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Heat Capacity of Aqueous Monoethanolamine, Diethanolamine, *N*-Methyldiethanolamine, and *N*-Methyldiethanolamine-Based Blends with Carbon Dioxide

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New data are reported on the heat capacity of CO_2-loaded, aqueous solutions of monoethanolamine (MEA), diethanolamine (DEA), *N*-methyldiethanolamine (MDEA), and aqueous MDEA-based blends with MEA and DEA.

Introduction

The work reported here was motivated by the need to quantify the effect of acid gas loading on the important physical properties of gas-sweetening solvents. Focus is on the effect of CO_2 loading on the specific heat of amine-treating solutions, in the form of both single amines and *N*-methyldiethanolamine-based blends. It should be pointed out, however, that dissolved H_2S, which we have not studied here, is likely also to have a no-less-important impact. Little or no data exist for the effect of H_2S loading on physical properties, and data are certainly needed.

Experimental Section

Heat capacity was determined by measuring the temperature rise of a known mass of sample in response to a known electrical energy input via an immersed ohmic resistance. Samples were contained in a stoppered and gently-stirred Dewar flask, and the equipment was calibrated (the cell constant determined) using water and various salt solutions as standards. This was not an isothermal experiment. Temperature measurements were started below 25 °C and continued to above this temperature so that measurements bracketing the desired temperature were made. The repeatability of the heat capacity measurements was ±1%. and test runs on standard systems with known heat capacities gave results also within ±1% of the reported values.

All the amine solutions on which heat capacity measurements were made were preloaded with known amounts of CO_2. For each amine of a specified concentration, a large batch of aqueous solution was made up and roughly one-half of it was saturated with CO_2 by sparging CO_2 into the solution through sintered glass disks. Aliquots from these two batches, one unloaded and the other saturated with CO_2 at atmospheric pressure, were mixed together in various proportions to make up a series of solutions all having the same amine to water ratio but each one having a different CO_2 loading. For each sample containing a single amine, the total amine concentration and the CO_2 loading were determined titrimetrically using the method of Weiland and Trass (1969). For mixtures of two amines, their individual concentrations could not be determined titrimetrically (an inherently high precision method of analysis compared, say, to gas chromatography), so we relied on careful, accurate weighing of the constituents and their mixing together to make the original solutions on a mass basis; however, the CO_2 loading was still determined titrimetrically for each sample on which data were taken. Several kilograms of each original CO_2-free solution was made, and each constituent was weighed with an accuracy of ±0.1 g. All heat capacities are reported at 25 °C.

Table 1. Heat Capacity ($J\ g^{-1}\ K^{-1}$) of CO_2-Loaded MDEA Solutions at 25 °C

loading (mol/mol)	30 mass % MDEA	40 mass % MDEA	50 mass % MDEA	60 mass % MDEA
0.00	3.787	3.585	3.407	3.174
0.05	3.761	3.531	3.366	
0.10	3.703	3.528	3.342	
0.13				3.087
0.15	3.684	3.526	3.298	
0.20	3.684	3.473	3.294	
0.25	3.636	3.460	3.208	3.005
0.30	3.607	3.384	3.163	
0.35	3.545	3.365	3.136	
0.38				2.976
0.40	3.496	3.350	3.132	
0.45	3.436	3.287	3.120	
0.50	3.436	3.240	3.094	
0.51				2.886
0.64				2.849

Table 2. Heat Capacity ($J\ g^{-1}\ K^{-1}$) of CO_2-Loaded DEA Solutions at 25 °C

loading (mol/mol)	10 mass % DEA	20 mass % DEA	30 mass % DEA	40 mass % DEA
0.00	4.047	3.915	3.778	3.566
0.05		3.878	3.699	3.535
0.10	4.034	3.850	3.663	3.486
0.15		3.834	3.648	3.465
0.20	3.987	3.798	3.639	3.416
0.25		3.792	3.616	3.405
0.30	3.965	3.761	3.565	3.372
0.35		3.763	3.547	3.239
0.40	3.946	3.740	3.527	3.315
0.45		3.729	3.515	3.295
0.50	3.923	3.711	3.474	3.278

