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Molar heat capacities of aqueous 2-amino-2-ethyl-1,3-propanediol solutions and their ternary mixtures containing piperazine or lithium salts

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ABSTRACT

The molar heat capacities of a primary sterically hindered amine 2-amino-2-ethyl-1,3-propanediol (AEPD) and its aqueous solutions, in the whole range of concentrations, were measured at temperatures from 303.15 K to 353.15 K by heat flow differential scanning calorimetry. The molar heat capacities of aqueous ternary solutions of AEPD with PZ or salt (LiCl or LiBr) at different amine and salt concentrations were also presented. The excess molar heat capacities of the binary solutions were determined, and the data were correlated with temperature and amine mole fraction using a Redlich–Kister-type equation. For the ternary systems, the heat capacity differences were obtained, and the heat capacity data were represented as a function of temperature and solute concentration using the Sohnel and Novotný equation. The applied correlations well represented the experimental data heat capacities of the studied solvents as suggested by the low values of average absolute deviation, which are 0.2%, 0.1%, and 0.2% for the pure, binary, and ternary systems, respectively.

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1. Introduction

Sterically hindered amines are amongst the industrially important types of amine solvents (e.g. 2-amino-2-methy-1-propanol (AMP)), which are utilized in gas purification [1,2]. Their application in the removal of CO_2 from process gases was first proposed by Sartori and Savage [3] who showed that steric hindrance could be introduced in the amine by placing a bulky substituent adjacent to its amino group. Such hindrance leads to formation of unstable carbamates, which favors its hydrolysis to bicarbonate and free amine; hence, increasing the amine's theoretical loading capacity to up to 1.0 mol CO_2 per mole amine – a key advantage of sterically hindered amines over primary and secondary amines whose loading capacities are limited to 0.5 [3]. Moreover, the low carbamate stability in the solvent promotes low energy requirements during regeneration. Also, compared to tertiary amines, hindered amines have significantly higher reaction rate with CO_2 [4]. In fact, they are commonly used as promoters in mixed amine and hot potassium carbonate systems and as principal agents in aqueous solutions for the selective absorption of H_2S in the presence of CO_2 [1].

One of the relatively known sterically hindered amines, which has been proposed as a potential CO_2 absorbent is 2-amino-2-ethyl-1,3-propanediol (AEPD). It has been reported that aqueous AEPD solutions (10 and 30 wt.%) have appreciable absorption capacity for CO_2, which is much better than MEAs at higher CO_2 partial pressures [5]. The absorption kinetics of CO_2 in aqueous AEPD at temperatures ranging from 303.15 to 318.15 K and concentrations 0.41 – 2.15 kmol/m^3 were also investigated, and the specific rate constants were measured [6]. However, data on the thermophysical properties of aqueous AEPD solutions, which are vital in the design and operation of CO_2 absorption processes, are still rather scarce. Data are limited to those reported by Yoon et al. [6,7] for density and viscosity of 5 wt.% to 25 wt.% AEPD solutions at 305.15 K, 313.15 K, and 315.15 K [6], density of 20 wt.% to 100 wt.% AEPD, and viscosity and surface tension of 20 wt.% to 80 wt.% AEPD at 303.15 K to 343.15 K [7]. Thermal properties (i.e. heat capacity) of these systems, which are required in the design of heat exchange equipment installed in absorption and stripping columns are not yet available in the literature.

In this work, we presented new data on molar heat capacity, C_P, of AEPD and its aqueous binary solutions at 303.15 K to 353.15 K and concentrations from 15 mol% to 90 mol% AEPD. We also measured the C_P of aqueous ternary solutions of AEPD with piperazine (PZ), a known amine activator, which has been shown to promote the reaction rate of other hindered amines (i.e. AMP) with CO_2 [8,9]. The C_P of aqueous ternary solutions of AEPD containing the salts

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Nomenclature

a_1, a_2	parameters of Eq. (1)
$b_{j,0}$, $b_{j,1}$	parameters of Eq. (3)
B_j	temperature-dependent pair parameter of the Redlich–Kister-type equation
C_P	molar heat capacity (J mol^{-1} K^{-1})
C_P^E	excess molar heat capacity (J mol^{-1} K^{-1})
C_{Pa}	molar heat capacity of the PZ or salt-free aqueous solution (J mol^{-1} K^{-1})
$C_P - C_{Pa}$	heat capacity difference (J mol^{-1} K^{-1})
$d_{j,0}$, $d_{j,1}$	parameters of Eq. (6)
D_j	temperature-dependent pair parameter of the Sohnel and Novotný equation
m_1	molality of ternary solution (mol salt or PZ per kg AEPD + H_2O)
T	temperature (K)
x_i	mole fraction of component i

LiCl and LiBr, which are expected to lower the vapor pressure and molar heat capacity of the aqueous amine solutions [10,11], were also reported. The experimental data were used to calculate excess molar heat capacities, $C_P{}^E$, of the binary solutions, and heat capacity differences, $C_P - C_{Pa}$, of the ternary systems. We also aimed to present suitable correlations, which can be used to represent the experimental data as a function of temperature and concentration.

