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Thermodynamic properties of mixtures containing linear and cyclic ketones

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ABSTRACT

Densities, ρ, speeds of sound, u and excess heat capacities, C_P^E (293.15, 298.15, 303.15, 308.15 K) and excess molar enthalpies, H^E (298.15 K) for the binary acetone (i) + cyclopentanone or cyclohexanone or cycloheptanone (j) mixtures have been measured as a function of composition at atmospheric pressure. The measured ρ and u data have been employed to determine excess molar volumes, V^E and excess isentropic compressibilities, κ_S^E. The V^E, κ_S^E, H^E, and C_P^E data of the investigated mixtures have been fitted to Redlich–Kister equation to obtain binary parameters and standard deviations. The analysis of thermodynamic data in terms of Graph theory suggests that V^E, κ_S^E, H^E, and C_P^E values predicted by the Graph theory compare well with their experimental values.

1. Introduction

One of the problems in distillation is the selection of separating agent as it influences on operation bounds and control of rectification sequence. The general method of the selection of separating agent involves the examination of liquids or their mixtures with specific functional groups and their physical and thermodynamic properties. In order to assess the liquids or liquid mixtures as good solvent, as well as separating agent, their 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, are required to obtain information about the molecular interactions existing in them [1–4]. Acetone serves as solvent in different chemical industries, cleaning solvent of glass ware, and also used in mining industries for safely store and transport of the highly explosive and flammable acetylene [5]. Cyclic ketones are important intermediates in the synthesis of many organic compounds important for the chemical, pharmaceutical, and cosmetic industries [6–8]. They are also used as solvents in a number of engineering areas. Thus the knowledge of thermodynamic properties of acetone (i) + cyclic ketone (j) mixtures will have relevance in the engineering process as well as in the other industrial sectors. A survey of literature has revealed that data on thermodynamic properties like V^E, κ_S^E, H^E, and C_P^E of binary acetone (i) + cyclopentanone or cyclohexanone or cycloheptanone (j) mixtures are not available in the literature. These considerations prompted us to measure densities ρ, speed of sound, u, excess molar enthalpies, H^E, and excess heat capacities, C_P^E of acetone (i) + cyclopentanone or cyclohexanone or cycloheptanone (j) mixtures.

2. Experimental

Acetone (Fluka, mass fraction: 0.992), cyclopentanone (Fluka, mass fraction: 0.991), cyclohexanone (Fluka, mass fraction 0.988), and cycloheptanone (Fluka, mass fraction: 0.986), were purified by standard methods [9,10]. The source of liquids, their purification methods, and purities are recorded in Table 1. The densities, ρ and speeds of sound, u of the pure liquids and their mixtures were measured by using density and sound analyzer (Model DSA 5000) in the manner described elsewhere [11,12]. The equipment was calibrated with doubly distilled, degassed water at 293.15 K. For this purpose temperature of cell was set to 293.15 K in "temperature setting" which in turn is control by a built in peltier thermostat within equipment. The mole fraction of mixture (made by mixing two components in an air-tight glass bottle) was obtained from the measured apparent masses of the components using an electric balance. The

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Table 1
Details of studied chemicals, CAS number, source, purification method, purity, and analysis method.

Chemical name	CAS number	Source	Purification method	Purity	Analysis method
Acetone	67-64-1	Fluka	Fractional distillation	0.992	GC[a]
Cyclo-pentanone	120-92-3	Fluka	Fractional distillation	0.991	GC
Cyclo-hexanone	108-94-1	Fluka	Fractional distillation	0.988	GC
Cyclo-heptanone	502-42-1	Fluka	Fractional distillation	0.986	GC

[a] GC = Gas chromatography.

uncertainty in mole fraction is 1×10^{-4}. The densities, speeds of sound, and heat capacities of the purified liquids at 298.15 K are reported in Table 2 and also compared well with their literature values [7,9,13–20]. 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 value is 0.1% and the uncertainty in temperature measurement is ±0.01 K.

The excess molar enthalpies, H^E, heat capacities, C_P of pure liquids, and excess heat capacities, C_P^E of the investigated mixtures were measured by using a micro differential scanning calorimeter supplied by the M/S SETARAM instrumentation, France [Model-μ DSC 7 Evo] in the manner as described elsewhere [21,22]. The calibration of equipment was done by the Joule effect method which in turn is controlled by the SETARAM software and checked measuring heat capacity of naphthalene (147.6 J g^{-1}). The uncertainty in measuring, H^E and C_P^E values are 1% and 0.3% respectively.

