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

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ABSTRACT

Excess heat capacities, $\left(C_{\mathrm{P}}^{\mathrm{E}}\right)_{123}$ of 1-methylpyrrolidin-2-one (1) + pyrrolidin-2-one (2) + *o*- or *m*- or *p*-chlorotoluene (3) ternary and $C_{\mathrm{P}}^{\mathrm{E}}$ 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 $C_{\mathrm{P}}^{\mathrm{E}}$ and $\left(C_{\mathrm{P}}^{\mathrm{E}}\right)_{123}$ 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,*** $C_{\mathrm{P}}^{\mathrm{E}}$ ***; 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 (CO_2 treatment process especially to the part that involves heat transfer[1]) 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 ± 0.5 $kg{\cdot}m^{-3}$ and 0.1 $m{\cdot}s^{-1}$ respectively. Further, uncertainty in the temperature measurement (DSA-5000) is ± 0.01 K. The molar heat capacities of the studied pure liquids and their mixtures were measured by high sensitivity differential scanning calorimeter Micro DSC (Model – µDSC 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 Jg^{-1}) comparable to 148.7 Jg^{-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 $\pm 10^{-5}$ g. The uncertainity in mole fraction is 1×10^{-4}. The uncertainity in measuring heat capacity is ± 0.3 %. The uncertainty in the temperature measurement (DSC) is ± 0.02 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 values[14-18] 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 equations[19] 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 $(C_P^E)_{123}^{(n)}(n=0-2)$ 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

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

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

{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).

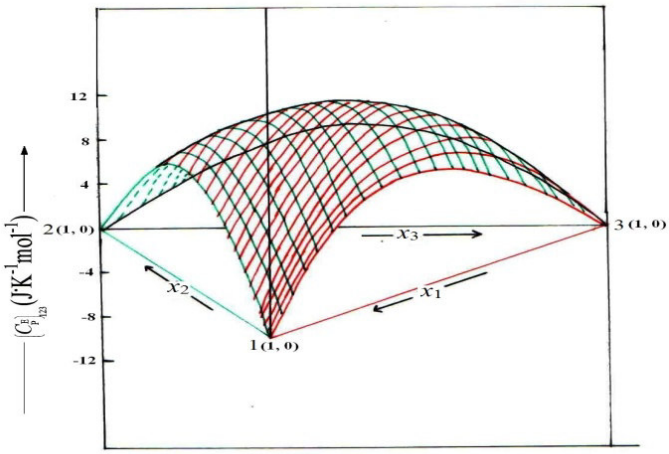

Figure 1

Excess heat capacities, $(C_P^E)_{123}$ for 1-methyl pyrrolin-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

[a]*GC = 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	ρ / kg·m^{-3}		u / m·s^{-1}		C_P / J·K^{-1}·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	-
m-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] 1069.4[18]	1306.55	-	175.66	-
p- 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/ K = (293.15, 298.15, 303.15) and Pressure p = 0.1 MPa

x_1	C_P / J·K^{-1}mol^{-1}	C_P^E / J·K^{-1} mol^{-1}	x_1	C_P / J·K^{-1} mol^{-1}	C_P^E / J·K^{-1} mol^{-1}
1-methyl pyrrolidin-2-one (1) + pyrrolidin-2-one (2)					
***T* / 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 / K = 298.15K					
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 / 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 ± 0.01 K;

Table 4

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

x_1	x_2	$\left(C_P^E\right)_{123}$	$\left(C_P^E\right)_{123}$ /J·K^{-1} mol^{-1}		
		/J·K^{-1} mol^{-1}	**Exptl.**	**Graph**	**Flory**
1-methyl pyrrolidin-2-one (1) + pyrrolidin-2-one (2) + *o*-Chlorotoluene (3)					
T / 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) + *m*-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) + *p*-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, σ($C_{\mathrm{P}}^{\mathrm{E}}$) 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
σ (C_P^E)/J·K^{-1} mol^{-1}	0.00	0.00	0.00

