

Densities and Viscosities of Solutions of Monoethanolamine + *N*-Methyldiethanolamine + Water and Monoethanolamine + 2-Amino-2-methyl-1-propanol + Water

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The densities and viscosities of aqueous mixtures of monoethanolamine (MEA) with *N*-methyldiethanolamine (MDEA) and MEA with 2-amino-2-methyl-1-propanol (AMP) have been studied at temperatures from 30 to 80 °C. For density measurements, four MEA + MDEA (a total of 20 mass %) + H₂O mixtures and eight MEA + AMP (20 and 30 mass %) + H₂O mixtures were studied. For viscosity measurements, ten MEA + MDEA + H₂O mixtures and eight MEA + AMP + H₂O mixtures were measured. A Redlich-Kister equation of the excess volume was applied to represent the density of the liquid mixtures. The equation of Grunberg and Nissan of liquid viscosity was used to correlate the viscosity data. Both density and viscosity calculations show satisfactory results.

Introduction

Alkanolamine aqueous solutions are frequently used for the removal of acidic gases, such as CO₂ and H₂S, from natural, refinery, and synthesis gas streams. Industrially important alkanolamines are monoethanolamine (MEA), diethanolamine (DEA), di-2-propanolamine (DIPA) and *N*-methyldiethanolamine (MDEA). Aqueous MEA solutions have been widely used due to their high reactivity, low solvent cost, ease of reclamation, and low absorption of hydrocarbons (1). For a gas stream that contains both CO₂ and H₂S, the aqueous MDEA solution is found to be an appropriate solution for the selective removal of H₂S from the gas stream (2, 3). Advantages of the use of MDEA solutions include their high loading capacity (about 1.0 mol of CO₂/mol of amine) and low heat of reaction with the acid gases (4). Sterically hindered alkanolamines have been proposed as commercially attractive solvents for removal of acid gases from gaseous streams (5). An example of the sterically hindered alkanolamines is 2-amino-2-methyl-1-propanol (AMP), which is the hindered form of MEA.

Recently the use of blended amines, a solution of two or more amines in varying compositions, finds considerable improvement in absorption and a great savings in energy requirements (6). Blends of primary and tertiary amines, such as mixtures of MEA and MDEA, have been suggested for CO₂ removal (6). Compared to the MDEA, the AMP has the same high CO₂ loading capacity (about 1 mol of CO₂/mol of amine) but has a larger reaction rate constant when reacting with CO₂ (5, 7, 8). Therefore, MEA + AMP + H₂O may be an attractive new solvent, in addition to MEA + MDEA + H₂O, for the acid gas treating process.

Solubility data of CO₂ and H₂S in blended alkanolamine aqueous solutions have been reported in the literature. The solubilities of CO₂ and H₂S in aqueous mixtures of MEA with MDEA have been reported in the literature (9-12). Besides solubility data, densities and viscosities of aqueous alkanolamine solutions are also essential in the rational design of the gas absorption units for removing acid gases from gas

Table 1. Comparison of the Densities of Aqueous MDEA Solutions Measured in This Work with Literature Values

t/°C	ρ /(g·cm ⁻³)			
	20 mass % MDEA		30 mass % MDEA	
	Al-Ghawas et al. (15)	this work	Li and Shen (11)	this work
30	1.0132	1.0133	1.0229	1.0223
40	1.0091	1.0089	1.0180	1.0171
50	1.0047	1.0040	1.0130	1.0116
60	0.9993	0.9983	1.0069	1.0057
av abs % dev		0.05		0.10

streams. Thus, it is the purpose of this research to study experimentally the density and viscosity of the MEA + MDEA + H₂O and MEA + AMP + H₂O systems at temperatures ranging from 30 to 80 °C.

Experimental Section

Alkanolamine aqueous solutions were prepared from distilled water. MEA is Riedel-de Haën reagent grade with a 99% (mol) purity, MDEA is Riedel-de Haën reagent grade with a 98.5% (mol) purity, and AMP is Riedel-de Haën reagent grade with a 98% (mol) purity.