Table 3. Heat Capacity ($J\ g^{-1}\ K^{-1}$) of CO_2-Loaded MEA Solutions at 25 °C

loading (mol/mol)	10 mass % MEA	20 mass % MEA	30 wt MEA	40 mass % MEA
0.00	4.061	3.911	3.734	3.634
0.05	4.015			
0.10		3.823	3.656	3.508
0.20	3.917	3.766	3.570	3.343
0.30	3.915	3.670	3.457	3.238
0.40	3.891	3.648	3.418	3.163
0.50	3.857	3.597	3.359	3.109

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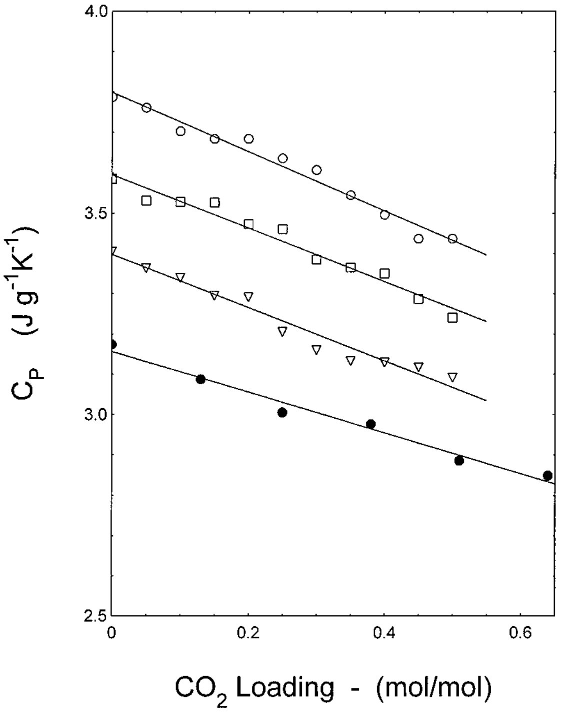

Figure 1. Heat capacity of CO_2-loaded MDEA solutions at 25 °C: ○, 30 mass % MDEA; □, 40 mass % MDEA; ▽, 50 mass % MDEA; ●, 60 mass % MDEA.

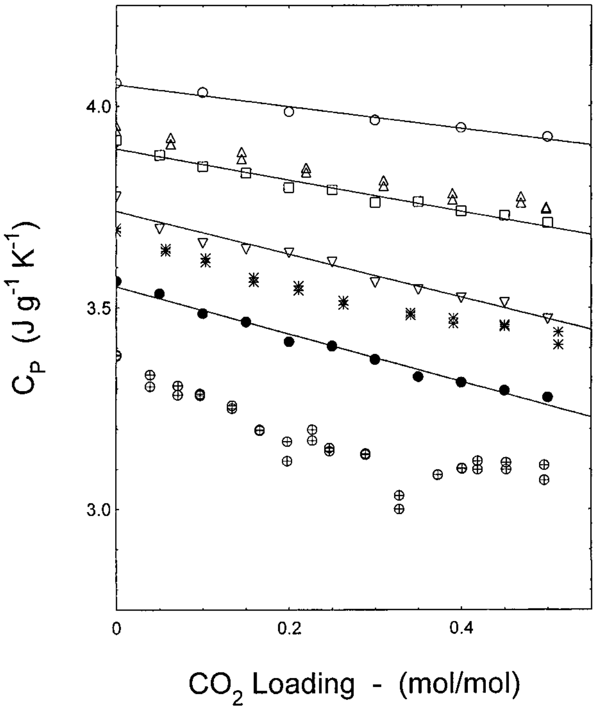

Figure 2. Heat capacity of CO_2-loaded DEA solutions at 25 °C; ○, 10 mass % DEA; □, 20 mass % DEA; ▽, 30 mass % DEA; ●, 40 mass % DEA; △, 20 mass % DEA, Kahrim & Mather (1980); *, 35.5 mass % DEA, Kahrim & Mather (1980); ⊕, 50 mass % DEA, Kahrim & Mather (1980).