The samples of binary mixtures for IR studies were prepared by mixing components in 1:1 (w/w) ratio and their IR spectra were recorded on a Perkin Elmer-Spectrum RX-1, FTIR spectrometer.

3. Results

The ρ, u, and C_P^E for acetone (i) + cyclopentanone or cyclohexanone or cycloheptanone (j) mixtures studied at 293.15, 298.15, 303.15, and 308.15 K over entire composition range are given in supplementary Tables S1–S2 and H^E for the same mixtures at 298.15 K are reported in supplementary Table S3. The observed ρ and u data were utilized to determine the excess molar volumes, V^E and the isentropic compressibilities, κ_S, and excess isentropic compressibilities, κ_S^E values by employing relations:

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

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

$$\kappa_S^E = \kappa_S - \kappa_S^{id} \quad (3)$$

where ρ and u are the density, speed of sound of mixture and x_i, M_i, and ρ_i are the mole fraction, molar mass, and density of component (i). Such V^E, κ_S, and κ_S^E values of the studied binary mixtures are reported in Table S1. The κ_S^{id} values were obtained in the manner suggested by Benson and Kiyohara [23]

$$\kappa_S^{id} = \sum_{i=i}^{j} \varphi_i \left[\kappa_{S,i} + \frac{T v_i \alpha_i^2}{C_{p,i}}\right] - T\left(\sum_{i=i}^{j} x_i v_i\right) \frac{\left(\sum_{i=i}^{j} \varphi_i \alpha_i\right)^2}{\left(\sum_{i=i}^{j} x_i C_{p,i}\right)} \quad (4)$$

where ϕ_i is the volume fraction of component (i) in the mixed state. $\kappa_{S,i}$, v_i, α_i, and $C_{p,i}$ are isentropic compressibility, molar volume, thermal expansion coefficient, and molar heat capacity respectively of the pure component (i). The α values were predicted by utilizing the density values at various temperatures in the manner as described elsewhere [24]. The graphical representations of the various thermodynamic properties for the investigated mixtures are provided in Figs. 1–4. For each mixture, the V^E, κ_S^E, C_P^E, and H^E data were fitted to Redlich–Kister equation [25]

$$\left(X^E\right)(X = V \text{ or } K_S \text{ or } H \text{ or } C_P) = x_i x_j \left[X^{(0)} + X^{(1)}(2x_i - 1) + X^{(2)}\left(2x_j - 1\right)^2\right]. \quad (5)$$

The $X^{(n)}$ (n = 0–2) are binary adjustable parameters. These parameters were determined by fitting (X^E) ($X = V$ or K_S or H or C_P) data to Eq. (5) by the least square methods and are reported in Table 3 along with the standard deviations $\sigma(X^E)$ ($X = V$ or K_S or H or C_P).

4. Discussion

The V^E, κ_S^E, H^E, and C_P^E data of acetone (i) + cyclopentanone or cyclohexanone or cycloheptanone (j) mixtures are not available in the literature for comparison with the measured results. The V^E and κ_S^E data for (i + j) mixtures are negative over entire mole fraction range and for an equimolar composition follow the order: cyclohexanone > cycloheptanone > cyclopentanone; and cyclopentanone > cyclohexanone > cycloheptanone respectively. The H^E data for various mixtures are positive over whole composition range and at an equimolar composition vary in the order: cycloheptanone > cyclohexanone > cyclopentanone. Further, the C_P^E values of the acetone (i) + cyclopentanone or cyclohexanone (j) mixtures are negative over entire composition range and for an equimolar composition follow the order: cyclohexanone > cyclopentanone. However, the sign and magnitude

Table 2
Comparison of densities, ρ, speeds of sound, u, and heat capacities, C_P 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.)
Acetone	298.15	784.41	785.41[13] 784.45[14]	1163.9	1163.76[17]	125.12	124.9[17]
Cyclo-pentanone	298.15	944.52	944.35[6] 945.3[15]	1393.2	1394.1[18]	154.69	154.5[9]
Cyclo-hexanone	298.15	942.90	942.15[16] 945.2[7]	1414.8	1408.0 [18] 1417.00[19]	178.37	177.97[20]
Cyclo-heptanone	298.15	947.63	–	1455.0	–	202.08	–