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Heat capacities of binary and ternary mixtures containing *o*-chlorotoluene, cyclic ether and aromatic hydrocarbons

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ABSTRACT

Molar heat capacities, $(C_P)_{123}$ and $(C_P)_{mix}$, have been measured for the ternary *o*-chlorotoluene (1) + tetrahydropyran (2) + benzene or toluene or *o*-xylene (3) and their binaries tetrahydropyran (1) + benzene or toluene or *o*-xylene (2) at 298.15, 303.15 and 308.15 K and atmospheric pressure. From the experimental results, excess heat capacities, C_P^E and $\left(C_P^E\right)_{123}$ values were calculated and fitted to Redlich–Kister equation to determine binary and ternary adjustable parameters along with standard deviations. The observed C_P^E and $\left(C_P^E\right)_{123}$ data have been analyzed by utilizing topology of the constituent molecules (Graph theory). The estimated C_P^E and $\left(C_P^E\right)_{123}$ values from Graph theory are in agreement with experimental values. The interaction parameters, χ^* and χ'_{12} for binary mixtures (simulated by Graph theory) have been discussed to obtain information about molecular interactions in mixtures.

1. Introduction

Heat capacity data of liquid mixtures is directly linked with temperature dependence of their thermodynamic properties and are therefore essential for the calculation of differences in these properties with different temperatures. Reliable heat capacity data for liquid or their mixtures are indispensable in thermodynamic calculations and engineering design [1,2]. The direct measurement of heat capacity at constant pressure is of academic and technical interest, especially for mixtures containing polar components [3,4]. Chlorotoluenes find important applications in the chemical industry as chemical intermediates in the production of pharmaceuticals, dyes and pesticides [5]. Tetrahydropyran, a member of technically important class of cyclic ethers, is used as a solvent in various chemical industries and for electrolytes in batteries having alkali metal negative electrodes [6]. Further the extraction of benzene, toluene, *o*-xylene, from refinery products such as naphtha, kerosene and fuel jets is very important for petrochemical industry. Consequently, thermodynamic properties of benzene or toluene or *o*-xylene with *o*-chlorotoluene and tetrahydropyran, may provide important basic data for use in petrochemical and chemical industries. In continuation of our work on thermodynamic properties of mixtures containing *o*-chlorotoluene and cyclic ethers [7], we report here excess heat capacities, $\left(C_P^E\right)_{123}$ of ternary *o*-chlorotoluene (1) + tetrahydropyran (2) + benzene or toluene or *o*-xylene (3) and C_P^E of their sub-binary tetrahydropyran (1) + benzene or toluene or *o*-xylene (2) mixtures at 298.15, 303.15 and 308.15 K. It would be of great interest to see how Graph theory describes the C_P^E and $\left(C_P^E\right)_{123}$ data of investigated binary and ternary mixtures. In recent studies, topology of the constituent molecules (Graph theory) has been successfully utilized to compute excess heat capacities of binary mixtures [7–9].

2. Experimental

2.1. Materials

o-Chlorotoluene (*o*-CT) (Fluka, mass fraction, 0.992; GC), tetrahydropyran (THP) (Fluka, mass fraction, 0.994; GC), benzene (Fluka, mass fraction, 0.995; GC), toluene (Fluka, mass fraction, 0.993; GC) and *o*-xylene (Fluka, mass fraction, 0.995; GC) were purified by the standard methods [10–12]. Details of chemical source, purification method, final purity and analysis method are listed in Table 1.

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List of symbols

ρ	density
u	speeds of sound
$(C_P)_{mix}$	molar heat capacity of binary mixture
$(C_P)_{123}$	molar heat capacity of ternary mixture
C_P^E	excess heat capacity of binary mixture
$(C_P^E)_{123}$	excess heat capacity of ternary mixture
x_i	mole fraction of the pure component ($i=1$ or 2 or 3)
C_P	molar heat capacity of the pure component
$C_P^{(n)}\ (n = 0-2)$	binary adjustable parameters
$\left(C_P^{(n)}\right)_{123}\ (n = 0-2)$	ternary adjustable parameters
${}^3\xi$	connectivity parameter of third degree of the constituent molecules
$\sigma\left(C_P^E\right)$	standard deviation in binary mixtures
$\sigma\left(C_P^E\right)_{123}$	standard deviation in ternary mixtures
$\sigma\left(C_P^E\right)_{Graph}$	deviation between experimental C_P^E and C_P^E estimated by Graph theory
$\sigma\left(C_P^E\right)_{123Graph}$	deviation between experimental $\left(C_P^E\right)_{123}$ and $\left(C_P^E\right)_{123}$ computed by Graph theory
χ_{11}	interaction energy parameter for the disruption of associated entity, 1_n
χ_{22}	interaction energy parameter for the disruption of associated entity, 2_n
χ_{12}	interaction energy parameter for unlike 1-2 contact formation
χ_{23}	interaction energy parameter for unlike 2-3 contact formation
χ_{13}	interaction energy parameter for unlike 1-3 contact formation
$\chi_{12}^{/}$	interaction energy parameter for molecular interactions forming 1:2 molecular complex
$\chi_{12}^{//}$	interaction energy parameter for molecular interactions forming 2:3 molecular complex
$\chi_{12}^{///}$	interaction energy parameter for molecular interactions forming 1:3 molecular complex

