Molar heat capacity of aqueous solutions of 1,3-diaminopropane and 1,4-diaminobutane and their piperazine blends

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ABSTRACT

The molar heat capacity, C_p, of aqueous 1,3-diaminopropane (DAP), 1,4-diaminobutane (DAB) and their corresponding blends with piperazine (PZ) were measured at temperatures from 303.2 K to 353.2 K by differential scanning calorimetry. The correlation of C_p of the aqueous binary mixtures with temperature and concentration was successfully described by a Redlich–Kister type equation using excess molar heat capacity data. A modified Sohnel and Novotny equation was used to represent the temperature and concentration dependence of C_p of the ternary mixtures. The average absolute deviations between the experimental and the predicted C_p data were 0.2% and 0.1% for the binary and ternary mixtures, respectively. The results suggest that the experimental data presented in this work were represented well by the proposed correlations.

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1. Introduction

Carbon dioxide removal from industrial flue gases is imperative because of the significant contribution of this greenhouse gas to global climate change. Nowadays, CO_2 removal is accomplished by chemical absorption using aqueous alkanolamine solutions. Although, currently available alkanolamine absorbents such as monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA) have been effectively used for such application, new amine solvents with favorable characteristics are still desirable. In recent years, significant efforts have been exerted to develop novel amine absorbents with high CO_2 absorption capacity, fast reaction kinetics, good thermal and chemical stability and low volatility, which can be better choice solvents for CO_2 capture [1–6].

Polyamines are amongst the amine solvents that are extensively investigated for potential application in CO_2 absorption. Because of the greater number of amine groups present in their structure, polyamines are expected to have higher binding capacity and faster reaction rate with CO_2 compared to solvents with single amine function [2,7,8]. In recent works, Singh et al. [9,10] have shown that the greater number of amine groups present in some polyamines increases the absorption capacity (in moles CO_2/mole amine) of the solvents. In particular, aqueous solutions of the diamines 1,3-diaminopropane (DAP) and 1,4-diaminobutane (DAB) were reported to have higher absorption capacity than aqueous MEA of the same concentration (2.5 M). Aqueous DAP was also shown to have much faster initial absorption rate compared with aqueous MEA. Such results are attributed to the increase in the number of amine groups in the diamines creating more reaction sites available for the reaction with CO_2 [10]. Xu et al. [5] demonstrated that the performance of aqueous DAB (3 M), based on its absorption capacity and absorption rate, was better compared with the other amine solvents they investigated. In another study, they blended DAB with the tertiary alkanolamine 2-(diethylamino)ethanol (DEEA) to improve the CO_2 absorption performance of the latter [11]. DAB was also used in combination with the cyclic diamine piperazine (PZ) [12]. PZ is described as a "state of the art" solvent for use in CO_2 capture with low vapor pressure, high reaction rate with CO_2, and high absorption capacity; however, have limited solubility in water. Rochelle et al. [12,13] propose that blending PZ with another diamine would widen its solubility window. It could then be expected that combining the above-mentioned diamines, DAP and DAB, with PZ would provide blends that have even better CO_2 absorption characteristics than the binary mixtures. Thus, such systems were also considered in the present work.

The objective of this work is to present experimental data on the heat capacity, C_p, of aqueous DAP and DAB and their corresponding ternary solutions with PZ. Heat capacity is one of the

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fundamental thermodynamic properties of a solvent system that is necessary in evaluating its potential application in CO_2 capture. Such data are important in estimating energy requirements associated with the solvent; hence, are vital in the design and optimization of the absorption process. To date, available data on the thermophysical properties of DAP and DAB are limited to vapor pressure [14], excess molar enthalpy (298.15 K) [15], C_p of pure solvents [16–18] and apparent C_p of aqueous DAB at $p = 28$ MPa [19]. In the present work, measurements were performed at temperatures from 303.2 K to 353.2 K, which covers the typical operating range during CO_2 absorption. For the binary solutions, measurements were done in the entire concentration range ($x_1 = 0.1$–1.0). The ternary mixtures used were at different DAB or DAP + PZ compositions with a total amine concentration of 30 wt%. The experimental data were also used to calculate excess molar heat capacities, C_p^E, of the binary solutions, and heat capacity difference, $C_p - C_{p,a}$, of the ternary systems. In addition, we correlated the temperature and composition dependence of C_p using a Redlich–Kister type expansion [20] and a modified Sohnel and Novonty [21] equation for the binary and ternary systems, respectively.

2. Experimental

2.1. Chemicals

1,3-Diaminopropane (DAP), 1,4-diaminobutane (DAB), and piperazine (PZ) were obtained from Acros Organics. Each had purity >99 wt% and used without further purification. The description of the amines used is given in Table 1. High-purity distilled water (resistivity = 18.3 mΩ), which was deionized in a Barnstead Thermolyne (model Easy Pure 1052) water purification system was used in the experiments. Aqueous samples were prepared by mass using a digital balance (Mettler Toledo model AL204) with accuracy $\pm 1 \times 10^{-4}$ g.

