Molar Heat Capacity of Aqueous Solutions of Tertiary Amine 1-Dimethylamino-2-propanol with Polyamine Diethylenetriamine

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Abstract—Heat capacities of ternary systems containing tertiary amine 1-dimethylamino-2-propanol (1DMAP) and polyamine diethylenetriamine (DETA) were measured at 30 wt% total amine concentration and temperature range of 303.15 to 353.15 K. Molar heat capacities of ternary systems were measured by using a differential scanning calorimeter (DSC). In this study, the heat capacities of binary aqueous 1DMAP solutions over the entire range of compositions were also determined. The obtained heat capacity data were correlated as a function of temperature and amine concentration using a modified Söhnel and Novotný equation and a Redlich-Kister expansion for the aqueous 1DMAP/DETA and aqueous 1DMAP solutions, respectively. The calculated molar heat capacities show a good agreement with the experimental data at average absolute deviation s of 0.05%, 0.57% and 0.2% for the pure, binary, and ternary systems, respectively. The heat capacities of aqueous mixtures of 1DMAP with DETA presented in this study are, in general, of sufficient accuracy for most engineering-design calculations.

Keywords- molar heat capacity, 1-dimethylamino-2-propanol, diethylenetriamine, Redlich-Kister expansion, Söhnel and Novotný equation

I. INTRODUCTION

A wide variety of alkanolamines, such as monoethanolamine (MEA), diethanolamine (DEA), N-methyldiethanolamine (MDEA), triethanolamine (TEA), and 2-amino-2-methyl-1-propanol (AMP), can be used as absorbents for the removal of CO2 and H2S from gas streams in the natural gas, petroleum chemical plants, and synthetic ammonia industries [1-3]. However, it is always an ongoing process to develop a better CO2 absorbers with better CO2 absorption performance, more economic, and less environmental impact.

Recently the use of blended amines, a solution of two or more amines in varying compositions, show considerable improvement in absorption and savings in energy requirements; blended amines combine the absorption characteristics of the constituent amines such as a higher loading capacity and faster reaction rates [2, 4-6].

The CO2 absorption properties by using the aqueous tertiary amine 1-dimethylamino-2-propanol (1DMAP) have been studied as an alternative CO2 absorbent. The aqueous 1DMAP has been shown to have a higher solubility and a lower absorption heat than those of MEA and MDEA, and a faster absorption rate than that of MDEA [6, 7].

Polyamines are known as absorption activators due to the additional amine functionalities that can potentially capture CO2. Polyamines such as diethylenetriamine (DETA) has been shown to have superior CO2 absorption rate and capacity as well as lower vapor pressure over MEA [8, 9].

Based on the encouraging results of 1DMAP and DETA, it is suggested that these blended amines, the aqueous 1DMAP/DETA systems, may have the potential to be an excellent CO2 absorbent, i.e., exhibits more effective, more economic, and less environmental impact.

Heat capacity data for alkanolamine solvents are necessary to be able to dimension heat exchangers used in gas-treating processes [1]. This property gives idea on energy requirement during operation. However, most experimental works regarding aqueous 1DMAP/DETA reported only on solvent performance, e.g. kinetics and absorption [6-8]. Information solely based on these is not enough for evaluating the practicability of the solvent. To the best of our knowledge, heat capacities of these systems are still limited or lacking and therefore it is necessary to accumulate a sufficient data bank for the CO2 absorption process design. Thus, the objective of this study is to measure heat capacity data of ternary systems containing 1DMAP and DETA. Heat capacity determinations were carried out at 30 wt% total amine concentration and temperature range of 303.15 to 353.15 K using the differential scanning calorimeter.