1. Density Measurement. The densities of MEA + MDEA + H₂O and MEA + AMP + H₂O solutions were measured by using a 25-mL Gay-Lussac pycnometer. The procedure used to determine the density of the solution is based on the ASTM D 3505 standard test method (13). The temperature of the thermostat is controlled by a TU-16A immersion circulator, made by Techne Inc., to within ±0.05 °C of the desired temperature. The density of the solution is calculated by the observed weight of the sample and that of the degassed pure water (13). The density of the pure water is adopted from the values reported in the *Chemical Engineer's Handbook* (14). The density measurements were made over the temperature range of 30-80 °C. The accuracy of the densities was estimated to be ±0.5% on the basis of comparisons with literature data.

2. Viscosity Measurement. The kinematic viscosities of MEA + MDEA + H₂O and MEA + AMP + H₂O systems

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Table 2. Densities of MEA + MDEA + H₂O

t/°C	$\rho/(\text{g}\cdot\text{cm}^{-3})$							
	mass % MEA/mass % MDEA				pure liquid			
	0/20	5/15	15/5	20/0	MEA ^a	MDEA ^a	AMP	water ^b
30	1.0133	1.0103	1.0061	1.0036	1.0098	1.0315	0.9267	0.9957
40	1.0089	1.0062	1.0018	0.9994	1.0009	1.0249	0.9179	0.9922
50	1.0040	1.0010	0.9968	0.9944	0.9929	1.0174	0.9096	0.9880
60	0.9983	0.9954	0.9912	0.9889	0.9849	1.0098	0.9011	0.9832
70	0.9921	0.9893	0.9853	0.9830	0.9771	1.0023	0.8922	0.9778
80	0.9860	0.9833	0.9793	0.9770	0.9683	0.9946	0.8841	0.9718

^a Values of Li and Shen (11). ^b Values reported by Perry and Chilton (14).

Table 3. Densities of MEA + AMP + H₂O

t/°C	$\rho/(\text{g}\cdot\text{cm}^{-3})$ (mass % MEA/mass % AMP)							
	0/30	6/24	12/18	18/12	24/6	0/20	5/15	15/5
30	0.9946	0.9977	1.0006	1.0034	1.0060	0.9941	0.9964	1.0012
40	0.9888	0.9921	0.9952	0.9984	1.0010	0.9896	0.9920	0.9968
50	0.9827	0.9861	0.9895	0.9928	0.9957	0.9840	0.9866	0.9919
60	0.9757	0.9797	0.9828	0.9867	0.9895	0.9778	0.9808	0.9863
70	0.9689	0.9728	0.9766	0.9802	0.9837	0.9713	0.9744	0.9813
80	0.9610	0.9658	0.9695	0.9737	0.9769	0.9649	0.9682	0.9742

Table 4. Comparison of the Calculated Densities with the Experimental Values

system	t/°C	no. of measurements	av abs % dev
MEA + H ₂ O	30–80	12	0.02
MDEA + H ₂ O	30–80	12	0.05
AMP + H ₂ O	30–80	12	0.03
MEA + MDEA + H ₂ O	30–80	36	0.02
MEA + AMP + H ₂ O	30–80	36	0.02

were measured by means of Cannon-Fenske routine viscometers over the temperature range 30–80 °C. These measurements were done according to the specifications and operating instructions of the ASTM D445 standard test method. The measurements were performed in a constant-temperature water bath, in which the temperature could be held constant to ± 0.05 °C. The absolute viscosity of fluid can be obtained by multiplying the kinematic viscosity by the density of the fluid. The accuracy of the kinematic viscosities was estimated to be $\pm 1.0\%$ on the basis of comparisons with literature values.

