

Density, Viscosity, and Solubility of CO₂ in Aqueous Solutions of 2-Amino-2-hydroxymethyl-1,3-propanediol

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The densities and viscosities of aqueous solutions of 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) were measured over the temperature range from (303.15 to 343.15) K and at the AHPD concentrations (5, 10, 15, 20, and 25) mass %. The solubilities of carbon dioxide in aqueous AHPD solutions were also measured at (313.15, 323.15, and 333.15) K over partial pressures of carbon dioxide ranging from (1 to 2000) kPa. The concentrations of aqueous AHPD solutions were (10 and 20) mass %. The thermodynamic characteristics of aqueous AHPD solution as a potential CO₂ absorbent were identified through measurements of these three key properties.

Introduction

The removal of acid gases from refinery and natural gases is of great importance. Aqueous solutions of alkanolamines have been widely used in gas treatment. Recently, the growing interest in aqueous solutions of sterically hindered amines for gas treatment processes might be due to their high cyclic capacity and relatively high absorption rates at high CO₂ loadings.¹ 2-Amino-2-ethyl-1-propanol (AMP) and 2-piperidineethanol (2-PE) are widely used sterically hindered amines. Because of the hindrance of the bulky group attached to the tertiary carbon atom, the unstable carbamate ions are formed in the reaction of the AMP solutions with CO₂, which results in a theoretical loading capacity up to 1.0 mol of CO₂/mol of amine. The solubility of carbon dioxide in aqueous AMP solutions has been reported, and it shows a higher CO₂ loading capacity than that of aqueous MEA solutions.^{2,3}

In the present study, an aqueous solutions of 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD), one of the sterically hindered amines, was chosen as a potential CO₂ absorbent. However, its thermodynamic characteristics must be known prior to practical application. Both the determination of reaction kinetics and the design of appropriate acid gas treatment equipment require essential physical properties such as density and viscosity of aqueous amine solutions. In addition, the equilibrium solubility data must be known for the feasible design and modeling of the gas treating process.

Experimental Section

Materials. Aqueous AHPD solutions were prepared with distilled water and 99+% 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) from Aldrich Chemical Co. All the chemicals were used without further purification. The

carbon dioxide and nitrogen gases provided for equilibrium solubility measurement were of commercial grade with a purity of 99.9%.

Density and Viscosity. Densities of aqueous AHPD solutions were measured by using calibrated pycnometers. To determine volumes of pycnometers at various temperatures from (303.15 to 343.15) K, triple-distilled water was used as a standard substance. The measurements were performed in a constant temperature water bath, in which the temperature could be controlled within ± 0.05 K with an external heater/cooler. Each temperature was measured with a calibrated mercury-filled glass-thermometer. A Sartorius R120S balance with a precision of ± 0.0001 g was used for weighing the amounts of amines and water. The uncertainty of the measured density was estimated to be within ± 0.0003 g·cm⁻³.

Viscosities of aqueous AHPD solutions were measured with several Ubbelohde viscometers (Witeg) having various capillary sizes. An appropriate viscometer was selected in consideration of the estimated values of kinematic viscosity. Measurements were made in a water bath whose temperature was kept constant within ± 0.05 K. Kinematic viscosities were calculated from the efflux times measured with an electronic stopwatch with an accuracy of 0.01 s. The kinematic viscosity values were reproducible within $\pm 1\%$. The dynamic viscosities were calculated by multiplying the kinematic viscosities with the density values of the same solutions.