II. EXPERIMENTAL

A. Chemicals

1-Dimethylamino-2-propanol (1DMAP, purity >99%) and diethylenetriamine (DETA, purity >99%) were obtained from Arcos Co., Ltd., and used without further purification. The description of the chemicals used is presented in Table I.
TABLE I. DESCRIPTION OF CHEMICALS USED

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Abbreviation</th>
<th>CAS no.</th>
<th>Molar mass</th>
<th>Chemical formula</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Dimethylamino-2-propanol</td>
<td>1DMAP</td>
<td>108-16-7</td>
<td>103.16</td>
<td>C₅H₁₃NO</td>
<td><img src="H3C%5Ctext%7BN%7D%5Ctext%7BH%7D2" alt="Chemical structure" /> \quad \text{N}\text{CH}3</td>
</tr>
<tr>
<td>Diethylenetriamine</td>
<td>DETA</td>
<td>111-40-0</td>
<td>103.17</td>
<td>C₄H₁₃N₃</td>
<td><img src="H3N%5Ctext%7BH%7D2%5Ctext%7BN%7D" alt="Chemical structure" /> \quad \text{H}\text{N}2</td>
</tr>
</tbody>
</table>

All solutions were prepared by mass using an analytical balance (Mettler Toledo, model AL204) having an accuracy of ±1×10⁻⁷ g. Distilled water of Type 1 reagent-grade (resistivity = 18.3 Ω·cm), which was deionized using a compact water purification system (Barnstead Thermodyne Easy Pure LF), was used in the experiments.

B. Heat Capacity Measurement

The measurement of heat capacity, \( C_P \), was performed using TA Instruments heat flow differential scanning calorimeter (DSC) (model DSC Q20), applying the sapphire method according to [10]. The DSC was equipped with a thermal analysis controller and operated in conjunction with a Refrigerated Cooling System (model RCS90) by TA Instruments. The DSC allows experiments within an operating temperature range of ambient to 998 K and with a temperature repeatability of ±0.1 K. It determines the temperature and heat flow associated with material transitions as a function of time and temperature. Based on gathered measurements, the calorimetric sensitivity was 1 μW with a precision of ±1%.

The purge gas was nitrogen (purity >99.9995%) with a flow rate of 50 mL·min⁻¹.

The liquid sample (sample mass range of 10-15 mg) was weighed in a Shimadzu (model AUW220D) analytical balance with an accuracy of ±1×10⁻⁷ g and encapsulated in an alodined aluminum hermetic pan using a press. The \( C_P \) of the sample was measured by comparing the differential heat flow curve of the sample with that of a reference standard material (sapphire), both of which were blank corrected. For each run, the method consisted a 2-min isothermal period at 15 °C, followed by a temperature ramp from (15 °C to 85 °C) at a heating rate of 5 °C·min⁻¹, and then an isothermal stage at 85 °C for 1 min. Five replicate runs were carried out for each measurement and average values were reported. Calibrations are checked periodically to ensure accuracy of measurements. The description of calibration details are the same as those described in previous works [11-13].

III. RESULTS AND DISCUSSION

To verify the accuracy of the method and equipment used, the molar heat capacities of water were measured and presented in Table II. The data were found to be in good agreement with the available data [14] with an average absolute deviation (AAD) of 0.05 %. The overall uncertainty of \( C_P \) measurements is estimated to be ±2 % based on validation with water, uncertainties of the measured weights and the repeatability of the measurements.

The experimental molar heat capacities of 1DMAP and its aqueous binaries for temperatures from 303.15 to 353.15 K and atmospheric pressure (\( P = 101.3 \text{ kPa} \)) are listed in Table III. As an effort to provide comparison, the measured data were plotted in Fig. 1, along with two estimated values using the group contribution methods [15, 16]. The behavior of the experimental \( C_P \) values for 1DMAP obtained in this work are in good agreement with the estimated value [16]. The obtained values of \( C_P \) of 1DMAP are expressed as a function of temperature, \( T \), as

\[
C_P(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = 276.51 - 0.0864 \cdot T(\text{K}) + 0.0008 \cdot T^2(\text{K}^2) \quad (1)
\]

The AAD between the experimental molar heat capacity data and the calculated values using (1) was 0.05 %. Equation (1) is shown as a solid line in Fig. 1.