Results and Discussion

For the density measurement, we have obtained data for the systems at which density data had been reported in the literature. Densities of 20 mass % MDEA and 30 mass % MDEA aqueous solutions have been studied by Al-Ghawas et al. (15) and Li and Shen (11). The results of density measurements for temperatures ranging from 30 to 60 °C are presented in Table 1. The average absolute percentage deviations of the density measurements are 0.05% and 0.1% for 20 mass % MDEA and 30 mass % MDEA aqueous solutions, respectively. Thus, the density data obtained in this study are in good agreement with the data of Al-Ghawas

et al. (15) and Li and Shen (11). For the MEA + MDEA aqueous systems, the systems studied for density measurement are 20 mass % MDEA, 5 mass % MEA + 15 mass % MDEA, 15 mass % MEA + 5 mass % MDEA, and 20 mass % MEA for temperatures ranging from 30 to 80 °C. The results are presented in Table 2. The densities of the pure fluids MEA, MDEA, AMP, and water are also listed in Table 2 for reference. For the MEA + AMP aqueous systems, the systems studied are 30 mass % AMP, 6 mass % MEA + 24 mass % AMP, 12 mass % MEA + 18 mass % AMP, 18 mass % MEA + 12 mass % AMP, 24 mass % MEA + 6 mass % AMP, 20 mass % AMP, 5 mass % MEA + 15 mass % AMP, and 15 mass % MEA + 5 mass % AMP. In Table 3, densities of eight MEA + AMP + H₂O systems are reported.

To correlate the densities of liquid mixtures, a Redlich-Kister-type equation for the excess molar volume is applied. For a binary system, the Redlich-Kister equation (16) has the form

$$V_{12}^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_1x_2 \sum_{i=0}^n A_i(x_1 - x_2)^i \quad (1)$$

where A_i are parameters that are temperature-dependent. The excess volume of the liquid mixture for a ternary system is assumed to be given by the following expression:

$$V^E = V_{12}^E + V_{13}^E + V_{23}^E \quad (2)$$

The excess volume of the liquid mixtures can be calculated by the measured density of the fluids

$$V^E = V_m - \sum x_i V_i^\circ \quad (3)$$

where V_m is the molar volume of the liquid mixture and V_i° is the molar volume of pure fluids at the temperature of the system. The molar volumes of the liquid mixtures are calculated by

$$V_m = \frac{\sum x_i M_i}{\rho_m} \quad (4)$$

Table 5. Binary Parameters of the Redlich-Kister Equation of the Excess Volume

params		binary system				
		MEA + H ₂ O	MDEA + H ₂ O	AMP + H ₂ O	MDEA + MEA	AMP + MEA
A ₀	a	-6.1623	8.8343 × 10 ¹	-4.2646 × 10 ¹	-2.0505 × 10 ³	-1.0299 × 10 ¹
	b	0.0257	-5.8995 × 10 ⁻³	1.9598 × 10 ⁻¹	1.2416 × 10 ¹	-2.4695 × 10 ⁻²
	c	-5.4778 × 10 ⁻³	9.1887 × 10 ⁻⁴	-3.1305 × 10 ⁻⁴	-1.8814 × 10 ⁻²	8.7215 × 10 ⁻⁶
A ₁	a	-1.0134 × 10 ⁻³	7.8825 × 10 ⁻¹	1.0000 × 10 ⁻⁶	3.3100 × 10 ⁻²	1.2576 × 10 ⁻²
	b	6.6014 × 10 ⁻³	-2.9301 × 10 ⁻³	2.0218 × 10 ⁻²	-1.8646	6.6225 × 10 ⁻¹
	c	0	0	0	5.7802 × 10 ⁻³	-2.4196 × 10 ⁻³
A ₂	a	0	0	0	0	3.2189 × 10 ⁻²
	b	0	0	0	0	1.8185 × 10 ²
	c	0	0	0	0	-5.7589 × 10 ⁻²

