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Heat Capacity of Sodium Aminoacetate Solutions before and after CO_2 Absorption

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The heat capacities of aqueous solutions of sodium aminoacetate (CAS no. 6000-44-8) and CO_2-loaded aqueous sodium aminoacetate solutions were measured for a range of sodium aminoacetate mass fractions $w = (0.01, 0.05, 0.10, 0.15, 0.20, \text{and } 0.30)$ and at a temperature range of $T = (298.15 \text{ to } 323.15)$ K. It was found that the heat capacity of the aqueous solution of sodium aminoacetate decreases as the concentration increases and increases with an increase in temperature. The heat capacity of CO_2-loaded aqueous sodium aminoacetate solution was found to increase with temperature and decrease with an increase in CO_2 loading. The heat capacities of the CO_2-loaded aqueous sodium aminoacetate solution were lower than those of the unloaded solutions.

Introduction

The most common process used for the removal of acid gases such as carbon dioxide and hydrogen sulfide from the natural gas is absorption using alkanolamines as reactive solvents. Currently, aqueous alkanolamine solutions have been preferred as reactive solvents because of their high reactivity, low cost, and high thermal stability. However, alkanolamines, especially monoethanolamine (MEA), have problems like degradation through oxidation of the amine, loss of the amine during the stripping process, and foaming.[1] As an alternative for alkanoalamines in the CO_2 absorption process, amino acid salts have been tested by researchers because of their molecular similarity[2−5] and their unique advantages of physical and chemical properties.[2,6] Even though the costs of amino acids are higher than amine solutions, they are safe for human in terms of toxicity. The volatility is also less when compared with the other amine-based solvents.

One of the amino acid salts which has a very high potential for the capture of CO_2 is sodium aminoacetate. The solubility of carbon dioxide in aqueous solutions of sodium aminoacetate at different pressures has also been studied experimentally.[7,8] To obtain a successful design and development of any absorption process for CO_2 using sodium aminoacetate as solvent, a priori knowledge of its physical properties is also required, besides its solubility data. Some physical properties of aqueous sodium aminoacetate as an absorbent for carbon dioxide removal have been studied previously.[9,10] One of the most important physical properties that is lacking in literature is the heat capacity of sodium aminoacetate solution. The heat capacity data is required for energy balance calculations as well as for the design of heat exchanger equipment.[11]

Heat capacity measurements using a differential scanning calorimeter (DSC) have been applied to determine the heat capacity of alkanolamines.[11−14] Hence, in the present work, heat capacity of aqueous solutions of sodium aminoacetate was measured using a DSC for a range of sodium aminoacetate mass fractions, $w = (0.01, 0.05, 0.10, 0.15, 0.20, \text{and } 0.30)$, and at a temperature range of $T = (298.15 \text{ to } 323.15)$ K. During the absorption of carbon dioxide from natural gas, some physical properties of the absorbent get altered. The physical properties of the absorbent after CO_2 absorption are need to be measured to quantify the effect of CO_2 loading on the physical properties of the absorbent. Hence, in the present work, the heat capacities of CO_2-loaded aqueous sodium aminoacetate solutions were also measured and reported.

Table 1. Heat Capacities of Water

T	C_p/kJ·kg^{-1}·K^{-1}				
		present study			
K	Osborne et al.[17]	run 1	run 2	run 3	average value
303.15	4.1785	4.185	4.181	4.172	4.179
308.15	4.1782	4.187	4.184	4.177	4.183
313.15	4.1786	4.186	4.186	4.181	4.184
318.15	4.1795	4.185	4.187	4.183	4.185
323.15	4.1807	4.183	4.188	4.186	4.185
328.15	4.1824	4.181	4.188	4.188	4.185
333.15	4.1844	4.179	4.188	4.190	4.186
338.15	4.1868	4.177	4.189	4.192	4.186
343.15	4.1896	4.176	4.190	4.195	4.187
348.15	4.1928	4.176	4.192	4.198	4.188
353.15	4.1964	4.175	4.193	4.201	4.190

