalpies²⁹⁻³⁰ for binary and ternary mixtures with respect to the temperature, T , excess heat capacities for binary, C_p^E and ternary, $(C_p^E)_{123}$ mixtures were expressed by

$$C_p^E = - \sum_{i=1}^2 \frac{x_i P_i^* \tilde{v}_i^* \alpha_i}{\tilde{v}_i} + \left(\frac{\alpha}{\tilde{v}} \right) \left[\left(\sum_{i=1}^2 x_i P_i^* \tilde{v}_i^* \right) - x_1 \tilde{v}_1^* \theta_2 \chi_{12}^{**} \right] \quad (15)$$

$$(C_p^E)_{123} = - \sum_{i=1}^3 \frac{x_i P_i^* \tilde{v}_i^* \alpha_i}{\tilde{v}_i} + \left(\frac{\alpha}{\tilde{v}} \right) \left[\sum_{i=1}^3 x_i P_i^* \tilde{v}_i^* - \sum_{i=1}^3 x_i \tilde{v}_i^* \theta_j \chi_{ij}^{**} \right] \quad (16)$$

Where \tilde{v}_i^* , P_i^* , \tilde{v}_i ($i = 1$ or 2 or 3) are the characteristic volume, characteristic pressure, reduced volume of pure component (i) and \tilde{v} is the reduced volume of mixture. All the terms have the same significance as described elsewhere.²⁹⁻³⁰ The Flory parameters for pure liquids are

reported in Table 10. Flory assumed that interaction energy parameter, χ_{12}^{**} for binary mixtures (which in turn is determined by using excess molar enthalpies, H^E data of binary mixtures at equimolar composition) of (1 + 2 + 3) ternary mixtures are independent of temperature by

Flory. However, Benson and D'Arcy³¹ suggested that χ_{12}^{**} for (1 + 2) mixtures should be a function of

temperature. The C_p^E and $(C_p^E)_{123}$ values for binary and ternary mixtures were then can be expressed by

$$C_p^E = -\sum_{i=1}^2 \frac{x_i P_i^* \tilde{v}_i^* \alpha_i}{\tilde{v}_i} + \left(\frac{\alpha}{\tilde{v}}\right) \left[\left(\sum_{i=1}^2 x_i P_i^* \tilde{v}_i^*\right) - x_1 v_1^* \theta_2 \chi_{12}^{**} \right] + \frac{x_1 v_1^* \theta_2}{\tilde{v}} \left(\frac{\partial \chi_{12}^{**}}{\partial T} \right) \quad (17)$$

$$(C_p^E)_{123} = -\sum_{i=1}^3 \frac{x_i P_i^* \tilde{v}_i^* \alpha_i}{\tilde{v}_i} + \left(\frac{\alpha}{\tilde{v}}\right) \left[\sum_{i=1}^3 x_i P_i^* \tilde{v}_i^* - \sum_{i=1}^3 x_i v_i^* \theta_j \chi_{ij}^{**} \right] + \sum_{i=1}^3 \frac{x_i v_i^* \theta_j}{\tilde{v}} \left(\frac{\partial \chi_{ij}^{**}}{\partial T} \right) \quad (18)$$

The reduced volumes, \tilde{v} and thermal coefficient, α of binary and ternary mixtures were calculated using

$$\tilde{v} = \left(V^E + \sum_{i=1}^2 x_i v_i \right) / \sum_{i=1}^2 x_i v_i^* \quad (19)$$

$$\tilde{v} = \left(V_{123}^E + \sum_{i=1}^3 x_i v_i \right) / \sum_{i=1}^3 x_i v_i^* \quad (20)$$

$$\alpha = \sum_{i=1}^2 x_i \alpha_i \quad (21)$$

$$\alpha = \sum_{i=1}^3 x_i \alpha_i \quad (22)$$

where V^E , V_{123}^E represent excess molar volumes of binaries (1 + 2), (2 + 3), (1 + 3) and ternary (1 + 2 + 3) mixtures and were taken from literature.⁶ The C_p^E and $(C_p^E)_{123}$ values determined via Eqs. (17-18) are reported in Tables 7 and 4 respectively, where they were compared with their corresponding experimental values. The values of χ_{12}^{**} etc. parameters for the various (1 + 2), (2 + 3), (1 + 3) mixture are listed in Table 9. A perusal of data in Tables 7 and 4 suggest that C_p^E and $(C_p^E)_{123}$ values predicted by Flory's theory are of same sign.

CONCLUSION

The heat capacities of binary NMP (1) + 2-Py (2); and ternary NMP (1) + 2-Py (2) + *o*- or *m*- or *p*-chlorotoluene (3) mixtures have been utilized to determine their excess heat capacities at 293.15, 298.15, 303.15 K. The excess heat capacities, C_p^E and $(C_p^E)_{123}$ of the present mixtures have been correlated with Redlich-Kister equation to obtain binary as well as ternary adjustable parameters along with standard deviations. The C_p^E and $(C_p^E)_{123}$ of the present binary and ternary mixtures are positive over entire mole fraction. The analysis of C_p^E

and $(C_p^E)_{123}$ data in terms of Graph and Flory's theories indicate that C_p^E and $(C_p^E)_{123}$ values calculated by Graph theory compare well with their experimental values. The knowledge of thermodynamic properties like excess molar volumes, V^E , excess isentropic compressibilities, κ_S^E , excess molar enthalpies, H^E and excess heat capacities, C_p^E of liquid mixtures is of practical interest to the industry in very different fields ranging from the chemical industry to petro, pharmaceutical and food technology industries, as these properties relate to temperature and pressure dependencies of used liquid mixtures e.g. in petro-chemical and automotive industries, an important point of interest is the influence of bi-components additives such as alcohols or ethers or esters on the properties of fuel and grease, thereby, increasing interest in mixtures of hydrocarbons with alcohols or ethers or esters.

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CONFLICT OF INTEREST

Conflict of interest declared none.

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