Results

The heat capacity data for *N*-methyldiethanolamine (MDEA), diethanolamine (DEA), and monoethanolamine (MEA) as a function of CO_2 loading are given in Tables 1−3 and in Figures 1−3. Corresponding data for aqueous DEA/MDEA and MEA/MDEA blends are shown in Tables 4 and 5 and Figures 4 and 5.

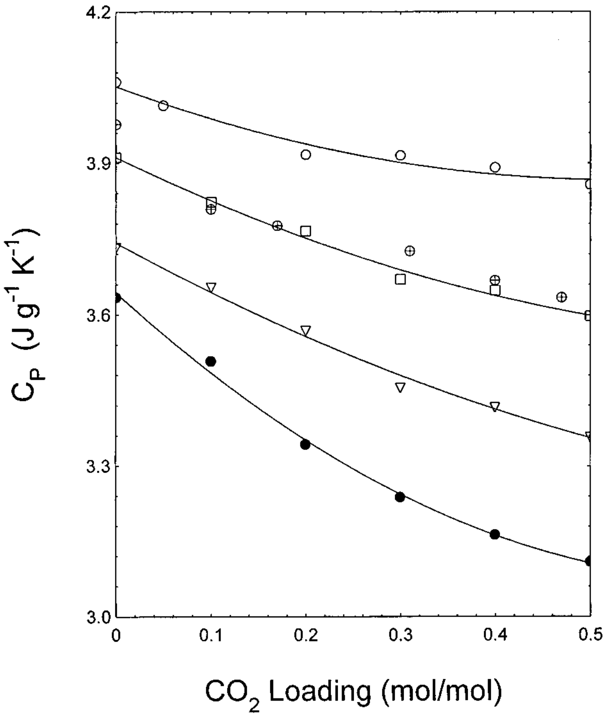

Figure 3. Heat capacity of CO_2-loaded MEA solutions at 25 °C: ○, 10 mass % MEA; □, 20 mass % MEA; ▽, 30 mass % MEA; ●, 40 mass % MEA; ⊕, 20 mass % MEA, Dow Chemical Company (1982).

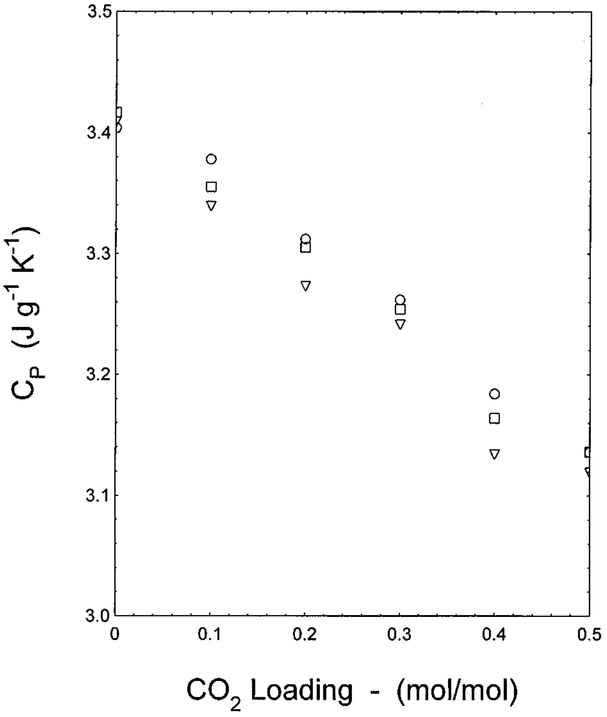

Figure 4. Heat capacity of CO_2-loaded DEA−MDEA blends at 25 °C: ○, 5 mass % DEA and 45 mass % MDEA; □, 10 mass % DEA and 40 mass % MDEA; ▽, 20 mass % DEA and 30 mass % MDEA

