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Topological studies of molecular interactions in binary and ternary liquid mixtures containing lactams and isomeric chlorotoluenes

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ABSTRACT

The densities, ρ, speeds of sound, u of 1-methylpyrrolidin-2-one (i) + pyrrolidin-2-one (j); 1-methylpyrrolidin-2-one or pyrrolidin-2-one (i) + *o*- or *m*- or *p*-chlorotoluene (j) binary and ρijk, $uijk$ data of 1-methylpyrrolidin-2-one (i) + pyrrolidin-2-one (j) + *o*- or *m*- or *p*-chlorotoluene (k) ternary mixtures have measured as a composition at 293.15, 298.15, 303.15, 308.15 K at atmospheric pressure. From the experimental densities and speeds of sound data excess molar volumes, V^E or $(V^E)ijk$, excess isentropic compressibilities, κ_S^E or $(\kappa_S^E)_{ijk}$ of binary and ternary mixtures respectively have been computed. Excess properties of the various binary and ternary mixtures have been related to Redlich–Kister equation and the binary and ternary parameters along with corresponding deviations are calculated. The results have also been analyzed in terms of Graph theory. It has been observed that V^E or $(V^E)ijk$; κ_S^E or $(\kappa_S^E)_{ijk}$ values predicted by Graph theory compare well with their experimental values. The IR studies also lend support to the proposed molecular entities and interactions in mixtures.

1. Introduction

Thermodynamic properties of liquid mixtures are extensively utilized in chemical engineering, design process, simulation, mass flow, fluid flow [1,2] along with testing of thermodynamic models [3–6]. Lactams are interesting compounds as they possesses a group which is the structural part of peptides, polypeptides, proteins and so, are vital for biological systems [7]. They are used in chemical industries as strong solubilizing agent [8], in purification and crystallization of drugs [9], and in petroleum industry to increase the selectivity and solvent power for extracting aromatic hydrocarbon [10]. These cyclic amides have excellent thermal and chemical stability and are used as absorbents of sour gases from crude natural gas. In these applications, mixtures of lactams with organic liquids can be preferred, if the mixed solvent functions effectively [11]. Chlorotoluenes are used as precursors in the pesticides, pharmaceutical and dye industries [12]. Knowledge of thermodynamic properties of lactams with isomeric chlorotoluenes mixtures can be useful in establishing efficient and economic conditions for various processes in chemical industries along with testing of thermodynamic models of solutions. A literature survey revealed that excess molar volumes and excess molar isentropic compressibilities that of 1-methylpyrrolidin-2-one (i) + pyrrolidin-2-one (j); 1-methylpyrrolidin-2-one or pyrrolidin-2-one (i) + o- or m- or p-chlorotoluene (j) binary and 1-methylpyrrolidin-2-one (i) + pyrrolidin-2-one (j) + o- or m- or p-chlorotoluene (k) ternary mixtures have not been reported in literature. These considerations prompted us to measure excess molar volume and excess molar isentropic compressibilities data of 1-methylpyrrolidin-2-one (i) + pyrrolidin-2-one (j), 1-methylpyrrolidin-2-one or pyrrolidin-2-one (i) + o- or m- or p-chlorotoluene (j) binary and excess molar volume, V_{ijk}^E, excess molar isentropic compressibilities, $(\kappa_S^E)_{ijk}$ data of 1-methylpyrrolidin-2-one (i) + pyrrolidin-2-one (j) + o- or m- or p-chlorotoluene (k) ternary mixtures.

2. Experimental

1-methylpyrrolidin-2-one (NMP) (Fluka 0.99 GC), pyrrolidin-2-one (2-Py) (Fluka 0.99 GC), *o*-chlorotoluene (Fluka, 0.98 GC), *m*-chlorotoluene (Fluka, 0.98 GC) and *p*-chlorotoluene (Fluka, 0.99 GC) were purified by standard methods [13–15]. The source of liquids, their purification methods and purities are recorded in Table 1. The density and speed of sound values for the purified liquids at 293.15, 298.15, 303.15 and 308.15 K are reported in Table 2 and are also compared with literature values [16–20].

Densities, ρ and speeds of sound, u values of the pure liquids and their binary as well as ternary mixtures were measured using a commercial density and sound analyzer apparatus (Anton Paar DSA 5000) in the manner as described elsewhere [21,22]. The uncertainties in the density and speed of sound measurements are 2×10^{-3} kg m^{-3} and 0.1 m·s^{-1} respectively. The uncertainty in V^E values calculated from density results is 0.1%. Further, uncertainty in the temperature measurement is ±0.01 K.

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Table 1
Details of studied chemicals, CAS number, source, water content, purification method, initial & final purity and analysis method.

Chemical name	CAS number	Source	Purification method	Initial purity	Final purity	Water content	Analysis method
1-Methylpyrrolidin-2-one	872-50-4	Fluka	Vacuum distillation	0.98	0.99	Nil	GC[a]
Pyrrolidin-2-one	616-45-5	Fluka	Vacuum distillation	0.98	0.99	Nil	GC
o-Chlorotoluene	95-49-8	Fluka	Fractional distillation	0.97	0.98	Nil	GC
m-Chlorotoluene	108-41-8	Fluka	Fractional distillation	0.97	0.98	Nil	GC
p-Chlorotoluene	106-43-4	Fluka	Fractional distillation	0.98	0.99	Nil	GC

[a] GC = Gas chromatography.