The validity of the procedure and apparatus for density and viscosity measurements was tested in our previous work.⁴

Solubility. The apparatus used for this work consisted of an equilibrium cell, a gas chromatograph, a pressure gauge and thermometer, a circulation pump, valves, and cylinders of carbon dioxide, nitrogen, and helium. The equilibrium cell was made of 316 stainless steel with an internal volume of about 450 mL. This cell was connected

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Table 1. Densities ($\rho/\text{g}\cdot\text{cm}^{-3}$) of Aqueous 2-Amino-2-hydroxymethyl-1,3-propanediol (AHPD) Solutions

T/K	ρ at the following conc of AHPD/mass %				
	5	10	15	20	25
303.15	1.0084	1.0210	1.0344	1.0474	1.0613
313.15	1.0047	1.0174	1.0306	1.0434	1.0571
323.15	1.0003	1.0131	1.0262	1.0390	1.0525
333.15	0.9951	1.0076	1.0200	1.0330	1.0470
343.15	0.9900	1.0022	1.0148	1.0275	1.0413

Table 2. Density Correlation Parameters and AAD% of Aqueous 2-Amino-2-hydroxymethyl-1,3-propanediol (AHPD) Solutions

	A_i	B_i	C_i
$i = 0$	0.7319	0.2053×10^{-2}	-0.3910×10^{-5}
$i = 1$	0.2359×10	-0.1309×10^{-2}	0.2038×10^{-4}
AAD(%)		0.04	

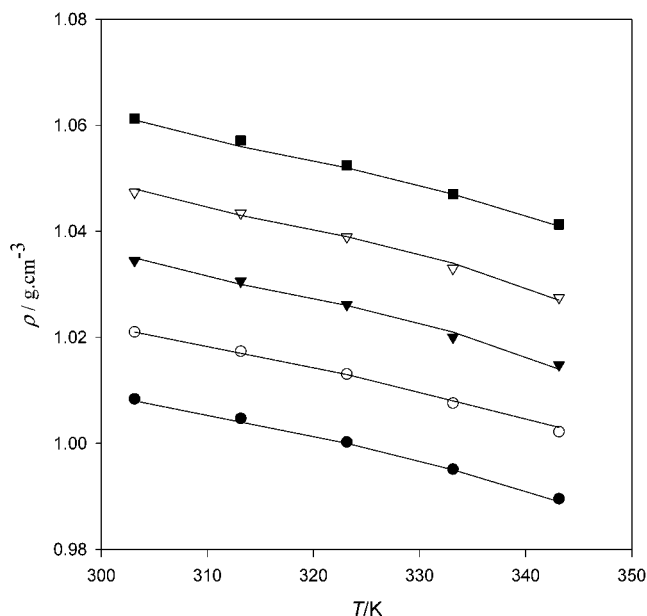
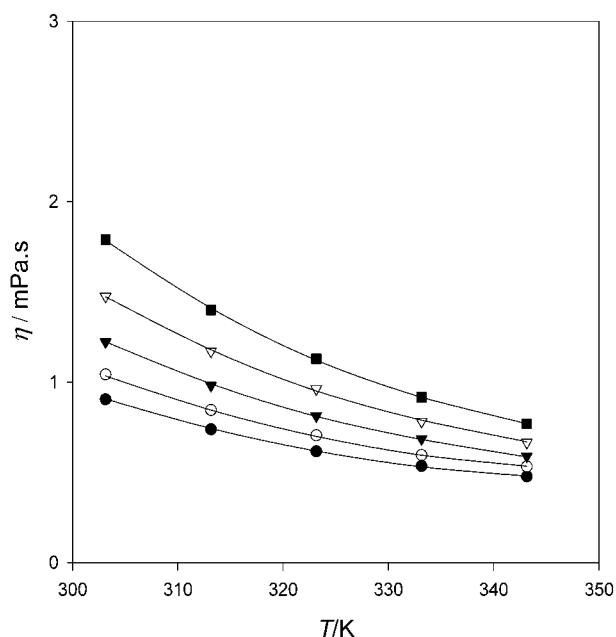
to a gas chromatograph (Hewlett-Packard, 5890 Series II Plus) with a vapor sampling valve (Rheodyne 7410) with a loop of about 500 μL . This sample was used to determine the composition of the vapor phase. For the gas chromatograph the column was 1.8 m by 3 mm diameter and packed with Porapak Q. Helium, carrier gas, with a flow rate of 30 mL/min and a thermal conductivity detector (TCD) were used for the GC analysis. The temperatures of the oven, injector, and detector in the gas chromatograph were (40, 120, and 120) $^{\circ}\text{C}$, respectively. The equilibrium cell was immersed in a water bath maintained at ± 0.1 $^{\circ}\text{C}$ of the set point temperature by a refrigerator/heater (Jeio Tech, RBC-20), and the temperature in the equilibrium cell was measured with a K-type thermocouple with an accuracy of ± 0.1 K. To measure the system pressure, a Heise gauge (CM 118324, (0 to 3500) kPa range) was used with an accuracy of $\pm 0.1\%$ of the gauge range.