Table 6. Comparison of the Viscosity of MDEA + H₂O with Literature Values

<i>t</i> /°C	η /(mPa·s)							
	Al-Ghawas et al. (15)				this study ^a			
	20 mass % MDEA	30 mass % MDEA	40 mass % MDEA	50 mass % MDEA	20 mass % MDEA	30 mass % MDEA	40 mass % MDEA	50 mass % MDEA
30	1.686	2.612	4.359	7.436	1.699	2.622	4.343	7.470
40	1.301	1.937	3.112	5.105	1.316	1.953	3.117	5.081
50	1.051	1.505	2.309	3.642	1.048	1.515	2.313	3.606
60	0.858	1.207		2.700	0.860	1.210		2.671

^a Average absolute percentage deviation 0.53.**Table 7. Viscosities of MEA + MDEA + H₂O**

<i>t</i> /°C	η /(mPa·s) (mass % MEA/mass % MDEA)									
	0/30	6/24	12/18	18/12	24/6	30/0	0/20	5/15	15/5	20/0
30	2.626	2.515	2.396	2.287	2.186	2.109	1.699	1.635	1.531	1.480
40	1.953	1.885	1.806	1.734	1.665	1.616	1.316	1.268	1.200	1.161
50	1.515	1.460	1.408	1.355	1.307	1.277	1.048	1.013	0.963	0.936
60	1.210	1.167	1.128	1.094	1.059	1.035	0.860	0.833	0.797	0.778
70	0.981	0.957	0.931	0.903	0.877	0.868	0.721	0.703	0.675	0.659
80	0.828	0.803	0.781	0.759	0.740	0.732	0.618	0.603	0.581	0.577

Table 8. Viscosities of MEA + AMP + H₂O

<i>t</i> /°C	η /(mPa·s) (mass % MEA/mass % AMP)							
	0/30	6/24	12/18	18/12	24/6	0/20	5/15	15/5
30	3.053	2.830	2.617	2.420	2.262	1.866	1.754	1.571
40	2.168	2.059	1.933	1.810	1.712	1.405	1.338	1.223
50	1.621	1.566	1.479	1.410	1.389	1.099	1.053	0.978
60	1.266	1.212	1.163	1.138	1.087	0.884	0.856	0.814
70	1.078	0.983	0.951	0.922	0.895	0.733	0.712	0.681
80	0.887	0.805	0.782	0.770	0.751	0.622	0.609	0.584

Table 9. Viscosities of the Pure Liquids

<i>t</i> /°C	η /(mPa·s)			
	MEA ^a	MDEA	AMP	water ^b
30	15.1088	57.8599	99.4748	0.8149
40	10.0209	34.3085	46.9258	0.6680
50	6.9715	21.6716	24.2108	0.5591
60	5.0473	14.3856	13.9977	0.4765
70	3.7793	9.9789	8.6418	0.4123
80	2.9120	7.0875	5.6485	0.3625

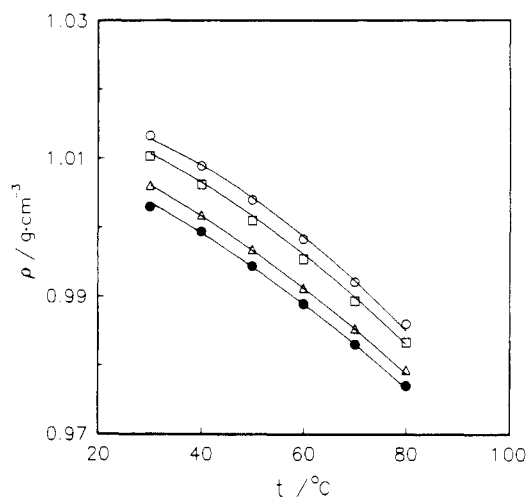
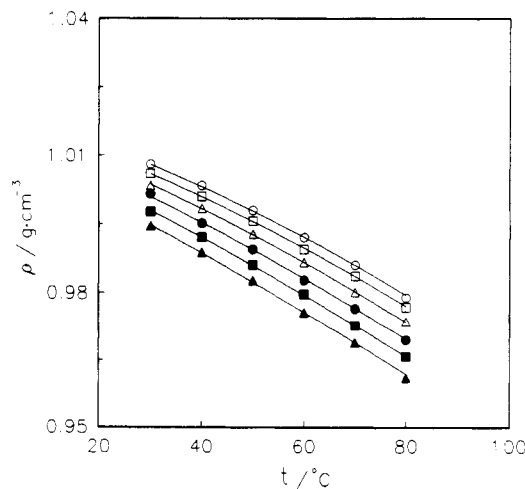
^a Data of DiGuilio et al. (17). ^b Values reported by Yaws et al. (18).**Table 10. Comparison of the Calculated Viscosities with Experimental Values**

