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Physical and Thermodynamic Properties of Aqueous 2-Amino-2-Methyl-1,3-Propanediol Solutions

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Densities and viscosities of mixtures of 2-amino-2-methyl-1,3-propanediol (AMPD)–water were measured at temperatures of 30, 40, 50, 60, and 70°C. The solubility of N_2O in the aqueous AMPD solutions was measured at temperatures of 30, 40, and 50°C. The concentrations selected for study were 10, 20, and 30 mass% AMPD for all three temperatures. The experimental values for density and viscosity were correlated as functions of temperature. The maximum deviations were less than 0.005% for densities and 0.3% for viscosities.

KEY WORDS: absorption; AMPD; carbon dioxide; density; solubility; viscosity.

1. INTRODUCTION

The absorption technology of acid gases such as CO_2, H_2S, and COS with aqueous solutions of alkanolamine has been widely used in the chemical industries to purify gas mixtures. Particularly the separation of CO_2 from the flue gas produced by burning fossil fuel has been of great interest owing to the global warming caused by the increase in the concentration of CO_2 in the atmosphere. Therefore, the separation of CO_2 by absorption with chemical absorbents such as alkanolamines has been considered as a challenging method.

Aqueous monoethanolamine (MEA) solutions are the most frequently used chemical absorbents because of high reactivity to such chemicals as carbon dioxide and hydrogen sulfide. However, highly MEA-concentrated aqueous solutions cannot be solely used for the removal of acid gases, since

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it can react with unrelated materials such as reactor vessels, tubing lines, and several process compartments. Industrially important other alkanolamines are diethanolamine (DEA), *N*-methyldiethanolamine (MDEA), and di-2-propanolamine (DIPA). MDEA aqueous solutions are better than MEA or DEA solutions in that they have the properties of high loading capacity (mol of CO_2/mol of amine) up to 1.0, less regeneration energy, and high resistance to thermal and chemical degradation. However, the slow reactivity of MDEA solutions with CO_2 limits their use. Recently, sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP) and 2-piperidineethanol (PE) have been proposed as new CO_2 absorbents because of their advantages in loading capacity, absorption rate, and regeneration energy [1, 2]. Because of the hindrance of the bulky group attached to the tertiary carbon atom, unstable carbamate ions are formed in the reaction of the AMP solutions with CO_2 resulting in a theoretical loading capacity up to 1.0.

In the previous work [3], we confirmed that 2-amino-2-methyl-1,3-propanediol (AMPD) could be used as an effective CO_2 absorbent and reported the equilibrium solubility of CO_2 in aqueous AMPD solutions at 30°C and a concentration of 10 mass% AMPD and at temperatures of 30, 40, and 60°C and a concentration of 30 mass% AMPD. In this study, we present experimental values of the density, viscosity, and solubility of N_2O in the aqueous AMPD solutions. These results provide the thermodynamic basis required for the study on kinetics of reaction between CO_2 and AMPD which is in progress in our laboratory.

2. EXPERIMENTAL

2.1. Densities

Densities were measured with a density meter (Anton Paar, DMA 58) with a hollow U-shaped tube having an internal volume of about 0.7 cm^3. The accuracy of the apparatus calibrated with air and water was ± 0.00001 $g \cdot cm^{-3}$. The temperature of the apparatus could be kept constant within ± 0.01 K by a built-in solid state thermostat. A Sartorius R120S balance with a precision of ± 0.0001 g was used for mass measurements of liquid mixtures. The density values were reproducible within ± 0.00004 $g \cdot cm^{-3}$.

2.2. Viscosities

Kinematic viscosities were measured with several Ubbelohde-type viscometers (Witeg) of various capillary sizes. The measurements were performed in a constant-temperature water bath controlled to within ± 0.05 K.

An electronic stop watch with an uncertainty of 0.01 s was used to measure the efflux times of liquid solutions. The efflux times for one liquid sample were measured, at least, five times. The accuracy of the measured kinematic viscosity was estimated to be within ±0.5%. The dynamic viscosities were calculated by multiplying the measured kinematic viscosities with the density values of the same solutions.