Table 6

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

Parameters	T/K		
	293.15	298.15	303.15
1-methyl pyrrolidin-2-one (1) + pyrrolidin-2-one (2) + *o*-chlorotoluene (3)			
$\left(C_P^E\right)_{123}^{(0)}$	123.65	165.45	204.87
$\left(C_P^E\right)_{123}^{(1)}$	127.76	147.34	185.65
$\left(C_P^E\right)_{123}^{(2)}$	-16767.40	-18857.20	-21083.22
$\sigma\left(C_P^E\right)_{123}$ /(J·K^{-1} mol^{-1})	0.03	0.04	0.05
1-methyl pyrrolidin-2-one (1) + pyrrolidin-2-one (2) + *m*-Chlorotoluene (3)			
$\left(C_P^E\right)_{123}^{(0)}$	98.34	99.22	91.06
$\left(C_P^E\right)_{123}^{(1)}$	1145.37	1178.90	1283.56
$\left(C_P^E\right)_{123}^{(2)}$	-8553.92	-8756.26	-9538.09
$\sigma\left(C_P^E\right)_{123}$ /(J K^{-1} mol^{-1})	0.04	0.04	0.05
1-methyl pyrrolidin-2-one (1) + pyrrolidin-2-one (2) + *p*-chlorotoluene (3)			
$\left(C_P^E\right)_{123}^{(0)}$	92.35	111.25	164.34
$\left(C_P^E\right)_{123}^{(1)}$	733.97	871.02	1092.01
$\left(C_P^E\right)_{123}^{(2)}$	-777.41	-414.22	90.08
$\sigma\left(C_P^E\right)_{123}$ /(J·K^{-1} 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 / J·K^{-1} 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 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 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 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 $\chi_{12}^{//}$ 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
$\chi_{12}^{//}$ / J·K^{-1} mol^{-1}	0.73	0.85	0.91
χ^* / J·K^{-1} mol^{-1}	0.72	0.73	0.82
$\sigma\left(C_P^E\right)_{Graph}$	0.03	0.04	0.03
χ_{12}^{**} / J·K^{-1} mol^{-1}	-1.32	-1.29	-1.32
$\sigma\left(C_P^E\right)_{Flory}$	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 $\left(C_P^E\right)_{123}$ at *T*/ K = 293.15, 298.15, 303.15 . Also included are the deviations, $\sigma\left(C_P^E\right)_{123Graph}$ and $\sigma\left(C_P^E\right)_{123Flory}$ between experimental values of $\left(C_P^E\right)_{123}$ and values obtained from Graph and Flory theories.

	T/K		
Parameters	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
χ_{12}^* / J·K^{-1} mol^{-1}	-48.35	80.53	94.59
χ_{23}^* / J·K^{-1} mol^{-1}	-128.21	81.05	84.03
χ_{13}^* / J·K^{-1} mol^{-1}	-62.35	37.29	39.56
χ^* / J·K^{-1} mol^{-1}	257.82	-156.45	-167.61
$\sigma\left(C_P^E\right)_{123Graph}$	0.44	0.50	0.29
χ_{12}^{**} / J·K^{-1} mol^{-1}	-1.32	-1.29	-1.32
χ_{23}^{**} / J·K^{-1} mol^{-1}	-0.20	-0.19	-0.18
χ_{13}^{**} / J·K^{-1} mol^{-1}	3.87	3.79	3.77
$\sigma\left(C_P^E\right)_{123Flory}$	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
χ_{12}^{*} / J·K^{-1} mol^{-1}	3.92	2.97	0.60
χ_{23}^{*} / J·K^{-1} mol^{-1}	-0.87	-3.50	-7.84
χ_{13}^{*} / J·K^{-1} mol^{-1}	58.53	57.35	56.14
χ^{*} / J·K^{-1} mol^{-1}	-21.47	-12.06	1.43
$\sigma\left(C_{\mathrm{P}}^{\mathrm{E}}\right)_{123\mathrm{Graph}}$	0.28	0.23	0.29
χ_{12}^{**} / J·K^{-1} mol^{-1}	-1.32	-1.29	-1.32
χ_{23}^{**} / J·K^{-1} mol^{-1}	-0.48	-0.46	-0.45
χ_{13}^{**} / J·K^{-1} mol^{-1}	6.67	6.54	6.51
$\sigma\left(C_{\mathrm{P}}^{\mathrm{E}}\right)_{123\mathrm{Flory}}$	9.75	9.25	10.34
1-methyl pyrrolidin-2-one (1) + pyrrolidin-2-one (2) + *p*-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
χ_{12}^{*} / J·K^{-1} mol^{-1}	19.59	31.88	48.34
χ_{23}^{*} / J·K^{-1} mol^{-1}	8.31	16.40	21.69
χ_{13}^{*} / J·K^{-1} mol^{-1}	34.10	36.42	40.18
χ^{*} / J·K^{-1} mol^{-1}	-18.01	-40.84	-66.16
$\sigma\left(C_{\mathrm{P}}^{\mathrm{E}}\right)_{123\mathrm{Graph}}$	0.18	0.24	0.24
χ_{12}^{**} / J·K^{-1} mol^{-1}	-1.32	-1.29	-1.32
χ_{23}^{**} / J·K^{-1} mol^{-1}	0.00	0.00	0.02
χ_{13}^{**} / J·K^{-1} mol^{-1}	3.43	3.36	3.34
$\sigma\left(C_{\mathrm{P}}^{\mathrm{E}}\right)_{123\mathrm{Flory}}$	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, ṽ used in Flory theory calculations at T/ K = (293.15, 298.15, 303.15)