system	<i>t</i> /°C	no. of measurements	av abs % dev
MEA + H ₂ O	30 to 80	12	0.53
MDEA + H ₂ O	30 to 80	12	1.49
AMP + H ₂ O	30 to 80	12	1.50
MEA + MDEA + H ₂ O	30 to 80	36	0.72
MEA + AMP + H ₂ O	30 to 80	36	1.41

where M_i is the molar mass of pure component i and ρ_m is the measured liquid density. The parameter A_i in eq 1 is temperature-dependent and is assumed to have the following form:

$$A_i = a + b(T/K) + c(T/K)^2 \quad (5)$$

The results of density calculation based on the Redlich-Kister equations, eqs 1, 2, and 5, are presented in Table 4, and the determined parameters are given in Table 5. The average absolute percentage deviations for density calculations are 0.03% and 0.02% for binary systems and ternary systems, respectively. The comparisons between the calculated and the measured densities are also shown graphically in Figures 1 and 2 for MEA + MDEA + H₂O and MEA + AMP + H₂O, respectively. Using the Redlich-Kister equation of the excess volume, the results of the density calculations are satisfactory for the systems tested.

**Figure 1. Densities ρ of MEA + MDEA + H₂O solutions at temperature t (mass % MEA/mass % MDEA): ○, 0/20; □, 5/15; △, 15/5; ●, 20/0. Lines are calculated by eq 3.****Figure 2. Densities ρ of MEA + AMP + H₂O solutions at temperature t (mass % MEA/mass % AMP): ○, 30/0; □, 24/6; △, 18/12; ●, 12/18; ■, 6/24; ▲, 0/30. Lines are calculated by eq 3.**

Viscosities of aqueous MDEA solutions for temperatures of 20–60 °C have been studied by Al-Ghawas et al. (15). For the viscosity measurement, viscosities of four MDEA + H₂O systems, 20, 30, 40, and 50 mass % MDEA, have been carried

Table 11. Binary Parameters of Viscosity Using the Grunberg and Nissan Equation

param	binary system				
	MEA + H ₂ O	MDEA + H ₂ O	AMP + H ₂ O	MDEA + MEA	AMP + MEA
a	3.7210 × 10 ²	-1.9933 × 10 ³	1.9618 × 10 ³	4.6814 × 10 ⁴	-1.0541 × 10 ⁵
b	-3.1100	1.8755 × 10 ¹	-1.7230 × 10 ¹	-4.2726 × 10 ²	9.5234 × 10 ²
c	8.8092 × 10 ⁻³	-5.8011 × 10 ⁻²	5.0803 × 10 ⁻²	1.2979	-2.8621
d	-8.3457 × 10 ⁻⁶	5.9402 × 10 ⁻⁵	-5.0036 × 10 ⁻⁵	-1.3125 × 10 ⁻³	2.8612 × 10 ⁻³