The dependence of the aqueous solution of 1DMAP with temperature and composition was also determined. According to [17], the excess molar heat capacity, \( \dot{C}_P^E \), of binary mixtures is defined as

\[
\dot{C}_P^E(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = C_P - \sum_{j} x_j C_{P,j} \quad (2)
\]

TABLE II. EXPERIMENTAL MOLAR HEAT CAPACITY OF WATER

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Heat capacity, ( C_P ) (J·mol⁻¹·K⁻¹)</th>
<th>( \text{Sabbah et al. [14]} )</th>
<th>This study</th>
</tr>
</thead>
<tbody>
<tr>
<td>303.15</td>
<td>75.3</td>
<td>75.4 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>308.15</td>
<td>75.3</td>
<td>75.3 ± 0.07</td>
<td></td>
</tr>
<tr>
<td>313.15</td>
<td>75.3</td>
<td>75.2 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>318.15</td>
<td>75.3</td>
<td>75.2 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>323.15</td>
<td>75.3</td>
<td>75.3 ± 0.13</td>
<td></td>
</tr>
<tr>
<td>328.15</td>
<td>75.3</td>
<td>75.4 ± 0.07</td>
<td></td>
</tr>
<tr>
<td>333.15</td>
<td>75.4</td>
<td>75.4 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>338.15</td>
<td>75.4</td>
<td>75.6 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>343.15</td>
<td>75.5</td>
<td>75.7 ± 0.09</td>
<td></td>
</tr>
<tr>
<td>348.15</td>
<td>75.5</td>
<td>75.6 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>353.15</td>
<td>75.6</td>
<td>75.7 ± 0.05</td>
<td></td>
</tr>
</tbody>
</table>

**AAD (%)** 0.05
TABLE III. Molar Heat Capacities of 1DMAP (1) + H₂O (2) Mixtures at Different Temperatures \( (P = 101.3 \text{ kPa}) \)

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( x_1 = 0.100 )</th>
<th>( x_1 = 0.300 )</th>
<th>( x_1 = 0.500 )</th>
<th>( x_1 = 0.700 )</th>
<th>( x_1 = 0.900 )</th>
<th>( x_1 = 1.000 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>303.15</td>
<td>101.0</td>
<td>148.1</td>
<td>181.0</td>
<td>207.1</td>
<td>232.4</td>
<td>246.6</td>
</tr>
<tr>
<td>308.15</td>
<td>101.3</td>
<td>149.4</td>
<td>182.7</td>
<td>209.0</td>
<td>234.5</td>
<td>247.9</td>
</tr>
<tr>
<td>313.15</td>
<td>101.6</td>
<td>150.7</td>
<td>184.4</td>
<td>211.1</td>
<td>236.9</td>
<td>249.6</td>
</tr>
<tr>
<td>318.15</td>
<td>102.1</td>
<td>152.2</td>
<td>186.4</td>
<td>213.1</td>
<td>239.2</td>
<td>251.5</td>
</tr>
<tr>
<td>323.15</td>
<td>102.5</td>
<td>153.3</td>
<td>188.1</td>
<td>215.4</td>
<td>241.1</td>
<td>253.5</td>
</tr>
<tr>
<td>328.15</td>
<td>102.7</td>
<td>154.6</td>
<td>190.0</td>
<td>217.4</td>
<td>243.2</td>
<td>255.1</td>
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<tr>
<td>333.15</td>
<td>103.0</td>
<td>155.9</td>
<td>191.8</td>
<td>219.6</td>
<td>245.3</td>
<td>256.5</td>
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<tr>
<td>338.15</td>
<td>103.3</td>
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<td>193.9</td>
<td>221.7</td>
<td>247.6</td>
<td>257.7</td>
</tr>
<tr>
<td>343.15</td>
<td>103.6</td>
<td>158.1</td>
<td>195.9</td>
<td>223.7</td>
<td>249.5</td>
<td>259.1</td>
</tr>
<tr>
<td>348.15</td>
<td>103.9</td>
<td>159.3</td>
<td>197.7</td>
<td>225.8</td>
<td>251.4</td>
<td>261.0</td>
</tr>
<tr>
<td>353.15</td>
<td>104.2</td>
<td>160.5</td>
<td>200.2</td>
<td>227.8</td>
<td>253.0</td>
<td>262.7</td>
</tr>
</tbody>
</table>