The cell, filled with 300 mL of aqueous AHPD solution, was completely purged with nitrogen gas to remove remaining air at first, and after that most of the nitrogen from the cell was vented to the atmosphere. Then the appropriate amount of carbon dioxide was fed into the cell. In particular, for the experiments at CO_2 partial pressures lower than atmospheric pressure, the mixed gas of carbon dioxide and nitrogen was used, as nitrogen did not react with aqueous AHPD solutions. The composition of carbon dioxide could then be accurately determined from gas chromatography. When the system pressure and vapor composition were constant, the liquid and vapor phases in the cell were considered to have reached equilibrium. The liquid samples withdrawn from the equilibrium cell were analyzed by the titration method.⁵

Results and Discussion

Density and Viscosity. Densities and viscosities of aqueous AHPD solutions were measured over the temperature range from (303.15 to 343.15) K and at the AHPD concentrations (5, 10, 15, 20, and 25) mass %. The experimental results are tabulated in Tables 1 and 3 and plotted in Figures 1 and 2, respectively, with empirical correlation equations. All data points were correlated as a function of temperature and concentration of AHPD by the following polynomial equations.

$$10^{-3}\rho/\text{g}\cdot\text{cm}^{-3} \text{ or } \eta/\text{mPa}\cdot\text{s} = \sum_{i=0}^n [A_i x^i + B_i x^i (T/\text{K}) + C_i x^i (T/\text{K})^2] \quad (1)$$

**Figure 1.** Densities ($\rho/\text{g}\cdot\text{cm}^{-3}$) of aqueous AHPD solutions (mass % AHPD): ■, 25; ▽, 20; ▼, 15; ○, 10; ●, 5. Solid lines are calculated with eq 1.**Figure 2.** Viscosities ($\eta/\text{mPa}\cdot\text{s}$) of aqueous AHPD solutions (mass % AHPD): ■, 25; ▽, 20; ▼, 15; ○, 10; ●, 5. Solid lines are calculated with eq 1.**Table 3. Viscosities ($\eta/\text{mPa}\cdot\text{s}$) of Aqueous 2-Amino-2-hydroxymethyl-1,3-propanediol (AHPD) Solutions**

T/K	η at the following conc of AHPD/mass %				
	5	10	15	20	25
303.15	0.905	1.042	1.221	1.475	1.789
313.15	0.738	0.846	0.981	1.170	1.399
323.15	0.616	0.705	0.811	0.962	1.129
333.15	0.534	0.596	0.685	0.782	0.916
343.15	0.477	0.531	0.588	0.665	0.769

where n is equal to 1 for the density and 2 for the viscosity correlation and x is mass fraction of AHPD. The calculated regression parameters and average absolute deviations (AAD%) are listed in Tables 2 and 4. The AADs of 0.04%