Experimental Section

Materials. The absorbent used in this study is sodium aminoacetate ($C_2H_4NO_2Na$). Aqueous sodium aminoacetate was prepared by neutralizing glycine (purity ≥ 99.7, Merck) and dissolving in distilled water, with an equimolar sodium hydroxide (purity ≥ 99, R&M Chemicals). The concentration of the amino acid salt was estimated by titrating with standard HCl solutions. The end point is the isoelectric point of glycine.[8] Solution concentrations ranging from $w = (0.01 \text{ to } 0.30)$ were used in the present study. All weight measurements were done using an analytical balance with an accuracy of ± 0.1 mg. The CO_2-loaded sodium aminoacetate solution was produced from the CO_2 absorption process using a SOLTEQ BP-22 high pressure solubility cell. The details of the solubility cell and the experimental procedures for CO_2 absorption are discussed in our earlier work.[8] The CO_2 content was determined using

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Table 2. Heat Capacities of Sodium Aminoacetate (1) + H_2O (2)

T	C_p/kJ·kg^{-1}·K^{-1}						
	present study						Song et al.[18]
K	$w_1 = 0.01$	$w_1 = 0.05$	$w_1 = 0.10$	$w_1 = 0.15$	$w_1 = 0.20$	$w_1 = 0.30$	$w_1 = 0.30$
298.15	4.140	4.084	3.946	3.840	3.635	3.391	3.441
303.15	4.141	4.085	3.947	3.842	3.661	3.417	3.445
308.15	4.143	4.088	3.950	3.845	3.692	3.444	3.450
313.15	4.147	4.092	3.953	3.849	3.723	3.471	3.454
318.15	4.151	4.096	3.956	3.853	3.753	3.500	3.459
323.15	4.152	4.103	3.960	3.859	3.786	3.528	3.463

Table 3. Correlation Coefficients and the SD for Equation 2

w_1	A_0	$10^3\ A_1$	R^2	SD
0.01	3.9774	0.5418	0.9721	0.00078
0.05	3.8536	0.7648	0.9618	0.00130
0.10	3.7749	0.5699	0.9781	0.00073
0.15	3.6134	0.7554	0.9648	0.00123
0.20	1.8256	6.0603	0.9989	0.00162
0.30	1.7528	5.4907	0.9996	0.00098

titration method. The uncertainty of the CO_2 loading is within ± 1 % on the basis of the uncertainty of the titration apparatus. High purity carbon dioxide and nitrogen (> 99.8) were used for the experiments. Pure water of Millipore quality was used for heat capacity calibration.

Apparatus and Procedure. The basic principle for heat capacity measurement using DSC consists of heating the test material at a controlled atmosphere through the region of interest. The difference in heat flow into the test material and a reference or blank due to energy changes in the material was continually monitored and recorded.[15] The DSC used in this study is Pyris 1 DSC, Perkin-Elmer (U.S.A.). The DSC operation range is T = (223.15 to 723.15) K. The condition of the test chamber was maintained by passing nitrogen as a purge gas with a flow rate of 10 mL·min^{-1} during heat capacity measurements. The accuracy of temperature measurement is within ± 0.001 °C. The liquid sample was placed within an aluminum hermetic sample pan (Perkin-Elmer) using the sample encapsulating press method. Samples of (5 to 10) mg were used for the experiments. The sample weight was measured using an analytical balance (Mettler Toledo Dragon 304) with an uncertainty of ± 0.0001 g. The temperature of the sample was raised at a fixed heating rate of 10 K·min^{-1}. The measurement method for heat capacity follows the procedure proposed by Chiu et al.[11] The heat capacity of aluminum oxide determined by Ditmars et al.[16] was used for heat capacity calibration. The heat capacity of the substance can be calculated using the following relation:[11]

$$C_p = \left[\frac{60E}{H_r}\right]\frac{\Delta H}{m} \tag{1}$$

where C_p is heat capacity, E is the cell calibration coefficient, H_r is the heating rate in K·min^{-1}, ΔH is the heat flow difference between the sample measurement and the baseline measurement in mW, and m is the sample mass in milligrams. The estimated uncertainty of the heat capacity measurement is ± 1 %.

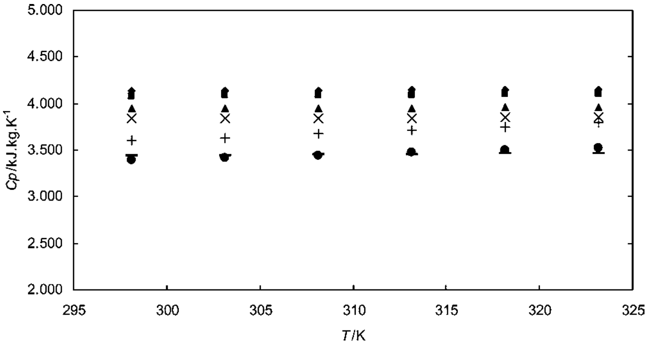

Figure 1. Heat capacity of sodium aminoacetate (1) + water (2) as a function of temperature for a range of sodium aminoacetate mass fractions; ◆, $w_1 = 0.01$; ■, $w_1 = 0.05$; ▲, $w_1 = 0.10$; ×, $w_1 = 0.15$; +, $w_1 = 0.20$; •, $w_1 = 0.30$; solid line, Song et al.,[18] $w_1 = 0.30$.