2.2. Apparatus and procedures

The densities, ρ and speeds of sound, u of pure liquids were measured using an Anton Paar vibrating tube digital density and sound analyzer (DSA-5000) in the manner as explained elsewhere [13,14]. The densities, ρ and speeds of sound, u values of the purified liquids are reported in Table 2 and compared with their literature values [5,10,15–38]. The standard uncertainties in densities, ρ and speeds of sound, u measurements are 0.5 kg m^{-3} and 0.1 m s^{-1} respectively.

The molar heat capacities, C_P of the pure liquids and their mixtures were measured by using micro differential scanning calorimeter [Model-µ DSC 7 Evo] in the manner as described elsewhere [8]. The calibration of the calorimeter (controlled by SETARAM software) was done by the Joule effect method. The Joule effect calibration was checked by measuring heat of fusion of naphthalene (147.78 J g^{-1}). The various compositions of binary or ternary liquid mixtures were made using an electric balance Mettler AX-205 Delta Range with an uncertainty of $\pm 10^{-5}$ g. Pure liquid or a mixture of known composition was taken in the experimental cell with the help of micropipette. A constant sweeping of nitrogen gas (0.8 bar pressure) was supplied. The equipment was scanned for temperature cycle 15 °C (initial temperature) and 45 °C (final temperature) at the scanning (heating or cooling) rate 0.4 °C/min. The stability in the calorimetric signal was produced by scanning (900 s) an isothermal level at the initial and final temperature. The temperature cycle and scanning rate of isothermal level was maintained by software. After scanning a graph between heat flow and calorimeter temperature along with C_P values was displayed. The standard uncertainties in temperature and heat capacities values are ±0.02 K and 0.3% respectively. Further, the standard uncertainty in mole fraction is 1×10^{-4}. The C_P values of the purified liquids are reported in Table 2 and compared with their literature values [17,22,30,34,39–43].

The reliability of the calorimeter was checked by measuring molar heat capacities for the pure liquids (reported in Table 2) as well as excess heat capacities of chloroform + tetrahydrofuran + cyclohexane mixture [44] and they agreed with corresponding experimental values within reported uncertainty.

3. Results

The molar heat capacities, $(C_P)_{mix}$ and $(C_P)_{123}$ of THP (1) + benzene or toluene or *o*-xylene (2) binary and *o*-CT (1) + THP (2) + benzene or toluene or *o*-xylene (3) ternary mixtures are listed in Supplementary information Table S1and Table 3 respectively. The excess heat capacities, C_P^E and $\left(C_P^E\right)_{123}$ data for binary as well as ternary mixtures were computed using:

$$C_P^E = (C_P)_{mix} - \sum_{i=1}^{2} x_i (C_P)_i \tag{1}$$

$$\left(C_P^E\right)_{123} = (C_P)_{123} - \sum_{i=1}^{3} x_i (C_P)_i \tag{2}$$

where x_i, $(C_P)_i$, ($i = 1$ or 2 or 3) are the mole fraction and molar heat capacities of the pure component (i). The $(C_P)_{mix}$ and $(C_P)_{123}$ the heat capacities of binary as well as ternary mixture respectively. Such C_P^E and $\left(C_P^E\right)_{123}$ data for binary and ternary mixtures, presented in Supplementary information Table S1and Table 3 respectively, were fitted to Redlich–Kister [45] equation

$$C_P^E = x_1 x_2 [C_P^{(0)} + C_P^{(1)}(2x_1 - 1) + C_P^{(2)}(2x_1 - 1)^2] \tag{3}$$

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	0.992	GC[a]
Tetrahydropyran	Fluka	Vacuum distillation	0.994	GC[a]
Benzene	Fluka	Fractional distillation	0.995	GC[a]
Toluene	Fluka	Fractional distillation	0.993	GC[a]
o-Xylene	Fluka	Fractional distillation	0.995	GC[a]

[a] GC = Gas chromatography.