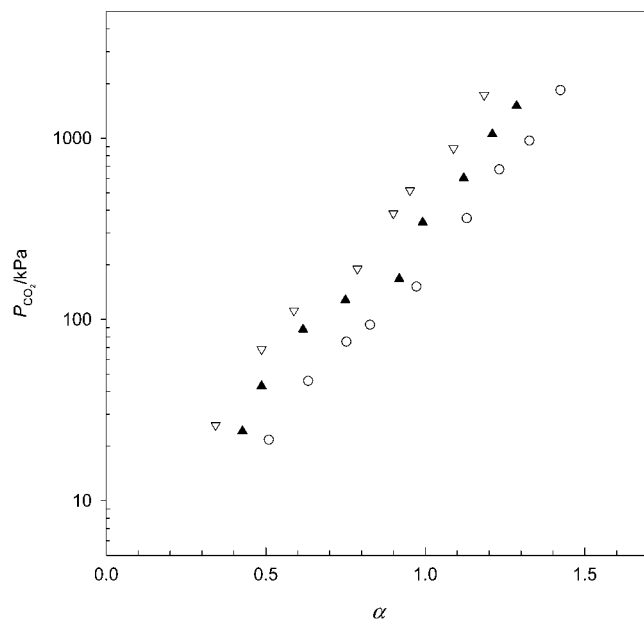
Table 4. Viscosity Correlation Parameters and AAD% of Aqueous 2-Amino-2-hydroxymethyl-1,3-propanediol (AHPD) Solutions

	A_i	B_i	C_i
$i = 0$	0.2334×10^2	-0.1310	0.1874×10^{-3}
$i = 1$	-0.2353×10^2	0.1541	-0.2442×10^{-3}
$i = 2$	0.5746×10^3	-0.3299×10	0.4761×10^{-2}
AAAD(%)		0.5	

Table 5. Solubility of Carbon Dioxide in AHPD Aqueous Solutions

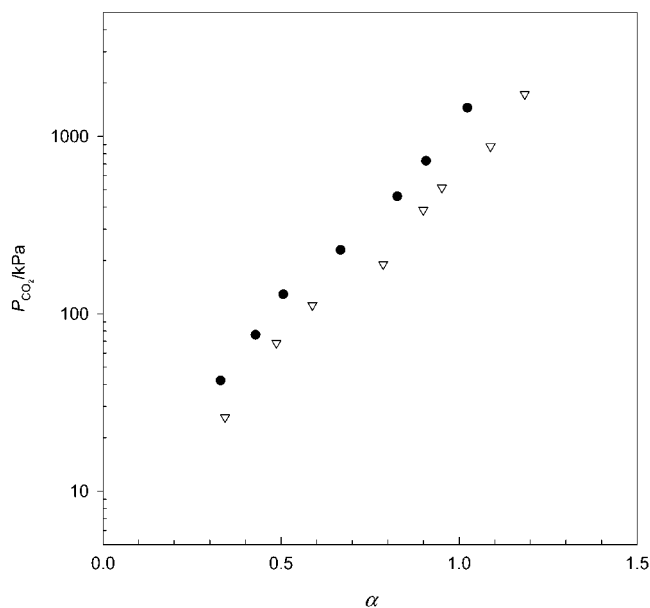
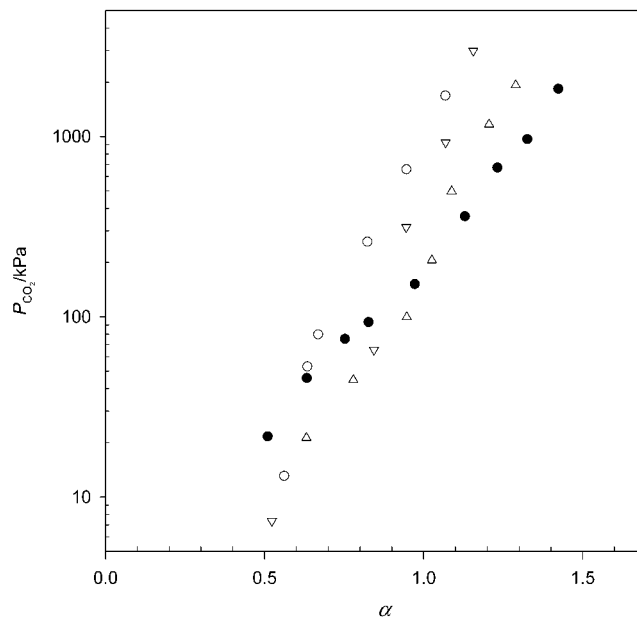
10 mass % AHPD				20 mass % AHPD			
313.15 K		323.15 K		333.15 K		333.15 K	
P/kPa	α^a	P/kPa	α^a	P/kPa	α^a	P/kPa	α^a
21.7	0.510	24.2	0.427	26.1	0.343	42.1	0.330
45.8	0.633	42.9	0.487	68.4	0.487	76.2	0.428
75.4	0.753	88.1	0.617	111.8	0.588	128.9	0.506
93.5	0.827	127.8	0.749	190.4	0.787	229.0	0.667
152.0	0.972	167.6	0.918	384.8	0.900	459.3	0.826
361.6	1.130	342.8	0.992	514.5	0.952	728.2	0.907
672.5	1.232	602.0	1.120	878.5	1.089	1451.5	1.023
968.3	1.326	1052.2	1.210	1728.6	1.184		
1839.8	1.423	1506.6	1.286				

