J. Chem. Thermodynamics 85 (2015) 1–12

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Excess heat capacities of mixtures containing 1-methylpyrrolidin-2-one, chlorotoluenes and benzene

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ARTICLE INFO

Article history:
Received 17 July 2014
Received in revised form 22 December 2014
Accepted 26 December 2014
Available online 5 January 2015

Keywords:
Molar heat capacity, C_P
Excess heat capacity, C_P^E
Connectivity parameter, ξ
Interaction energy parameter, χ
1-Methylpyrrolidin-2-one

ABSTRACT

Excess heat capacities, $(C_P^E)_{ijk}$ of {1-methylpyrrolidin-2-one (i) + benzene (j) + *o*- or *m*- or *p*-chlorotoluene (k)} and C_P^E of their sub-binary {1-methylpyrrolidin-2-one (i) + benzene (j)}; {benzene (i) + *m*- or *p*-chlorotoluene (j)} mixtures have been determined using their measured heat capacities data at $T = (293.15, 298.15, 303.15)$ K and 0.1 MPa using micro differential scanning calorimeter. The results are discussed in terms of Graph (which deals with the topology of the constituent molecules) theory. The results suggest that C_P^E and $(C_P^E)_{ijk}$ values commuted by Graph theory compare well with experimental values.

1. Introduction

The design and operation of chemical reactors, pumps, heat transfer equipment such as refrigeration systems and the industrial equipment requires knowledge of heat capacities of liquids used in the various processes [1,2]. The heat capacity data of liquid mixtures are required for the collection of heat balances around the absorber regenerators, and heat exchangers used in gas treating industries [3]. The heat capacities data of liquids mixtures can also provide information whether they can be used as heat transfer fluids for large scale solar energy collectors to be used for electric power generator or not. Furthermore, change in enthalpy, entropy and Gibb's free energy at any temperature can be calculated from results obtained at various temperatures [4]. 1-Methylpyrrolidin-2-one, ε-caprolactam is a stable, dipolar aprotic, and powerful solvent. Such properties of liquids are important in chemical reactions where an inert medium is needed [5]. 1-Methylpyrrolidin-2-one is used in pharmaceutical and medicinal fields for improving the transdermal flux of both hydrophilic and hydrophobic drugs [6]; in petroleum industry to increase the selectivity and solvent power for extracting aromatic hydrocarbon [7]. It is also used as absorbents of sour gases from crude natural gas [8]. Benzene is widely used in chemical and petroleum industry [9]. Chlorotoluenes are important chemical intermediates and are used for the production of pesticides, pharmaceutical and dyes [10,11]. The increasing use of 1-methylpyrrolidin-2-one, benzene and chlorotoluenes in industries has greatly increased the need for the extensive information on thermodynamic properties of liquid mixtures containing the said components. The present study is in continuous of our systematic studies [12–15] on thermodynamic properties of liquid mixtures containing cyclic amides as one of the component. A survey of literature has indicated that heat capacities data of {1-methylpyrrolidin-2-one (i) + benzene (j) + *o*- or *m*- or *p*-chlorotoluene (k)} mixtures are not available in the literature. The Graph theory has recently been utilized to predict C_P^E of binary mixtures. It was of interest to see how theory describes the C_P^E of ternary mixtures.

2. Experimental

1-Methylpyrrolidin-2-one (NMP) (mass fraction: 0.99), benzene (mass fraction: 0.99), *o*-chlorotoluene (mass fraction: 0.98), *m*-chlorotoluene (mass fraction: 0.98), *p*-chlorotoluene (mass fraction: 0.99) were purified by standard methods [16–18]. The source of liquids, their purification methods and final purity are reported in table 1. The densities, ρ and speeds of sound, u values of the pure liquids were measured using a density and sound analyzer apparatus (Anton Paar DSA 5000) in the manner as described elsewhere [19,20]. The uncertainties in the density and speed of sound measurements are ±0.5 kg · m^{-3} and 0.1 m · s^{-1} respectively. Further, uncertainty in the temperature measurement (DSA-5000) is

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http://dx.doi.org/10.1016/j.jct.2014.12.022
0021-9614/

T = ±0.01 K. The investigated liquids, namely, *o*- or *m*- or *p*-chlorotoluene with same physical properties [12] were used in the current study. Further, ρ and u values for 1-methylpyrrolidin-2-one and benzene at T = (293.15, 298.15, and 303.15) K along with their literature values [21–23,8,24–28] are presented in table 2.

The molar 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 [13]. The calibration of equipment was done by Joule effect method which in turn was controlled by SETARAM software. The calibration was checked by measuring heat of fusion of naphthalene (148.18 $J \cdot g^{-1}$) comparable to 148.7 $J \cdot g^{-1}$ [29]. For a scanning sequence initial (15 °C) and final temperature (45 °C) were supplied along with heating rate of 0.4 $K \cdot min^{-1}$. The liquid or liquid mixture under investigation was taken in standard batch cell (made up of Hastelloy C276) of capacity 1 ml. The mole fraction of each liquid mixture was made by measuring masses of the components of mixtures in air tight glass bottles using an electric balance Mettler AX-205 Delta Range with an uncertainty of $\pm 10^{-5}$ g. The uncertainty in mole fraction is $1 \cdot 10^{-4}$. The uncertainty in measuring heat capacity is ±0.3%. The uncertainty in the temperature measurement (DSC) is ±0.02 K. The molar heat capacities of 1-methylpyrrolidin-2-one and benzene are recorded in table 2, where they are compared with literature values [30,31].