2.2. Measurement of heat capacity

Heat capacity measurement was carried out using a TA instruments heat flow differential scanning calorimeter (model DSC-2010), and the sapphire method was applied [22]. Details of the experimental setup and procedure including the validation tests (using water and dipropylene glycol) were discussed in our previous works [23–26]. In each measurement, the differential heat flow curve of the sample was compared with that of standard sapphire with both curves blank corrected. The sample used was weighed in a Shimadzu (model AUW220D) analytical balance with an accuracy of $\pm 1 \times 10^{-4}$ g and encapsulated in an alodined aluminum hermetic pan. The purge gas used was nitrogen (purity > 99.9995%), and the optimum flow rate of 40 mL min⁻¹. To ensure the accuracy of the measurements, the DSC was calibrated periodically. Temperature and cell constant calibration was done using indium as calibration material. The standard uncertainty of the measured temperature was ± 0.2 K. At least five replicate measurements were performed for each sample. Based on tests performed with water and taking into account the uncertainties of the measured weights and the repeatability of the measurements, the overall expanded uncertainty ($k = 2$) of the reported C_p was estimated to be $\pm 3.0\%$.

3. Results and discussion

The molar heat capacities of pure and aqueous diamines, DAP and DAB, were measured at temperatures from 303.2 to 353.2 K and atmospheric pressure ($p = 101.3$ kPa). The results are given in Tables 2 and 3, for DAP and DAB, respectively. The experimental
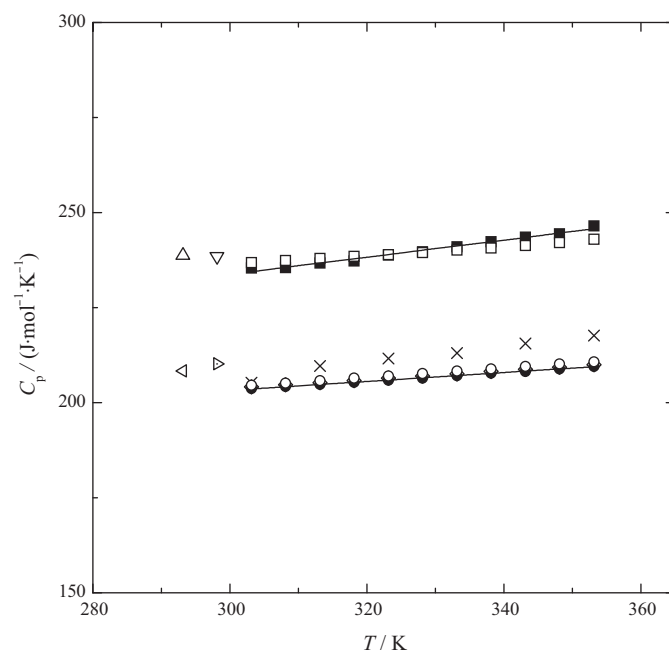
Fig. 1. Molar heat capacity of pure diamines at different temperatures. For DAP: ●, this work (expt.); ◇, Goralski and Tkaczyk (expt.) [16]; ○, Domanska et al. [18], ×, Rayer et al. (expt.) [17]; ◁, Chueh and Swanson (calc.) [27]; ▷, Missenard (calc.) [28]; For DAB: ■, this work (expt.); □, Goralski and Tkaczyk (expt.) [16]; △, Chueh and Swanson (calc.) [27]; ▽, Missenard (calc.) [28]; lines, calculated using Eq. (1).

data for the pure diamines are also plotted as function of temperature in Fig. 1 to provide a comparison with available literature data [16–18,27,28]. It can be observed that the data reported in the present work conform with those reported by Goralski and Tkaczyk [16] (for DAP:AAD = 0.2%; for DAB:AAD = 0.6%) and Domanska et al. [18] (for DAP:AAD = 0.5%). As expected, the heat capacity of DAB is higher than that of DAP at the same temperature, which is due to the longer alkyl chain of DAB than DAP's. The increasing values of C_p as temperature increased are due to higher degrees of freedom available at higher temperatures.

For the pure diamines, the dependence of C_p with temperature is represented by a linear equation as in Eq. (1).

$$C_P/\text{J mol}^{-1}\,\text{K}^{-1} = A_1 + A_2(T/\text{K}) \tag{1}$$

Here T is the temperature and A_1 and A_2 are adjustable coefficients obtained by fitting the equation with the experimental data using the least squares method. The values of which are given in Table 4. The absolute average deviation (AAD) between the experimental and predicted data from Eq. (1) is less than 0.1%.

Likewise, the heat capacity of the aqueous binary solutions was correlated with temperature and concentration. It is noticeable that for both aqueous DAP and aqueous DAB systems, C_p increased as amine concentration and temperature increased. The correlation was done by calculating the excess molar heat capacity of each sample and representing the obtained data as function of temperature and amine mole fraction using a Redlich–Kister type equation. The excess molar heat capacity, C_p^E, was calculated from the following relation:

$$C_p^E/\text{J mol K}^{-1} = C_p - \sum_i x_i C_{p,i} \tag{2}$$

where C_p and $C_{p,i}$ are the molar heat capacity of the mixture and pure component i, respectively and x_i is the mole fraction. The obtained values of C_p^E from the experimental C_p data for selected temperatures are plotted as points in Figs. 2 and 3 for aqueous DAP and aqueous DAB, respectively. As shown in the figures, C_p^E values