Excess molar volumes and excess isentropic compressibilities of binary and ternary mixtures of o-chlorotoluene with cyclic ether and amides or cyclohexane at different temperatures

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A B S T R A C T

Densities and speeds of sound data for ternary o-chlorotoluene (i) + tetrahydropyran (j) + N-methylformamide or N,N-dimethylformamide or cyclohexane (k) and their sub-binary o-chlorotoluene or (tetrahydropyran + cyclohexane) mixtures have been measured at temperatures (298.15, 303.15, 308.15) K and 0.1 MPa. The excess molar volumes, V_{ijk}^{E}, V^{E} and excess isentropic compressibilities, $(\kappa_{S}^{E})_{ijk}$, κ_{S}^{E} for ternary and binary mixtures respectively have been determined from the experimental densities, speeds of sound values and fitted to Redlich–Kister equation to calculate ternary and binary adjustable parameters along with standard deviations. The excess properties, V_{ijk}^{E} and $(\kappa_{S}^{E})_{ijk}$ have been tested in terms of (i) Graph; and (ii) Prigogine–Flory–Patterson (PFP) theories.

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1. Introduction

Thermodynamic properties of multi-component liquid mixtures are essential for process designing as well as for understanding structural and packing changes in mixtures. The design and operation of processes that involve non-electrolyte mixtures require knowledge of rigorous models or experimental data to represent the non-ideality of mixtures. The highest quality of density and speed of sound data and their analysis provide information required for improving the parameters for the predictive models which in turn are also used in simulation packages, design processes in chemical and biological industries [1–3]. o-Chlorotoluene is used as an intermediate in the chemical industry and as a solvent for chemical processing as well as a solvent for the formulation of agricultural pesticides. o-Chlorotoluene breaks down to intermediates such as cresols, 2-chlorobenzaldehyde, mixed dichlorotoluenes, 2-chlorobenzoic acid, 2-chlorobenzonitrile and 2-chlorobenzylchloride which are further used in the production of coloring agents, agrochemicals, and pharmaceuticals [4,5]. Tetrahydropyran is used as a reaction medium solvent for organic and biological processes, a solvent for plastics and polymers and as a dispersing agent for textile processes [6]. N-methylformamide

(NMF) a polar and protic solvent is used in the pharmaceutical industry and organic synthesis. Anticancer properties have also been credited to N-methylformamide molecule. N,N-dimethylformamide (DMF) a polar and aprotic solvent is used in the industry of synthetic fibers, leathers, films and during the coating processes [7]. Cyclohexane is a main ingredient among medicines and chemical waste liquids. It is widely used as a solvent, polar additive, dilution initiator, structure regulator, and active additive in the synthesis of copolymer, resins and rubber [8]. Consequently, densities and speeds of sound data of o-chlorotoluene with tetrahydropyran and N-methylformamide or N,N-dimethylformamide or cyclohexane mixtures may be of vital importance for industries. Further, survey of literature has shown that the densities and speeds of sound of o-chlorotoluene (i) + tetrahydropyran (j) + N-methylformamide or N,N-dimethylformamide or cyclohexane (k) mixtures are not available in literature. This prompted us to measure densities and speeds of sound of the present mixtures.

2. Experimental

o-Chlorotoluene (o-CT) (Fluka, mass fraction, 0.993; GC), tetrahydropyran (THP) (Fluka, mass fraction, 0.996; GC), N-methylformamide (NMF) (Fluka, mass fraction, 0.994; GC), N,N-dimethylformamide (DMF) (Fluka, mass fraction, 0.998; GC), cyclohexane (Fluka, mass fraction, 0.996; GC) were purified by standard methods [9–11]. The source of chemicals, their purification and

analysis methods along with final purity are listed in table 1. The densities and speeds of sound values of the purified liquids at $T = (298.15, 303.15, 308.15)$ K are recorded in table 2, where they are compared with literature [7,9,12–39] values.

The density and sound analyzer apparatus (Anton Paar DSA 5000) was used to measure densities and speeds of sound values of the purified liquids and their mixtures as described elsewhere [40,41]. The equipment was calibrated at $T = 293.15$ K with doubly distilled, deionized and degassed water. The various mole fractions of binary or ternary liquid mixtures were prepared by measuring masses of the components in air tight glass bottle of capacity ~5 ml using an electric balance (Model: Mettler AX-205 Delta Range) with a sensitivity of $\pm 10^{-5}$ g. The uncertainty in mole fraction is $1 \cdot 10^{-4}$. 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. The uncertainty in V^E values calculated from density results is 0.1% and uncertainty in the temperature measurement is ± 0.01 K.

3. Results

The measured densities, ρ_{ijk}, ρ and speeds of sound, u_{ijk}, u of ternary o-CT (i) + THP (j) + NMF or DMF or cyclohexane (k) and their sub-binaries o-CT or THP (i) + cyclohexane (j) at (298.15, 303.15, 308.15) K are listed in tables 3 and 4 respectively. The excess molar volumes, V^E_{ijk}, V^E; isentropic compressibilities, $(\kappa_S)_{ijk}, \kappa_S$; and excess isentropic compressibilities $(\kappa^E_S)_{ijk}, \kappa^E_S$ for the ternary and binary mixtures respectively were calculated using the equations

$$V^E_{ijk} = \sum_{i=i}^{k} x_i M^*_i (\rho_{ijk})^{-1} - \sum_{i=i}^{k} x_i M^*_i (\rho^*_i)^{-1}, \tag{1}$$

$$V^E = \sum_{i=i}^{j} x_i M^*_i (\rho)^{-1} - \sum_{i=i}^{j} x_i M^*_i (\rho^*_i)^{-1}, \tag{2}$$

$$(\kappa_S)_{ijk} = (\rho_{ijk} u^2_{ijk})^{-1}, \tag{3}$$

$$\kappa_S = (\rho u^2)^{-1}, \tag{4}$$

$$(\kappa^E_S)_{ijk} = (\kappa_S)_{ijk} - \kappa^{id}_S, \tag{5}$$

$$\kappa^E_S = \kappa_S - \kappa^{id}_S, \tag{6}$$

where x_i, M^*_i and ρ^*_i are the mole fraction, molar mass and density of pure component (i), respectively. The ρ_{ijk}, ρ and u_{ijk}, u are the densities and speeds of sound of ternary and binary mixtures respectively.