3. Results

The molar heat capacities, C_p and $(C_P)_{ijk}$ of {NMP (i) + benzene (j)}; {benzene (i) + *o*- or *m*- or *p*-chlorotoluene (j)} binary and {NMP (i) + benzene (j) + *o*- or *m*- or *p*-chlorotoluene (k)} ternary mixtures measured over entire mole fraction range at T = (293.15, 298.15, 303.15) K are listed in tables 3 and 4 respectively. Excess heat capacities, C_P^E and $(C_P^E)_{ijk}$ data of the studied binary and ternary mixtures were calculated from relations

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

$$(C_P^E)_{ijk} = (C_P)_{ijk} - \sum_{i=i}^{k} x_i (C_P)_i, \tag{2}$$

where x_i ($i = i - k$), $(C_p)_i$ ($i = i - k$) are the mole fraction and molar heat capacity of pure component respectively. The C_P^E and $(C_P^E)_{ijk}$ data of {NMP (i) + benzene (j)}; {benzene (i) + *o*- or *m*- or *p*-chlorotoluene (j)} binary and {NMP (i) + benzene (j) + *o*- or *m*- or *p*-chlorotoluene (k)} ternary mixtures at the studied temperatures (recorded in tables 3 and 4 respectively) were fitted to Redlich–Kister equations [32] to observe the composition dependence

$$C_P^E = x_i x_j \left[C_P^{(0)} + C_P^{(1)} (2x_i - 1) + C_P^{(2)} (2x_i - 1)^2 \right], \tag{3}$$

$$\begin{aligned}(C_P^E)_{ijk} = {} & x_i x_j \left[\sum_{n=0}^{2} (C_P)_{ij}^{(n)} (x_i - x_j)^n \right] + x_j x_k \left[\sum_{n=0}^{2} (C_P)_{jk}^{(n)} (x_j - x_k)^n \right] \\ & + x_k x_i \left[\sum_{n=0}^{2} (C_P)_{ik}^{(n)} (x_k - x_i)^n \right] \\ & + x_i x_j x_k \left[\sum_{n=0}^{2} (C_P)_{ijk}^{(n)} (x_j - x_k)^n x_i^n \right],\end{aligned} \tag{4}$$

where $(C_P)_{ij}^{(n)}$ (n = 0 to 2) etc. and $(C_P)_{ijk}^{(n)}$ (n = 0 to 2) are adjustable parameters of binaries ($i + j$), ($j + k$), ($i + k$) and ($i + j + k$) ternary mixtures. These parameters were determined by fitting C_P^E and $(C_P^E)_{ijk}$ data to equations (3) and (4) using least-squares method. The binary adjustable parameters for {NMP (i) + *o*- or *m*- or *p*-chlorotoluene (j)}; {benzene (i) + *o*-chlorotoluene (j)} were taken from literature [12,33]. The calculated values of $(C_P)_{ij}^{(n)}$ and $(C_P)_{ijk}^{(n)}$ parameters along with their standard deviations, $\sigma(C_P^E)$ and $\sigma(C_P^E)_{ijk}$ defined by

$$\sigma(C_P^E) = \left[\sum \left(\left(C_P^E \right)_{\{exptl\}} - \left(C_P^E \right)_{\{calc.\ equation\ (3)\}} \right)^2 \Big/ (m - n) \right]^{0.5}, \tag{5}$$

$$\sigma\left((C_P^E)_{ijk} \right) = \left[\sum \left((C_P^E)_{ijk\{exptl\}} - (C_P^E)_{ijk\{calc.\ equation\ (4)\}} \right)^2 \Big/ (m - n) \right]^{0.5}, \tag{6}$$

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

Chemical name	Source	Purification method	Final purity	Analysis method
1-Methyl pyrrolidin-2-one	Fluka	Vacuum distillation	0.99	GC[a]
Benzene	Fluka	Fractional distillation	0.99	GC
o-Chlorotoluene	Fluka	Fractional distillation	0.98	GC
m-Chlorotoluene	Fluka	Fractional distillation	0.98	GC
p-Chlorotoluene	Fluka	Fractional distillation	0.99	GC

[a] GC = gas chromatography.

TABLE 2
Comparison of densities, ρ, speeds of sound, u, and molar heat capacities, C_P of pure component (i) with their literature values at T/K = 293.15, 298.15, 303.15 and p = 0.1 MPa.

Liquids	T/K	ρ/(kg · m^{-3})		u/(m · s^{-1})		C_P/J · K^{-1} · mol^{-1})	
		(Exptl.)	(Lit.)	(Exptl.)	(Lit.)	(Exptl.)	(Lit.)
1-Methyl pyrrolidin-2-one	293.15	1033.3	1033.23[21]	1565.6	1565.50[23]	165.44	
	298.15	1028.3	1028.23[21]	1546.1	1546.06[8]	166.22	166.1[24]
	303.15	1023.5	1023.47[22]	1527.3	1527.21[23]	166.92	
Benzene	293.15	878.89	879.00[24]	1322.6	1323.30[27]	133.58	133.63[30]
	298.15	873.54	873.56[25]	1299.4	1299.2 [28] 1299.73[27]	135.28	135.76[31]
	303.15	868.20	868.21[26]	1276.2	1276.37[27]	136.58	136.62[30]

The standard uncertainty in density $u(\rho)$ = ±0.5 kg · m^{-3}; the standard uncertainty in speed of sound $u(u)$ = 0.1 m · s^{-1}; the standard uncertainty in heat capacity, $u(C_p)$ = ±0.3%; the standard uncertainty in temperature (DSA) $u(T)$ = ±0.01 K; the standard uncertainty in temperature (DSC) $u(T)$ = ±0.02 K; the standard uncertainty in pressure $u(p)$ = ±100 Pa.