\[
C_P^E (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = C_P - \sum x_i C_{P,i} \tag{2}
\]

where \( x_i \) and \( C_{P,i} \) are the mole fraction and molar heat capacity of component \( i \), respectively. This calculation was followed by a correlation of the \( C_P^E \) with composition and temperature using a Redlich-Kister equation [18] as follows,

\[
C_P^E (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = x_i \sum_{i=1}^{n} A_i (x_i - x_j)^{i-1} \tag{3}
\]

where \( A_i \) is assumed to follow (4) below

\[
A_i = a_{i0} + a_{i1} T(K) \cdot \tag{4}
\]

A least-squares regression was used to determine the values of the adjustable parameters \( a_{i0} \) and \( a_{i1} \) in (4). The determined parameters are summarized in Table IV. The AADs for \( C_P \) and \( C_P^E \) are 0.57% and 5.5%, respectively. The calculated \( C_P \) and \( C_P^E \) values are represented as solid lines in Fig. 2 and Fig. 3. In Fig. 2, it is observed that \( C_P \) values increase with temperature and amine concentration. Increase of \( C_P \) with amine concentration is due to higher heat capacities of the amine over water. Moreover, it is shown in Fig. 3 that \( C_P^E \) values are all positive for the entire composition range and follow an increasing behavior with temperature for a constant \( x_1 \). Both figures depict good agreement of the experimental and calculated results.

Figure 1. Comparison of experimental molar heat capacity of 1DMAP with estimation methods: ●, Chueh and Swanson (cald) [16]; ▲, Missenard (cald) [15]; ■, this study; line, calculated by (1).

Figure 2. Molar heat capacities of 1DMAP + H₂O mixtures as a function of temperature: □, H₂O by Sabbah et al. [14]; ■, \( x_1 = 0.10 \); ●, \( x_1 = 0.30 \); ▲, \( x_1 = 0.50 \); □, \( x_1 = 0.70 \); ●, \( x_1 = 0.90 \); ○, \( x_1 = 1.0 \). Lines, calculated values.
Figure 3. Excess molar heat capacities of 1DMAP (1) + H2O (2) systems at different temperatures: ■ 303.15 K; ▲ 313.15 K; ▶ 323.15 K;  ▼ 333.15 K; ▣ 343.15 K; ● 353.15 K; lines, calculated using (3).

TABLE IV. FITTED PARAMETERS OF REDLICH-KISTER EQUATION FOR THE EXCESS MOLAR HEAT CAPACITIES AND HEAT CAPACITIES OF AQUEOUS BINARY SYSTEMS

<table>
<thead>
<tr>
<th>i</th>
<th>Parameters</th>
<th>No. of data points</th>
<th>AAD (%)</th>
<th>C_P^a</th>
<th>C_P</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>a1 0</td>
<td>65</td>
<td>5.5</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>b1 0</td>
<td>65</td>
<td>1.7</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>

a. AAD(%) = 100/n \sum_{i=1}^{n} \left| \frac{C_{exp} - C_{calc}}{C_{exp}} \right|, where n is the number of data points.

The fitted parameters of the Redlich-Kister equation are given in Table IV. These parameters allow for the calculation of excess molar heat capacities of aqueous binary systems using Eq. (3).