2.3. Solubility

The solubility of N_2O in aqueous AMPD solutions was measured by using the apparatus shown schematically in Fig. 1. The equilibrium flask

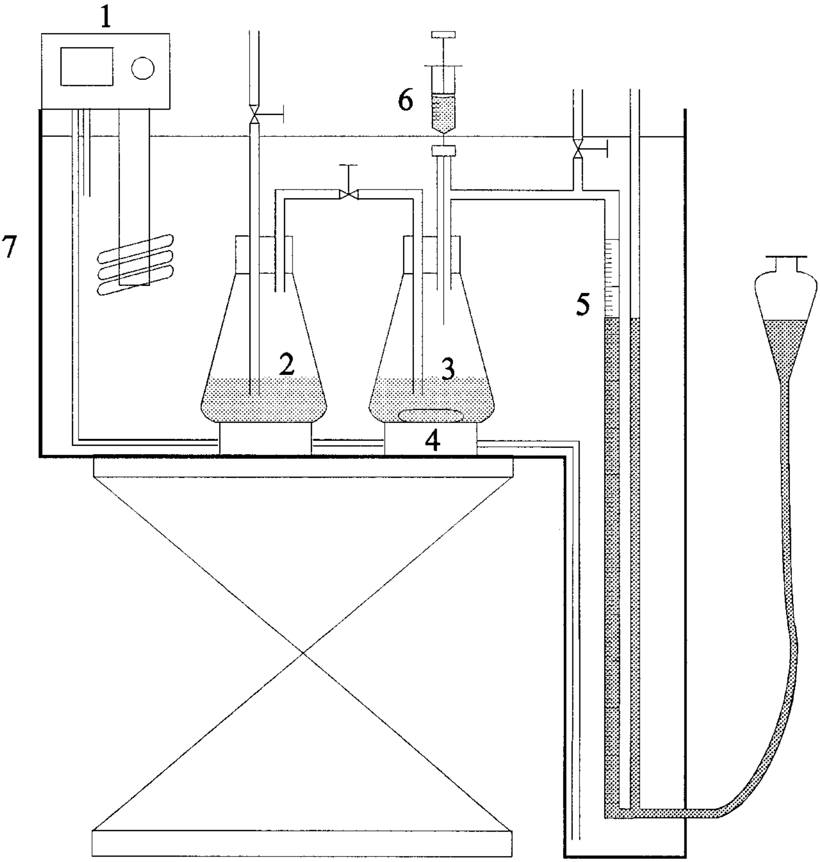

Fig. 1. Schematic diagram of solubility apparatus:(1) immersion circulator; (2) saturation flask; (3) absorption flask; (4) magnetic stirrer; (5) barometric leg; (6) liquid sample injection.

with an internal volume of about 125 ml was kept at ±0.1°C of the set point temperature by a constant-temperature water bath. The temperature in the flask was measured by a K-type thermocouple with a digital thermometer (OMEGA, MDSS41-TC) of which the resolution is ±0.1°C. Initially, the apparatus was purged with saturated N_2O gas to remove remaining air and heated to the desired temperature. Then liquid samples of about 30 ml were carefully introduced into the equilibrium flask. For rapid equilibration, aqueous alkanolamine solutions in the equilibrium flask were stirred with a magnetic spinbar with an external magnet. The system volume and pressure were changed by the effect of N_2O gas absorbed in the liquid sample. The system pressure was controlled at atmospheric pressure by the barometric leg until equilibrium was reached. When the system volume and pressure were stable for 30 min, the system was considered to be at equilibrium. It generally takes 5 to 10 min to reach equilibrium. The experimental error in the measured gas solubility is estimated to be ±3%. More detailed descriptions of the experimental procedure are given elsewhere [4–6].

2.4. Materials

The chemical absorbents used in this study were obtained from Sigma-Aldrich Chemical Co. with a minimum purity of 99+% and were used without further purification. All solutions were prepared with distilled water. N_2O and CO_2 gases with a purity of 99.99% were supplied from commercial cylinders.

