Topological investigations of excess heat capacities of binary liquid mixtures containing lactams and cycloalkanone

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ABSTRACT

The excess heat capacities, C_P^E, of binary 1-Methylpyrrolidin-2-one or pyrrolidin-2-one (i) + cyclopentanone or cyclohexanone or cycloheptanone or cyclohexane (j) mixtures were obtained over the entire mole fraction range using micro-differential scanning calorimeter (Model − μDSC 7 Evo) in the temperature range from 293.15 to 308.15 K at atmospheric pressure. The observed data have been fitted to Redlich–Kister equation to calculate adjustable parameters and standard deviations. The Moelwyn–Huggins concept of interactions between the components of mixture has been utilized using the topology of the constituent molecules (Graph theory) to determine excess heat capacities, C_P^E of the studied mixtures. The results obtained indicate that C_P^E values calculated by Graph theory are in agreement with experimental values.

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1. Introduction

Thermodynamic properties of liquids are often utilized to solve chemical engineering problems related to heat transfer, mass transfer and heat flow [1]. Heat capacities of liquids or their mixtures are directly linked with temperature derivatives of basic thermodynamic functions and are, therefore, utilized for the determination of difference in these functions at different temperatures. Such study is used in chemical engineering for establishing energy balances [2]. The excess heat capacity is an important thermodynamic property to obtain information about structural change in liquid mixtures, in the design and optimization of industrial processes [3–5] along with development/ testing of theories/models. The variation in heat capacities or excess heat capacities of liquid or liquid mixtures serves as a sensitive indicator for phase transitions [2]. Cyclic amides are of a great interest because a ring composed of methyl group links the nitrogen and carbon atoms of peptide bond. These compounds have generated special interest because the amide group is the structural part of the peptides, polypeptides and proteins. 1-Methyl-2-pyrrolidinone is an aprotic and dipolar solvent of high selectivity [6]. The structure of these compounds is related to many structural problems in molecular biology [7]. Cyclic ketones like cyclopentanone, cyclohexanone, and cycloheptanone are miscible with organic solvents and serve as a good solvent for paints, cellulose ethers, etc. [8]. The C_P^E data of mixtures with 1-methyl-2-pyrrolidinone or 2-pyrrolidinone and cycloalkanone or cyclohexane

molecules may be helpful in the environment of interior of proteins and applied research points of view in addition to industries or organic synthesis [6]. In recent studies Graph theory (which in turn deals with topology of a molecule) has been utilized to predict excess molar volume, V^E, excess molar enthalpies, H^E, excess Gibbs free energy, G^E, and excess isentropic compressibilities, κ_S^E, of binary as well as ternary mixtures [9–13]. An attempt has been made to employ Moelwyn–Huggins concept of interactions between the components of mixture to determine excess heat capacities of the investigated liquid mixtures by employing the topology of the constituent molecules in mixtures [14].

2. Experimantal

1-Methylpyrrolidin-2-one (NMP) (Fluka 0.99 GC), pyrrolidin-2-one (2-Py) (Fluka, 0.99 GC), cyclopentanone (Fluka, 0.99 GC), cyclohexanone (Fluka, 0.99 GC), cycloheptanone (Fluka, 0.95 GC), and cyclohexane (A R Grade, 0.98 GC) were purified by standard methods [15–18]. The vibrating tube densimeter and sound analyzer manufactured by Anton Paar, model DSA 5000 with a built in thermostat was used for the measurement of densities, ρ, and speeds of sound, u, of the pure liquids. The detail regarding the experimental methodology is described elsewhere [19,20]. The densities and speed of sound of the purified liquids at 298.15 ± 0.01 K are reported in Table 1 and also compared well with their literature values [21–28]. The uncertainties in the density and speed of sound measurements are 0.5 kg m^{-3} and 0.1 m s^{-1} respectively.

The 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 [29]. The

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Table 1
Comparison of densities, ρ, speeds of sound, u, and heat capacities, C_P^E, of pure liquids with their literature values at T/K = 298.15.

Liquids	T/K	ρ/kg m^{-3}		u/m s^{-1}		C_P/(J K^{-1} mol^{-1})	
		(Expt.)	(Lit.)	(Expt.)	(Lit.)	(Expt.)	(Lit.)
1-Methylpyrrolidin-2-one	298.15	1028.23	1028.23[21]	1546.15	1546.02[21]	166.35	166.22[30]
Pyrrolidin-2-one	298.15	1107.20	1107.2[21]	1634.13	1633.92[21]	169.99	169.55[30]
Cyclo-pentanone	298.15	944.515	944.350[22]	1393.21	1394.1[24]	154.69	154.5[17]
			945.300[23]				
Cyclohexanone	298.15	942.904	–	1414.75	1408.0[24]	178.37	177.97[31]
					1417.0[25]		
Cycloheptanone	298.15	947.633	–	1455.02	–	202.08	–
Cyclohexane	298.15	773.91	773.85[26]	1254.7	1254.4[28]	157.23	156.01[26]
			773.89[17]		1255.0[27]		
			773.94[27]				

calibration of equipment was done by Joule effect method which in turn is controlled by SETARAM software and checked by measuring heat capacity of naphthalene (147.78 J g^{-1}). For a scanning sequence initial and final temperatures were supplied along with heating rate of 0.4 K·min^{-1}. The uncertainty in measuring heat capacity is ±0.3%. The heat capacities of the pure liquids are recorded in Table 1 and also compared with literature values [17,26,30,31].