The ideal isentropic compressibilities, κ^{id}_S values for ternary and binary mixtures were calculated using Benson and Kiyohara [42] equation

$$\kappa^{id}_S = \sum_{i=i}^{j \text{ or } k} \phi_i \left[\kappa_{S,i} + \frac{TV_{m,i} \alpha^{*2}_i}{C^*_{p,i}} \right] - T \left(\sum_{i=i}^{j \text{ or } k} x_i V_{m,i} \right) \frac{\left(\sum_{i=i}^{j \text{ or } k} \phi_i \alpha^*_i \right)^2}{\left(\sum_{i=i}^{j \text{ or } k} x_i C^*_{p,i} \right)}. \tag{7}$$

The $\phi_i, \kappa_{S,i}, V_{m,i}, \alpha^*_i, T$ and $C^*_{p,i}$ (i = i or j or k) are the volume fraction, isentropic compressibility, molar volume, thermal expansion coefficient, temperature and molar heat capacity of pure component (i). The α^*_i values for various liquid were calculated using experimental density data in the manner described elsewhere [16]. The $C^*_{p,i}$ values for o-CT, THP, NMF, DMF and cyclohexane were taken from literature [43–45]. The $V^E_{ijk}, (\kappa^E_S)_{ijk}$ and V^E, κ^E_S values for ternary and binary mixtures are given in tables 3 and 4 respectively. Using Redlich–Kister [46] equations

$$X^E_{ijk}(X = V \text{ or } \kappa_S)$$

$$= x_i x_j \left[\sum_{n=0}^{2} \left(X^{(n)}_{ij} \right) (x_i - x_j)^n \right] + x_j x_k \left[\sum_{n=0}^{2} \left(X^{(n)}_{jk} \right) (x_j - x_k)^n \right]$$

$$+ x_i x_k \left[\sum_{n=0}^{2} \left(X^{(n)}_{ik} \right) (x_i - x_k)^n \right]$$

$$+ x_i x_j x_k \left[\sum_{n=0}^{2} \left(X^{(n)}_{ijk} \right) (x_j - x_k)^n x_i^n \right], \tag{8}$$

$$X^E(X = V \text{ or } \kappa_S) = x_i x_j \left[X^{(0)} + X^{(1)}(2x_i - 1) + X^{(2)}(2x_i - 1)^2 \right], \tag{9}$$

excess molar volumes and excess isentropic compressibilities data for the present ternary and binary mixtures were fitted by least squares optimization method. The $X^{(n)}_{ijk}$ ($X = V$ or κ_S) (n = 0 to 2) and $X^{(n)}_{ij}, X^{(n)}_{jk}, X^{(n)}_{ik}$ (n = 0 to 2) etc. are parameters characteristic of (i + j + k) ternary and sub-binaries (i + j), (j + k), (i + k) of (i + j + k) mixtures. The $X^{(n)}_{ij}$ ($X = V$ or κ_S) (n = 0 to 2) etc. for o-CT + THP or NMF or DMF; THP + NMF or DMF were taken from literature [43,44,47,48]. The standard deviations, $\sigma(V^E_{ijk})$, $\sigma(V^E)$ and $\sigma(\kappa^E_S)_{ijk}$, $\sigma(\kappa^E_S)$ of the fit defined by

$$\sigma\left(X^E_{ijk} \right)(X = V \text{ or } \kappa_S)$$

$$= \left\{ \left[\sum \left(X^E_{ijk} \right)_{expt} - X^E_{ijk(calc\ equation\ 8)} \right]^2 \middle/ (m - n) \right\}^{0.5}, \tag{10}$$

$$\sigma(X^E)(X = V \text{ or } \kappa_S)$$

$$= \left\{ \left[\sum (X^E)_{expt} - X^E_{(calc\ equation\ 9)} \right]^2 \middle/ (m - n) \right\}^{0.5}, \tag{11}$$

{where m, n are the number of experimental points and number of adjustable parameters of equations (8) and (9)} along with ternary and binary parameters are recorded in tables 5 and 6. The various surfaces generated [49] by V^E_{ijk} and $(\kappa^E_S)_{ijk}$ values {computed by employing equation (8)} for the ternary mixtures at $T = 298.15$ K are shown in figures 1–6 respectively. In figure 1 V^E_{ijk} values (corresponding to i–j axis) were obtained by keeping x_k constant and varying the values of x_i and x_j (shown as blue line); V^E_{ijk} values (corresponding to j–k axis) were obtained by keeping x_i constant and varying the values x_j and x_k (shown as red line).

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

Chemical name	Source	Purification method	Final purity (mass fraction)	Analysis method
o-Chlorotoluene	Fluka	Fractional distillation	0.993	GC[a]
Tetrahydropyran	Fluka	Vacuum distillation	0.996	GC
N-methylformamide	Sigma Aldrich	Vacuum distillation	0.994	GC
N,N-dimethylformamide	Sigma Aldrich	Vacuum distillation	0.998	GC
Cyclohexane	Fluka	Fractional distillation	0.996	GC

GC[a] = Gas chromatography.