Components	*T*/ K	*V** /cm^3·mol^{-1}	*P** /J·cm^{-3}	*α*(×10^{-3}) /K^{-1}	*V* /cm^3·mol^{-1}	*ṽ* /cm^3·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
o-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
m-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
p-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 $\left(C_{\mathrm{P}}^{\mathrm{E}}\right)_{123}$ data of the studied ternary mixtures were not available in the literature. The $\left(C_{\mathrm{P}}^{\mathrm{E}}\right)_{123}$ values of NMP (1) + 2-Py (2) + *o*- or *m*- or *p*-chlorotoluene (3) mixtures are positive over entire mole fractions range. The positive $\left(C_{\mathrm{P}}^{\mathrm{E}}\right)_{123}$ 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 $\left(C_{\mathrm{P}}^{\mathrm{E}}\right)_{123}$ 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 $(\partial C_{\mathrm{P}}^{\mathrm{E}} / \partial T)$ and $(\partial (C_{\mathrm{P}}^{\mathrm{E}})_{123} / \partial T)$ 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, $\kappa_{\mathrm{S}}^{\mathrm{E}}$ 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 entities[6]. 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 $\chi_{12}, \chi_{11}, \chi_{22}$ and $\chi_{12}^{/}$ are molar interactions 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, $C_{\mathrm{P}}^{\mathrm{E}}$ due to processes (i) – (iii) was given[21-26] by

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

Where ${}^3\xi_i$ (i = 1 or 2) is the connectivity parameter of third degree, ${}^3\xi$ of a molecule defined[27] 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

$$C_{\mathrm{P}}^{\mathrm{E}} = \left[\frac{x_1 x_2 \left({}^3\xi_1 / {}^3\xi_2\right)}{x_1 + x_2 \left({}^3\xi_1 / {}^3\xi_2\right)}\right]\left[(1+x_2)\chi_{12}^{//} + 2x_1\chi^*\right] \quad (9)$$

Two parameters $\chi_{12}^{//}$ and χ^* were determined by using $C_{\mathrm{P}}^{\mathrm{E}}$ data at two compositions and were then used to evaluate $C_{\mathrm{P}}^{\mathrm{E}}$ values of mixture at various mole fractions. The predicted $C_{\mathrm{P}}^{\mathrm{E}}$ values and $\chi_{12}^{//}$, χ^* parameters for (1 + 2) mixture are reported in Tables 7-8 respectively. Examination of data in Table 7 suggests that $C_{\mathrm{P}}^{\mathrm{E}}$ 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}; $\chi_{11}, \chi_{22}, \chi_{33}, \chi_{12}^{/}, \chi_{12}^{//}$ and $\chi_{12}^{///}$ 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 given[21-26] by

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

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

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

Then total change in ΔC_P

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

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

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

Eq. (14) involves four unknown $\chi_{12}^{*}, \chi_{23}^{*}, \chi_{13}^{*}, \chi^{*}$ parameters and were determined by utilizing $\left(C_P^E\right)_{123}$ data at four arbitrary compositions. Such parameters were then subsequently employed to $\left(C_P^E\right)_{123}$ data at other values of x_1 and x_2. The $\left(C_P^E\right)_{123}$ values (calculated via Eq. 14) are listed in Table 4. The $\chi_{12}^{*}, \chi_{23}^{*}, \chi_{13}^{*}, \chi^{*}$ parameters are reported in Table 9. Examination of data in Table 4 has indicated that $\left(C_P^E\right)_{123}$ values determined by Graph theory agree well with experimental values.

Flory's Theory

Differentiating Flory's expression for excess molar enthalpies[29-30] for binary and ternary mixtures with respect to the temperature, *T*, excess heat capacities for binary, C_P^E and ternary, $\left(C_P^E\right)_{123}$ mixtures were expressed by

$$C_p^E = -\sum_{i=1}^{2}\frac{x_i P_i^{*}\tilde{v}_i^{*}\alpha_i}{\tilde{v}_i} + \left(\frac{\alpha}{\tilde{v}}\right)\left[\left(\sum_{i=1}^{2}x_i P_i^{*}v_i^{*}\right) - x_1 v_1^{*}\theta_2\chi_{12}^{**}\right] \quad (15)$$

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

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' Arcy[31] suggested that χ_{12}^{**} for (1 + 2) mixtures should be a function of temperature. The C_P^E and $\left(C_P^E\right)_{123}$ values for binary and ternary mixtures were then can be expressed by

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

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

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

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

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

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

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

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 $\left(C_P^E\right)_{123}$ 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 $\left(C_P^E\right)_{123}$ 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 $\left(C_P^E\right)_{123}$ 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 $\left(C_P^E\right)_{123}$ of the present binary and ternary mixtures are positive over entire mole fraction. The analysis of C_P^E and $\left(C_P^E\right)_{123}$ data in terms of Graph and Flory's theories indicate that C_P^E and $\left(C_P^E\right)_{123}$ 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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