2. Experimental

2.1. Chemicals

2-Amino-2-ethyl-1,3-propanediol (AEPD, purity >98 wt.%) was supplied by Tokyo Chemical Industry, Co. Ltd., piperazine (PZ, purity >99 wt.%) and LiBr (purity >99 wt.%) were purchased from Acros Organics, and LiCl (purity >99.9 wt.%) was obtained from Prochem, Inc. They were used in the experiments without further purification. The list of chemicals used in this work is given in Table 1. High-purity distilled water (resistivity/mΩ = 18.3) deionized using a Barnstead Thermolyne (model Easy Pure 1052) water purification system was used in the experiments. Weight measurements were performed in a Mettler Toledo digital balance (model AL204) having an accuracy of ±1 × 10^{-4} g.

2.2. Apparatus and procedures

The heat capacity of each sample was measured using a TA Instruments heat flow differential scanning calorimeter (DSC) (model DSC-2010) equipped with a thermal analysis controller, and employing the well-known sapphire method. The experimental setup and method we used are the same as those we applied and described in detail in our earlier works [12–15].

For each measurement, we used 10–15 mg of the sample (encapsulated in an aluminum hermetic pan). The differential heat flow curve of the sample was compared with that of standard sapphire. Both curves were blank corrected. We used nitrogen (purity >99.9995%), as purge gas, at a flow rate of 40 mL/min. The repeatability of the temperature measurement was ±0.1 °C. To ensure the accuracy of the measurements, periodic calibration of the DSC was conducted using an indium calibrant. C_P measurements were done in three to five replicates. The apparatus and applied method were validated by measuring the heat capacity of dipropylene glycol (DPG) as test sample. The validation results, which we have reported in our recent work [16], were found to be in good agreement with the data reported in the literature [17–19] with an average absolute deviation (AAD) of less than 1%. Taking these results into account, the estimated overall uncertainty of the measurements was ±2%.

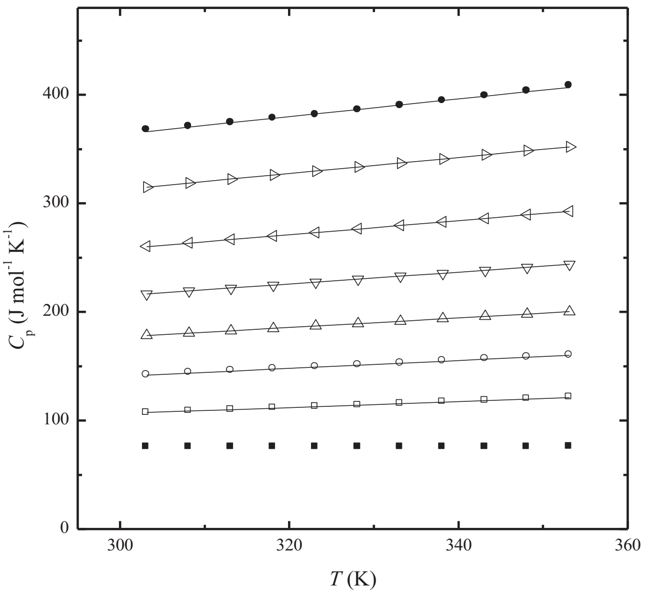

Fig. 1. Molar heat capacity of AEPD (1) + H_2O (2) systems: ■, H_2O by Osborne et al. [24]; □ x_1 = 0.1494; ○, x_1 = 0.3002; △, x_1 = 0.4502; ▽, x_1 = 0.5992; ◁, x_1 = 0.7505; ▷, x_1 = 0.8989; ●, x_1 = 1.0000; lines, calculated.

3. Results and discussion

Table 2 presents the experimental molar heat capacities, C_P, of pure and aqueous AEPD at temperatures from T = (303.15–353.15) K. The data are plotted in Fig. 1 to show the variation of C_P with temperature and amine mole fraction. As expected, the C_P of the samples, at all concentrations, slightly increased with increasing temperature. It can also be observed that at the same temperature, the C_P increased as the mole fraction of the amine in the binary solution increased, which is a manifestation of the higher C_P of the pure amine than that of water. It can also be deduced that the C_P exhibited greater variation with concentration than with temperature.

Table 1
Description of chemicals used.

Chemical name	Source	Purity (mass fraction)	Purification method
2-Amino-2-ethyl-1,3-propanediol (AEPD)	Tokyo Chemical Industry, Co. Ltd.	>0.98	None
Dipropylene glycol (DPG)	Acros Organics	>0.99	None
Piperazine (PZ)	Acros Organics	>0.99	None
Lithium bromide (LiBr)	Acros Organics	>0.99	None
Lithium chloride (LiCl)	Prochem, Inc.	>0.999	None
Water	In-house purification	Pure (resistivity = 18.3 mΩ)	Distillation, deionization

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