3. RESULTS AND DISCUSSION

The densities and viscosities of pure MDEA were measured over the temperature range of 30 to 70°C and are listed in Table I along with literature data [7–9]. The difference between this study and the literature

Table I. Densities and Viscosities of Pure *N*-Methyldiethanolamine

	ρ ($g \cdot cm^{-3}$)		η ($mPa \cdot s$)		
t (°C)	This work	Lit. [7]	This work	Lit. [8]	Lit. [9]
30	1.03228	1.0315	57.37	57.86	
40	1.02475	1.0249	34.60	34.31	34.02
50	1.01708	1.0174	21.59	21.67	21.50
60	1.00941	1.0098	14.43	14.39	
70	1.00167	1.0023	9.906	9.979	

Table II. Densities ρ ($g \cdot cm^{-3}$) of AMPD (1)–Water (2)

	w_1/w_2		
t (°C)	10/90	20/80	30/70
30	1.00915	1.02348	1.03853
40	1.00546	1.01939	1.03394
50	1.00107	1.01471	1.02894
60	0.99606	1.00943	1.02313
70	0.99050	1.00358	1.01702

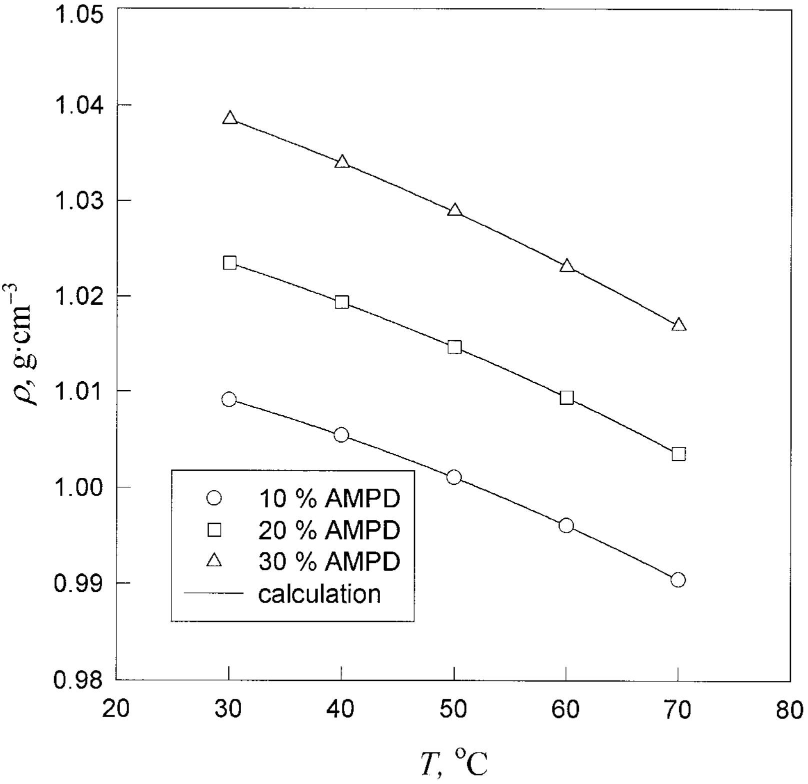

Fig. 2. Densities ρ of AMPD–water solutions as a function of temperature. Solid lines are calculated by Eq. (1).

Table III. Viscosities η (mPa · s) of AMPD (1)–Water (2) Systems

	w_1/w_2		
t (°C)	10/90	20/80	30/70
30	1.127	1.683	2.681
40	0.9018	1.307	1.999
50	0.7417	1.045	1.567
60	0.6225	0.8584	1.253
70	0.5326	0.7218	1.026

values was 0.045% for densities and 0.74% for viscosities in average absolute deviations (AAD). The measured densities and viscosities were found to be in good agreement with the literature data. This result reveals that our experimental apparatus and procedures can provide reliable data.