out, and the results are presented in Table 6. The overall average absolute percent deviation for 15 data points is 0.53%. Thus, the viscosities obtained in this study are in good agreement with the viscosity data of Al-Ghawwas et al. (15). For MEA + MDEA + H₂O solutions, the viscosities of 10 systems, 30 mass % MDEA, 6 mass % MEA + 24 mass % MDEA, 12 mass % MEA + 18 mass % MDEA, 18 mass % MEA + 12 mass % MDEA, 24 mass % MEA + 6 mass % MDEA, 30 mass % MEA, 20 mass % MDEA, 5 mass % MEA + 15 mass % MDEA, 15 mass % MEA + 5 mass % MDEA, and 20 mass % MEA, have been studied for temperatures of 30–80 °C, and the results are presented in Table 7. In Table 8, the viscosities of eight MEA + AMP + H₂O solutions for temperatures of 30–80 °C have also been presented. In Table 9, the viscosities of the pure fluids MEA, MDEA, AMP, and water are presented. The viscosity data of MEA and water are adopted directly from the literature values (17, 18).

The model of Grunberg and Nissan (19) for the viscosity of liquid mixtures is utilized to correlate the viscosity data. The equation of Grunberg and Nissan has the following form:

$$\ln \eta_m = \sum_i x_i \ln \eta_i + \sum_{i \neq j} x_i x_j G_{ij} \quad (6)$$

where η_i is the viscosity of the *i*th pure fluid. For a binary system, one has

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \quad (7)$$

For a ternary system,

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_3 \ln \eta_3 + x_1 x_2 G_{12} + x_1 x_3 G_{13} + x_2 x_3 G_{23} \quad (8)$$

G_{ij} in eq 7 is temperature-dependent and is assumed to have the form

$$G_{ij} = a + b(T/K) + c(T/K)^2 + d(T/K)^3 \quad (9)$$

The results of viscosity calculations based on the model of Grunberg and Nissan, eqs 7–9, are presented in Table 10. The average absolute percentage deviations are 1.2% and 1.1% for binary and ternary systems, respectively. The determined binary parameters of the viscosity equation of Grunberg and Nissan are given in Table 11. The comparisons between the calculated and the experimental viscosities for MEA + AMP + H₂O systems are also shown in Figure 3. The results of viscosity calculations are quite satisfactory.

Conclusion

The densities and viscosities of aqueous solutions of mixtures of MEA with MDEA and MEA with AMP have been studied experimentally for temperatures from 30 to 80 °C. The densities of four MEA + MDEA + H₂O solutions and eight MEA + AMP + H₂O solutions have been studied. For the ten MEA + MDEA + H₂O and eight MEA + AMP + H₂O solutions, the viscosity measurements have been performed. The density data were represented by the Redlich–Kister equation of the excess volume. The equation of Grunberg and Nissan for the viscosities of liquid mixtures was used to represent the viscosity data. Satisfactory results

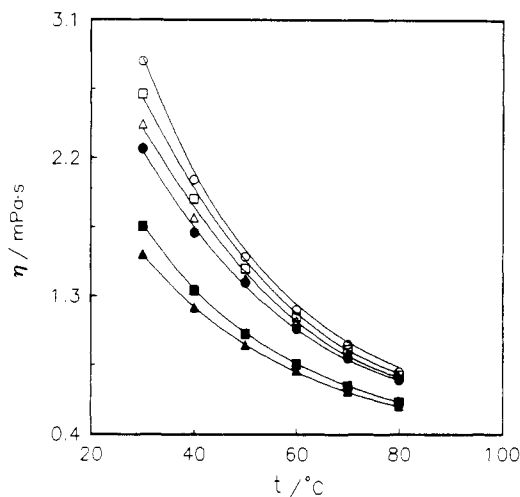


Figure 3. Viscosities η of MEA + AMP + H₂O solutions at temperature t (mass % MEA/mass % AMP): \circ , 6/24; \square , 12/18; \triangle , 18/12; \bullet , 24/6; \blacksquare , 5/15; \blacktriangle , 15/5. Lines are calculated by eq 9.

were obtained for the calculations of density and viscosity for the MEA + MDEA + H₂O and the MEA + AMP + H₂O systems.

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