3. Results

The excess heat capacities, C_P^E, data of the investigated mixtures were determined from the following relation

$$C_P^E = C_P - \sum_{i=i}^{j} x_i (C_P)_i \qquad (1)$$

where C_P, $(C_P)_i$, ($i = i$ or j), and x_i ($i = i$ or j) denote heat capacity of the mixture, heat capacity of pure components and mole fraction of components respectively. The observed excess heat capacities, C_P^E, for NMP or 2-Py (i) + cyclopentanone or cyclohexanone or cycloheptanone or cyclohexane (j) at 293.15, 298.15, 303.15 and 308.15 K are reported in Table 2 and are graphically represented in Figs. 1–4. The results for each mixture were fitted with Redlich–Kister equation [32]

$$C_P^E = x_i(1-x_i)\left[C_P^{(0)} + C_P^{(1)}(2x_i-1) + C_P^{(2)}(2x_i-1)^2\right] \qquad (2)$$

by the least-squares optimization. Values of adjustable parameters, $C_P^{(n)}$ (n = 0–2) and the standard deviations, $\sigma(C_P^E)$ defined by

$$\sigma\left(C_P^E\right) = \left[\sum \left(C_{P(\text{exptl.})}^E - C_{P(\text{calc.Eq.2})}^E\right)^2 / (m-n)\right]^{0.5} \qquad (3)$$

where m is the number of data points and n is the number of adjustable parameters in Eq. (2) that are reported in Table 3.

4. Discussion

We are unaware of any C_P^E data of the presented mixtures with which measured results can be compared. Measured heat capacities of pure liquids are in agreement with their literature values [17,26,30,31]. The C_P^E values of NMP or 2-Py (i) + cyclopentanone or cyclohexanone or cycloheptanone (j); 2-Py (i) + cyclohexane (j) mixtures are positive over the entire composition range. However, C_P^E data for NMP (i) + cyclohexane (j) mixture are negative over the entire mole fraction range. The C_P^E values at equimolar composition for NMP (i) + cyclopentanone or cyclohexanone or cycloheptanone (j) mixtures follow the order: cyclohexanone > cyclopentanone ≈ cycloheptanone.

The sign and magnitude of C_P^E values are cumulative effect of contributions due to molecular structure breakdown of associated entities and complexity among the constituent molecules. While the former leads negative later yields positive contribution to C_P^E. The positive C_P^E values for these mixtures imply that contribution due to complexity between NMP and cycloalkanone molecules far outweighs the contribution due to breakdown of associated entity (NMP) due to the addition of NMP to cycloalkanone or vice versa. The C_P^E values of NMP (i) + cyclohexanone (j) are more than that of NMP (i) + cyclopentanone (j) mixture. This may be due to the reason that cyclohexanone is more basic in character than cyclopentanone [33] and also possesses chair form with almost no strain. Thus cyclohexanone gives relatively more packed packing in NMP as compared to cyclopentanone. The strong interactions and more closed packing in cyclohexanone mixture as compared to cyclopentanone lead to increase in non-randomness and hence higher values of C_P^E. Further, C_P^E values of NMP (i) + cycloheptanone (j) mixture are lower than those of NMP (i) + cyclohexanone (j) mixture. It may be explained on the basis that cycloheptanone is more stable in twisted chair form, and due to strain π-electrons on >c=o group of cycloheptanone it interacts slowly with NMP as compared to cyclohexanone (π-electrons of >c=o group in non-twisted chair form).

The C_P^E data of 2-Py (i) + cyclopentanone or cyclohexanone or cycloheptanone (j) mixtures at equimolar composition vary as: cyclopentanone > cyclohexanone > cycloheptanone. The C_P^E data for these mixtures suggest that the addition of cycloheptanone to 2-Py breaks down the associated molecular entity (2-Py) and leads to more randomness in comparison to cyclopentanone or cyclohexanone.

5. Graph theory

5.1. Conceptual aspects of Graph theory and results

Structure activity relations are models that relate structural aspects of a molecule to its physico-chemical or biological properties. The problem in the development of relation can be attributed to the non-qualitative nature of structure of compound. Since the structure of compound depends on the connectivity of its constituent atoms, the topological ideas can reveal structural information of a molecule [34–37]. Randic et al. [38,39] have noted that while on one hand hundreds of topological indices are known, on the other hand, the interpretation of topological indices has received little attention. One of the current tendencies in physico-chemical and chemical investigations is the determination of physico-chemical and bio-logical properties of chemical compound and drugs from their structures [40–45]. Various topological indices have been utilized to obtain a correlation between the topological indices and physico-