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

3. Data processing and results

The experimental densities, ρ or ρijk; speeds of sound, u or $uijk$ of binary NMP (i) + 2-Py (2), NMP or 2-Py (i) + *o*- or *m*- or *p*-chlorotoluene (j) and ternary NMP (i) + 2-Py (j) + *o*- or *m*- or *p*-chlorotoluene (k) mixtures respectively at 293.15, 298.15, 303.15 and 308.15 K (reported in Tables 3–4) were utilized to determine their excess molar volumes, V^E, V^E_{ijk} and isentropic compressibilities, κ_S, $(\kappa_S)_{ijk}$ using

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

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

$$(\kappa_S) = \left(\rho u^2\right)^{-1} \tag{3}$$

$$(\kappa_S)_{ijk} = \left(\rho_{ijk} u^2_{ijk}\right)^{-1} \tag{4}$$

where x_i, M_i and ρ_i are the mole fraction, molar mass and density of component (i) and ρ,ρ_{ijk}, u, u_{ijk} are the densities and speeds of sound of binary and ternary mixtures respectively. In evaluating κ_S values, the speed of sound has been considered as a thermodynamic property, provided that a negligible amount of ultrasonic absorption of the acoustic waves of low frequency and of low amplitude is observed [23].

Excess isentropic compressibilities, κ^E_S and $(\kappa^E_S)_{ijk}$ for the binary as well as ternary mixtures were calculated using relation:

$$\kappa^E_S = \kappa_S - \kappa^{id}_S \tag{5}$$

κ^{id}_S values for binary and ternary mixtures were obtained using Benson and Kiyohara [24]

$$\kappa^{id}_S = \sum_{i=i}^{jork} \phi_i \left[\kappa_{S,i} + \frac{T v_i \alpha_i^2}{C_{p,i}}\right] - T\left(\sum_{i=i}^{jork} x_i v_i\right) \frac{\left(\sum_{i=i}^{jork} \phi_i \alpha_i\right)^2}{\left(\sum_{i=i}^{jork} x_i C_{p,i}\right)} \tag{6}$$

where ϕ_i, $\kappa_{S,i}$, v_i, α_i and $C_{p,i}$ (i = i or j or k) are the volume fraction, isentropic compressibility, molar volume, thermal expansion coefficient and molar heat capacity of pure component (i). The α values for NMP, 2-Py, *o*- or *m*- or *p*-chlorotoluene were calculated using experimental density data in the manner described elsewhere [25] and are listed in Table 2. The C_p values for NMP, 2-Py, *o*- or *m*- or *p*-chlorotoluene were taken from literature [26]. The V^E, κ^E_S (plotted in Figs. 1–2) and V^E_{ijk} $(\kappa^E_S)_{ijk}$ values for the studied mixtures are recorded in Tables 3–4.

Table 2
Comparison of densities, ρ, speeds of sound, u, coefficient of thermal expansion, α, of pure liquids with their literature values at temperature 293.15, 298.15, 303.15 and 308.15 K.

Liquid	T/K	ρ (kg m^{-3})		u (m s^{-1})		$\alpha \times 10^3$ (K^{-1})
		Expt	Lit.	Expt	Lit.	Expt
1-Methylpyrrolidin-2-one	293.15	1033.28	1033.23[16]	1565.59	1565.52[16]	0.951
	298.15	1028.26	1028.23[16]	1546.09	1546.02[16]	0.950
	303.15	1023.49	1023.46[16]	1527.31	1527.24[16]	0.934
	308.15	1018.69	1018.66[16]	1507.49	1507.38[16]	0.942
	293.15	1111.28	1111.28[16]	1651.44	1650.13[16]	0.743
Pyrrolidin-2-one	298.15	1107.15	1107.15[16]	1635.02	1633.92[16]	0.746
	303.15	1103.06	1103.02[16]	1618.70	1617.14[16]	0.748
	308.15	1098.96	1098.90[16]	1602.44	1601.87[16]	0.749
	293.15	1082.22	–	1316.77	–	0.901
o-Chlorotoluene	298.15	1077.34	1076.40[17]	1298.70	1299.06[18]	0.905
	303.15	1072.46	–	1280.66	–	0.911
	308.15	1067.57	–	1262.68	–	0.915
	293.15	1072.12	–	1313.63	–	0.913
m-Chlorotoluene	298.15	1067.23	1067.29[18]	1295.46	1298[18]	0.917
	303.15	1062.33	1062.81[18]	1277.31	1280[18]	0.923
	308.15	1057.43	–	1259.22	–	0.927
	293.15	1069.27	1069.1 [19] 1069.4 [20]	1306.55	–	0.918
p-Chlorotoluene	298.15	1064.37	–	1288.37	1289[18]	0.922
	303.15	1059.46	–	1270.29	1271[18]	0.928
	308.15	1054.54	–	1252.47	–	0.932