The density values of 10, 20, and 30 mass% AMPD solutions are listed in Table II. The data were regressed using the following polynomial:

$$\rho/(\mathrm{g \cdot cm^{-3}}) = a_1 + a_2(T/\mathrm{K}) + a_3(T/\mathrm{K})^2 \tag{1}$$

The determined parameters and AAD between the measured and calculated values are presented in Table IV. The maximum deviation was found to be less than 0.005%. Figure 2 shows the comparison of the experimentally measured and calculated densities for 10, 20, and 30 mass% AMPD solutions.

The viscosities of 10, 20, and 30 mass% AMPD solutions are listed in Table III. The data were regressed using the following simple expression:

$$\eta/(\mathrm{mPa \cdot s}) = \exp\left[b_1 + \frac{b_2}{T/\mathrm{K} + b_3} \right] \tag{2}$$

Table IV. Parameters and AAD for Density Correlations for AMPD (1)–Water (2) Systems

	w_1/w_2		
	10/90	20/80	30/70
a_1	0.82677	0.86820	0.91564
$10^3 a_2$	1.5457	1.4044	1.2390
$10^6 a_3$	−3.1143	−2.9429	−2.7500
AAD (%)	0.002	0.001	0.004

Table V. Parameters and AAD for Viscosity Correlations for AMPD (1)–Water (2) Systems

	w_1/w_2		
	10/90	20/80	30/70
b_1	−3.438	−3.337	−3.154
b_2	533.1	548.0	551.0
b_3	−153.3	−161.1	−170.1
AAD (%)	0.02	0.06	0.28

Table V includes the fitted parameters and the AAD between the measured and calculated values. The maximum deviation was found to be less than 0.3%. The comparison between the calculated and measured viscosities is also graphically shown in Fig. 3.

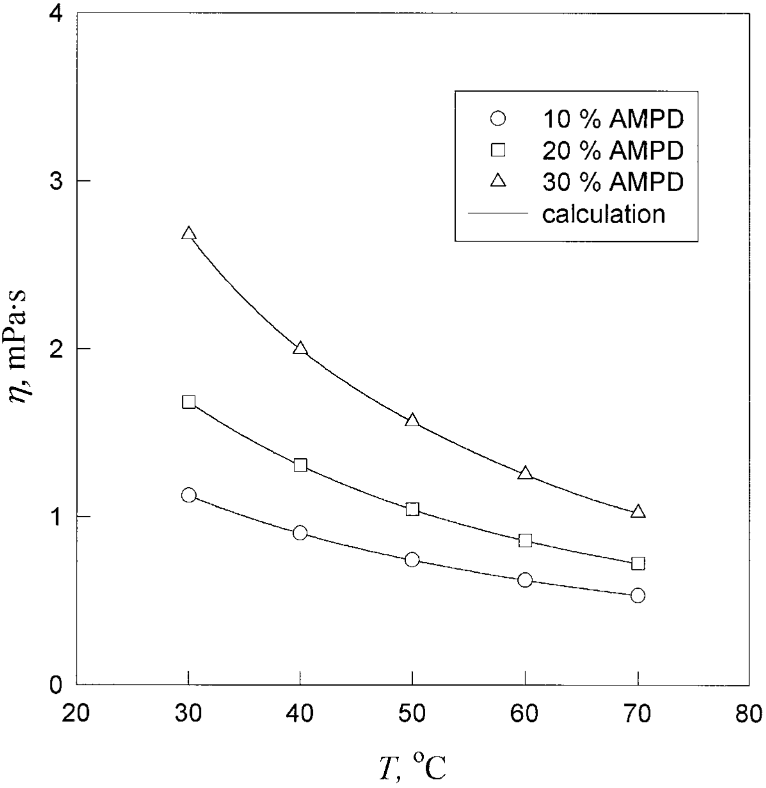

Fig. 3. Viscosities η of AMPD–water solutions as a function of temperature. Solid lines are calculated by Eq. (2).