Discussion

As shown in Figures 1−3, measured heat capacities are always a decreasing function of loading, and the higher the amine concentration the greater the sensitivity to CO_2 content. The lines in Figures 1 and 2 are least-squares linear fits to our data; the lines in Figure 3 are least-squares quadratic fits to our data. As shown in Figure 2,

Table 4. Heat Capacity (J g^{-1} K^{-1}) of CO_2-Loaded DEA/MDEA Blends at 25 °C

loading (mol/mol)	5 mass % DEA 45 mass % MDEA	10 mass % DEA 40 mass % MDEA	20 mass % DEA 30 mass % MDEA
0.00	3.404	3.417	3.410
0.10	3.378	3.355	3.340
0.20	3.312	3.305	3.274
0.30	3.262	3.254	3.242
0.40	3.184	3.164	3.135
0.50	3.136	3.136	3.120

Table 5. Heat Capacity (J g^{-1} K^{-1}) of CO_2-Loaded MEA/MDEA Blends at 25 °C

loading (mol/mol)	5 mass % MEA 45 Mass% MDEA	10 mass % MEA 40 mass % MDEA	20 mass % MEA 30 mass % MDEA
0.00	3.440	3.384	3.445
0.10	3.374	3.315	3.319
0.20	3.257	3.246	3.234
0.30	3.205	3.161	3.158
0.40	3.112	3.079	3.074
0.50	3.064	3.013	2.992

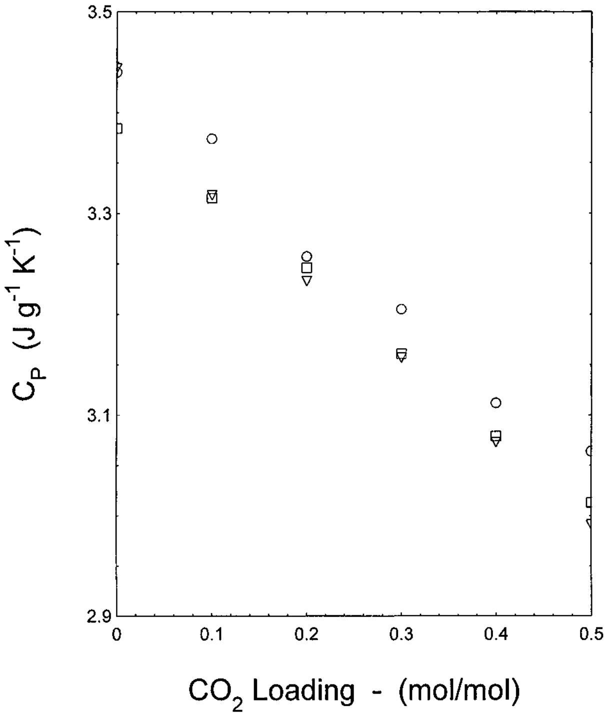

Figure 5. Heat capacity of CO_2-loaded MEA–MDEA blends at 25 °C: ○, 5 mass % MEA and 45 mass % MDEA; □, 10 mass % MEA and 40 mass % MDEA; ▽, 20 mass % MEA and 30 mass % MDEA.

our data for DEA tend to fall slightly below the data of Kahrim and Mather (1980) for 20 mass % DEA. Their data for 35.5 mass % and 49.7 mass % DEA at 25 °C are shown also in the same figure. In Figure 3 our data for 20 mass % MEA are compared with data provided by Dow Chemical Company, and, to within the scatter in the measurements, the two data sets appear to be in substantial agreement.

In mixed amines (Figures 4 and 5), the data show that at a given, constant, total amine concentration there is no consistent dependence of heat capacity on the relative proportions of the two amines constituting the blend, at least to within the inherent scatter in the data. Just as for single amines, the heat capacity of amine mixtures decreases approximately linearly with CO_2 loading.

Acknowledgment

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