Table V and Table VI list the molar heat capacities of the 1DMAP + DETA + H2O solutions at the same temperature range for 30 wt% total amine. It can be deduced that the C_P increases with increasing temperature as a result of higher degrees of freedom with higher temperatures. It is also shown that addition of DETA to the aqueous binary 1DMAP solutions tends to reduce the measured C_P, which can be due to the lower heat capacity of DETA compared to 1DMAP. The graphical representation for this behavior is presented in Fig. 4.

For the aqueous ternary systems, the modified Söhnel and Novotný [19] equation was used to represent the measured data as a function of temperature and concentration as follows,

\[ C_P (J \cdot mol^{-1} \cdot K^{-1}) = C_{P,a} + \sum_{i=1}^{n} B_i \left( m_2 (mol \cdot kg^{-1}) \right) \]  

where C_P,a is the previously calculated molar heat capacity of the polyamine-free aqueous solution (via the Redlich-Kister equation) and m_2 is the molality (in terms of mol polyamine per kg of 1DMAP + water solution). Here, the B_i's are temperature dependent pair-parameters defined as

\[ B_i = b_{i,0} + b_{i,1} T(K) \]  

where b_{i,0} and b_{i,1} are empirical constants presented in Table VI, which were calculated by fitting the experimental data in Eqs. (5) and (6). The determined AADs of 0.2% and 1.7% for the C_P and C_P - C_P,a respectively, suggest good agreement of the experimental data and the corresponding calculated values.

Figure 4. Molar heat capacity of 1DMAP (1) + DETA (2) + H2O (3) solutions as function of temperature (30 wt% total amine concentration): ■ 25 wt% 1DMAP/5 wt% DETA/70 wt% H_2O; ▲ 20 wt% 1DMAP/10 wt% DETA/70 wt% H_2O; ▶ 15 wt% 1DMAP/15 wt% DETA/70% H_2O;  ▼ 5% 1DMAP/25% DETA/70 wt% H_2O; lines, calculated using (5).

TABLE VI. FITTING PARAMETERS OF THE SÖHNEL AND NOVOTNY EQUATION FOR THE AQUEOUS TERNARY SYSTEMS

<table>
<thead>
<tr>
<th>i</th>
<th>Parameters</th>
<th>No. of data points</th>
<th>AAD (%)</th>
<th>C_P - C_P,a</th>
<th>C_P</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>b_{i,0}</td>
<td>b_{i,1}</td>
<td>88</td>
<td>1.7</td>
<td>0.2</td>
</tr>
</tbody>
</table>

a. AAD(%) = 100/n \sum_{i=1}^{n} \left| \frac{C_{exp} - C_{calc}}{C_{exp}} \right|, where n is the number of data points.

The fitting parameters of the Söhnel and Novotný equation for the aqueous ternary systems are given in Table VI. These parameters allow for the calculation of molar heat capacities of aqueous ternary systems using Eq. (5).
The obtained heat capacity differences, $C_P - C_P,a$, of the aqueous ternaries are graphically shown in Fig. 5. It can be seen in these figures that the values of $C_P - C_P,a$ systematically increase with the polyamine (DETA) concentration. However, a decreasing behavior with temperature was obtained at lower 1DMAP concentrations, and shifts to increase at higher amounts of 1DMAP in the solution. This observation may be attributed to the great dependence of $C_P - C_P,a$ values on the 1DMAP concentration.

IV. CONCLUSION

A new set of molar heat capacity data for the tertiary amine, 1DMAP, and its aqueous binary were presented. Experimental molar heat capacity of the aqueous ternary system of 1DMAP with DETA at 30 wt% total amine were also reported. The applied models were suitable which was suggested by the acceptable AADs of 0.57% for the binary systems using the Redlich-Kister equation and 0.2% for the ternaries applying the Söhnel and Novotný equation. Thus, the result of this study can be applied in the design calculations for CO$_2$ absorption process using the aqueous 1DMAP + DETA as the CO$_2$ absorbent.

REFERENCES