Table VI. Solubility of N_2O and CO_2 in Water

t (°C)	H (kPa · m^3 · kmol^{-1}) N_2O	CO_2	Ref.
30	4568	3332	[10]
	4406	3382	[11]
	4465	3420	[12]
	4350	3394	[4]
	4835	3428	This work
40	5811	4133	[10]
	5725	4227	[11]
	5822	4226	[12]
	5021	4250	[4]
	6108	4306	This work
50	7282	5058	[10]
	7264	5136	[11]
	5369	5167	[4]
	7445	5234	This work

To establish the reliability of the experimental apparatus and procedure for the N_2O analogy, the solubility of N_2O and CO_2 in water was measured at temperatures of 30, 40, and 50°C. Table VI compares the solubility of N_2O and CO_2 in water determined in this work with the values reported by several researchers. The measured solubilities of both N_2O and CO_2 in water are in reasonable agreement with literature values. The solubility of N_2O in 10, 20, and 30 mass% AMPD solutions at temperatures of 30, 40, and 50°C is listed in Table VII and depicted in Fig. 4. As shown in Fig. 4, Henry's constant is a strong function of both the concentration and temperature. It is found that Henry's constant increases

Table VII. Solubility of N_2O in Aqueous AMPD Solutions

t (°C)	H (kPa · m^3 · kmol^{-1}) 10% AMPD	20% AMPD	30% AMPD
30	5064	5350	5645
40	6454	6590	7062
50	7503	7821	8351

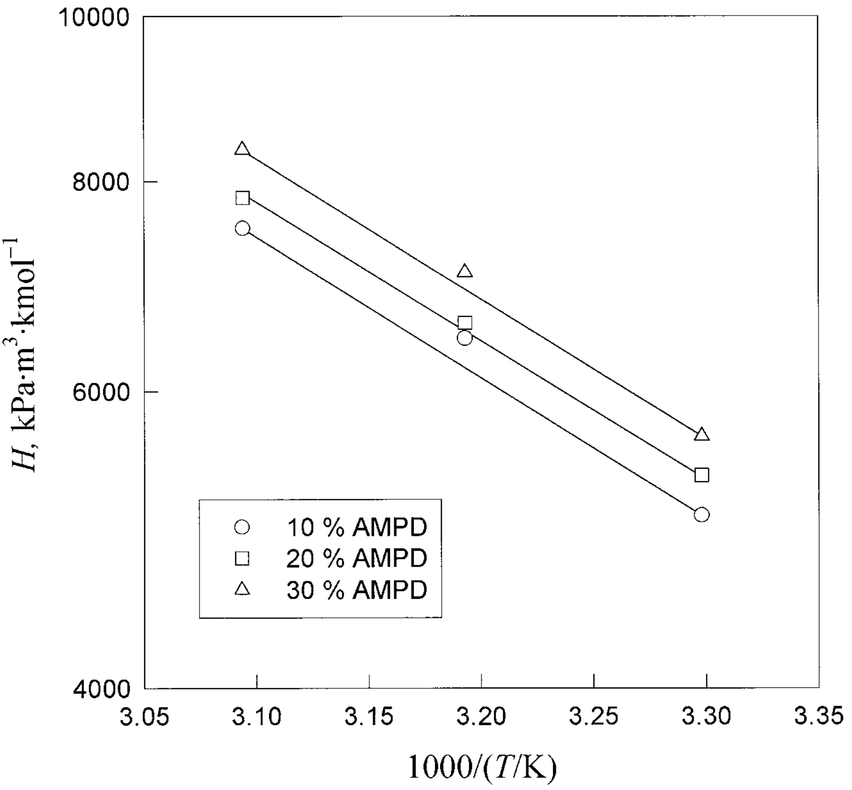

Fig. 4. Solubility of N_2O in AMPD–water solutions.

with an increase in the concentration of AMPD as well as with the system temperature.

3. CONCLUSION

The densities and viscosities of aqueous AMPD solutions were measured at several temperatures. The experimental values for these properties were correlated as functions of temperature. The maximum deviations between the measured and calculated results were less than 0.005% for densities and 0.3% for viscosities. The solubility of N_2O in the aqueous AMPD solutions was also measured to estimate the physical solubility of CO_2 in the alkanolamine solutions. It was found that Henry's constant increased with an increase in the concentration of AMPD as well as with the system temperature.

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