^a Mole of CO₂/mole of AHPD.

**Figure 3.** Solubilities of carbon dioxide in aqueous 10 mass % AHPD solutions at various temperatures: ○, 313.15 K; ▼, 323.15 K; ▽, 333.15 K.

for the density and 0.5% for the viscosity show a good agreement between measured and calculated values.

Solubility. The solubilities of carbon dioxide in aqueous (10 and 20) mass % AHPD solutions were measured at (313.15, 323.15, and 333.15) K and over partial pressures of carbon dioxide ranging from (1 to 2000) kPa. The experimental solubility data points are presented in Table 5 and plotted in Figures 3 and 4. The temperature dependence on the solubility of carbon dioxide in aqueous AHPD solutions is shown in Figure 3. As temperature increased, the solubilities of carbon dioxide in aqueous AHPD solutions decreased. The influence of AHPD concentrations on the solubility is shown in Figure 4. The tendencies shown in Figures 3 and 4 are very similar to the case of aqueous AEPD solutions, which were studied in a previous work.⁶

**Figure 4.** Solubilities of carbon dioxide in aqueous 10 mass % and 20 mass % AHPD solutions at 333.15 K: ▽, 10 mass %; ●, 20 mass %.**Figure 5.** Solubilities of carbon dioxide in aqueous 10 mass % alkanolamine solutions at 313.15 K: ●, AHPD; △, AEPD; ▽, AMPD; ○, MEA.

The solubilities of carbon dioxide in aqueous 10 mass % AHPD solutions at 313.15 K were compared with those in aqueous solutions of various amines such as MEA,⁶ AMPD,⁷ and AEPD⁶ in Figure 5. The CO₂ loading capacity of aqueous AHPD solutions was much higher than that of aqueous MEA solutions at high partial pressures of carbon dioxide. AMPD, AEPD, and AHPD are all sterically hindered amines, and Figure 5 shows that aqueous solutions of these amines have better CO₂ loading capacity than aqueous MEA solution in the order AHPD > AEPD > AMPD. As CO₂ partial pressures decreased, solubilities of carbon dioxide in aqueous AHPD solutions decreased rapidly and eventually became lower than those in aqueous MEA solutions below 50 kPa. This tendency is somewhat similar to the behavior of physical solvents. For a physical solvent, the acid gas (CO₂) solubility is small at low

pressures, but it becomes quite large at high pressures.⁸ At relatively high CO₂ partial pressures, the aqueous AHPD solutions may be more advantageous than aqueous solutions of conventional amines.

Conclusions

In this work 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD) was proposed as a potential CO₂ absorbent. The densities and viscosities of aqueous AHPD solutions were measured over the temperature range from (303.15 to 343.15) K and at the AHPD concentrations (5, 10, 15, 20, and 25) mass %. The solubilities of carbon dioxide in aqueous AHPD solutions were measured at (313.15, 323.15, and 333.15) K over partial pressures of carbon dioxide ranging from (1 to 2000) kPa. As a result of comparing the solubilities of carbon dioxide in aqueous 10 mass % AHPD solutions at 313.15 K with those in aqueous solutions of various amines such as MEA, AMPD, and AEPD, the CO₂ loading capacity of aqueous AHPD solutions was much better than that of aqueous solutions of other amines at high CO₂ partial pressures.

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