Results and Discussion

A. Heat Capacity of Aqueous Sodium Aminoacetate Solution. To justify the accuracy of the heat capacity measured using Pyris 1 DCS, the heat capacity of pure water (Millipore) was measured. Three test runs were conducted for the measurement of the heat capacity of water, and the average values are reported in Table 1 along with the available literature data,[17] which shows a good agreement.

The present experimental data on the heat capacity of aqueous sodium aminoacetate solutions are presented in Table 2. The heat capacity data for sodium aminoacetate mass fraction $w_1 = 0.30$ is compared with the available literature data[18] in Figure 1. The heat capacities of sodium aminoacetate mass fraction $w_1 = 0.30$ show a very good agreement with the data of Song et al.[18] The effect of temperature on the heat capacity of aqueous sodium aminoacetate solutions could be represented by the following equation:

$$C_p = A_0 + A_1 T \tag{2}$$

where C_p is the heat capacity in J·g^{-1}·K^{-1}, T is the temperature in K, and A_0, and A_1 are the correlation constants. The standard

Table 4. Heat Capacity of CO_2-Loaded Sodium Aminoacetate (1) + H_2O (2) as a Function of Temperature at Various α (mol CO_2/mol SG) for $w_1 = 0.01$

T	C_p/kJ·kg^{-1}·K^{-1}						
K	α = 0.000	α = 2.313	α = 2.688	α = 3.188	α = 3.375	α = 3.563	α = 4.063
298.15	4.140	4.028	3.983	3.938	3.907	3.897	3.832
303.15	4.141	4.048	4.007	3.968	3.941	3.933	3.872
308.15	4.143	4.068	4.032	4.005	3.977	3.975	3.917
313.15	4.147	4.088	4.061	4.039	4.013	4.014	3.964
318.15	4.151	4.108	4.091	4.068	4.051	4.048	4.013
323.15	4.152	4.128	4.112	4.100	4.090	4.087	4.068

Table 5. Heat Capacity of CO_2-Loaded Sodium Aminoacetate (1) + H_2O (2) as a Function of Temperature at Various α (mol CO_2/mol SG) for $w_1 = 0.05$

T	C_p/kJ·kg^{-1}·K^{-1}						
K	α = 0.000	α = 1.238	α = 1.363	α = 1.375	α = 1.438	α = 1.413	α = 1.525
298.15	4.084	3.953	3.859	3.836	3.790	3.792	3.713
303.15	4.085	3.979	3.876	3.881	3.841	3.841	3.765
308.15	4.088	4.005	3.913	3.932	3.901	3.892	3.822
313.15	4.092	4.031	3.958	3.978	3.958	3.945	3.885
318.15	4.096	4.058	4.010	4.019	4.004	4.002	3.950
323.15	4.103	4.084	4.079	4.064	4.041	4.060	4.010

Table 6. Heat Capacity of CO_2-Loaded Sodium Aminoacetate (1) + H_2O (2) as a Function of Temperature at Various α (mol CO_2/mol SG) for $w_1 = 0.10$

T	C_p/kJ·kg^{-1}·K^{-1}						
K	α = 0.000	α = 0.969	α = 1.156	α = 1.281	α = 1.319	α = 1.363	α = 1.431
298.15	3.946	3.741	3.720	3.632	3.597	3.568	3.515
303.15	3.947	3.775	3.765	3.672	3.621	3.609	3.560
308.15	3.950	3.817	3.814	3.716	3.652	3.649	3.609
313.15	3.953	3.855	3.860	3.766	3.701	3.699	3.666
318.15	3.956	3.885	3.891	3.822	3.778	3.771	3.743
323.15	3.960	3.911	3.896	3.882	3.895	3.883	3.863

Table 7. Heat Capacity of CO_2-Loaded Sodium Aminoacetate (1) + H_2O (2) as a Function of Temperature at Various α (mol CO_2/mol SG) for $w_1 = 0.15$

T	C_p/kJ·kg^{-1}·K^{-1}						
K	α = 0.000	α = 0.929	α = 1.013	α = 1.046	α = 1.054	α = 1.113	α = 1.138
298.15	3.840	3.620	3.552	3.489	3.468	3.420	3.384
303.15	3.842	3.640	3.601	3.547	3.528	3.486	3.453
308.15	3.845	3.674	3.649	3.610	3.601	3.553	3.525
313.15	3.849	3.713	3.697	3.672	3.690	3.632	3.601
318.15	3.853	3.754	3.746	3.732	3.770	3.716	3.679
323.15	3.859	3.812	3.794	3.793	3.792	3.777	3.758

Table 8. Heat Capacity of CO_2-Loaded Sodium Aminoacetate (1) + H_2O (2) as a Function of Temperature at Various α (mol CO_2/mol SG) for $w_1 = 0.20$

T	C_p/kJ·kg^{-1}·K^{-1}						
K	α = 0.000	α = 0.703	α = 0.941	α = 0.991	α = 1.022	α = 1.116	α = 1.134
298.15	3.635	3.490	3.298	3.253	3.232	3.154	3.143
303.15	3.661	3.526	3.367	3.325	3.303	3.247	3.223
308.15	3.692	3.571	3.451	3.400	3.376	3.324	3.311
313.15	3.723	3.618	3.524	3.477	3.454	3.393	3.401
318.15	3.753	3.664	3.581	3.555	3.537	3.473	3.492
323.15	3.786	3.714	3.643	3.633	3.627	3.589	3.587

Table 9. Heat Capacity of CO_2-Loaded Sodium Aminoacetate (1) + H_2O (2) as a Function of Temperature at Various α (mol CO_2/mol SG) for $w_1 = 0.30$

T	C_p/kJ·kg^{-1}·K^{-1}						
K	α = 0.000	α = 0.623	α = 0.906	α = 0.958	α = 0.967	α = 0.985	α = 1.031
298.15	3.391	3.173	3.016	2.861	2.833	2.820	2.775
303.15	3.417	3.207	3.080	2.946	2.912	2.877	2.859
308.15	3.444	3.241	3.156	3.032	2.998	2.966	2.952
313.15	3.471	3.278	3.226	3.121	3.091	3.062	3.055
318.15	3.500	3.316	3.283	3.213	3.193	3.167	3.169
323.15	3.528	3.356	3.334	3.307	3.307	3.303	3.295

deviation (SD) of the data was calculated by the following equation:[19]

$$\mathrm{SD} = \left(\frac{\sum_{1}^{n} (X_{\mathrm{exp}} - X_{\mathrm{cal}})^2}{n} \right)^{0.5} \tag{3}$$

where X_{exp}, X_{cal}, and n are the experimental values, calculated values using the equation, and the number of measurements, respectively. It was found that the heat capacity of aqueous solutions of sodium aminoacetate decreases with the increase in concentration and increases with temperature. The values of the correlation constants, R^2, and the SD for eq 2 are presented in Table 3.

A. Heat Capacity of CO_2-Loaded Aqueous Sodium Aminoacetate Solution. The heat capacity data of CO_2-loaded aqueous sodium aminoacetate solution for sodium aminoacetate mass fraction $w_1 = (0.01$ to $0.30)$, as a function of the loading factor (α = mol CO_2/mol SG), are given in Tables 4, 5, 6, 7, 8, and 9. The heat capacities of aqueous sodium aminoacetate solutions are also included in the tables for the comparison of unloaded solution (loading factor = 0). From the tables it is very clear that the heat capacity of CO_2-loaded solution increases with temperature but decreases with CO_2 loading. Therefore, the heat capacity of the CO_2-loaded aqueous sodium aminoacetate solution was found to be lower than that of unloaded solution.

Conclusion

In the present work, it was found that the heat capacity of aqueous solutions of sodium aminoacetate decreases as the concentration increases and increases with an increase in temperature. The heat capacity of CO_2-loaded aqueous sodium aminoacetate solution increases with temperature but decreases with that of CO_2 loading. The heat capacity of the CO_2-loaded aqueous sodium aminoacetate solution was always found to be lower compared to unloaded solution. These present data must be useful for the enthalpy calculation for absorption as well as the stripping process.

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