Viscosity, Density, and Surface Tension of Binary Mixtures of Water and *N*-Methyldiethanolamine and Water and Diethanolamine and Tertiary Mixtures of These Amines with Water over the Temperature Range 20–100 °C

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The density and viscosity of aqueous solutions of *N*-methyldiethanolamine were measured over the temperature range 60–100 °C. The density and viscosity of aqueous solutions of diethanolamine and diethanolamine + *N*-methyldiethanolamine were measured over the temperature range 20–100 °C. The surface tension of aqueous solutions of the above mixtures was measured over the temperature range 20–80 °C. The concentration ranges were 10–50 mass % *N*-methyldiethanolamine, 10–30 mass % diethanolamine, and 50 mass % total amine concentration with mass ratios of 0.0441–0.5883 (diethanolamine to *N*-methyldiethanolamine). The measured quantities were found to be in agreement with the literature where data were available.

Introduction

Aqueous solutions of *N*-methyldiethanolamine (MDEA) and diethanolamine (DEA) are widely used in the industrial treatment of acid gas streams containing H_2S and CO_2. MDEA is generally used for selective removal of H_2S in the presence of CO_2, while DEA is a common solvent for removal of CO_2. Aqueous solutions containing a mixture of DEA and MDEA, however, are considered to be excellent solvents for simultaneous absorption of CO_2 and H_2S in situations where a specified amount of CO_2 is to be removed.

The physical properties of aqueous solutions of MDEA, DEA, and DEA + MDEA, such as density, viscosity, and surface tension, are necessary for the design of acid gas treatment equipment and for measuring other physical properties such as liquid diffusivities, free-gas solubility, and reaction rate constants. Al-Ghawas et al. (*1*) measured the density and viscosity of aqueous solutions of 10–50 mass % MDEA over the temperature range 15–60 °C. Li and Shen (*2*) reported densities of 30 mass % MDEA from 30 to 80 °C. Oyevaar et al. (*3*) measured the densities and dynamic viscosities of 20 and 30 mass % DEA at 25 °C. Versteeg and van Swaaij (*4*) reported dynamic viscosity correlations for 10–30 mass % MDEA over the temperature range 20–60 °C. Sada et al. (*5*) measured the dynamic viscosity of 10–30 mass % DEA at 25 °C. Littel et al. (*6*) reported dynamic viscosity correlations for 10–30 mass % DEA over the temperature range 30–60 °C.

The objective of this work was to measure the density, viscosity, and surface tension of aqueous solutions of MDEA, DEA, and DEA + MDEA over the temperature range of 20–100 °C. However, the viscosity and density of MDEA were only measured over the temperature range 60–100 °C because the measurements at lower temperatures had been measured previously in this laboratory (*1*). Also, the surface tension was only measured up to 80 °C because of equipment limitations at higher temperatures. The concentration ranges considered in this work were 10–50 mass % MDEA, 10–30 mass % DEA, and DEA + MDEA blends of 50 mass % total amine concentration with mass ratios of 0.0441, 0.2206, 0.4413, and 0.5883 DEA to MDEA.

Experimental Section

The aqueous amine solutions were prepared with distilled-deionized water. The MDEA was obtained from Union Carbide Corp. with a purity greater than 99 mass %, and the DEA was obtained from Fisher Scientific also with a purity better than 99 mass %. The composition of each solution was measured by titration with HCl to an equivalence point of pH equal to 4.5 (*1*). All solutions were found to be within ±0.2 mass % of the stated concentration.

Density. The density of the amine solutions was measured using 25 cm^3 (at 20 °C) pycnometers of the Gay-Lussac type obtained from Fisher Scientific. The pycnometers containing the amine solutions were immersed in a large constant-temperature bath which was maintained to within +0.02 K by a constant-temperature circulator which was accurate to ±0.02 K. After the solutions reached the desired temperature, they were weighed to within ±0.0002 g with a Mettler H18 balance. Each reported value was the average of at least three measurements with a maximum deviation in the reported density of approximately ±0.05%.

Viscosity. The viscosity was measured using two Cannon-Fenske-type viscometers (sizes 50 and 100) and one Ubbelohde-type viscometer (size 0). The viscometers were immersed in a large bath. The temperature was controlled with a constant-temperature circulator to within ±0.02 K. The efflux time was measured manually with a digital stopwatch. With the efflux time, the kinematic viscosity was calculated from the equation

$$\nu = Ct \qquad (1)$$

where ν is the kinematic viscosity, C is a constant specific to the viscometer, and t is the efflux time. End effect corrections were neglected in the calculation of the kinematic viscosity. The constant, C, in eq 1 was determined for the Cannon-Fenske viscometers using water (size 50) and aniline (size 100). The aniline used in this work was certified ACS grade. The Ubbelohde viscometer was purchased with a calibration. Each reported measurement was the average of at least three runs with a maximum deviation in the kinematic viscosity of approximately ±0.05%. The dynamic viscosity was calculated by multiplying the kinematic viscosity by the corresponding

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Table 1. Density, Viscosity, and Surface Tension of Aqueous MDEA Solutions

mass % MDEA	T/°C	ρ/(g cm^{-3})	η/(mPa s)	σ/(mN m^{-1})
10	20			62.24
10	40			58.08
10	60	0.9904	0.627	53.31
10	80	0.9782	0.469	49.94
10	100	0.9651		
20	20			58.47
20	40			54.56
20	60	0.9974	0.836	51.20
20	80	0.9854	0.593	47.90
20	100	0.9702	0.460	
30	20			55.27
30	40			51.47
30	60	1.0042	1.119	49.34
30	80	0.9915	0.766	46.03
30	100	0.9767	0.550	
40	20			52.61
40	40			49.85
40	60	1.0125	1.706	47.81
40	80	0.9988	1.128	44.65
40	100	0.9826	0.766	
50	20			50.28
50	40			47.72
50	60	1.0185	2.565	45.44
50	80	1.0041	1.579	42.21
50	100	0.9850	1.048	

density. The maximum estimated error in the dynamic viscosity was within ±0.3%.

Surface Tension. The apparatus used to measure the surface tension of the amine solutions was a Rosano surface tensiometer, by Roller-Smith, which employs the Wilhelmy plate principle. The tensiometer is built around a 500-mg precision balance which was calibrated at each temperature with distilled-deionized water. The surface tension data for water were obtained from the *Handbook of Chemistry and Physics* (*7*). A wettable platinum blade with a perimeter of 5.00 cm was immersed in an amine solution and slowly withdrawn to measure the vertical force which is related to the surface tension by

$$\sigma = Fg/W \qquad (2)$$

where σ is the surface tension, F is the measured vertical force, g is the acceleration of gravity, and W is the perimeter of the blade. The amine solutions were placed in wide-mouthed Erlenmeyer flasks which were immersed in a large temperature bath. The temperature was maintained to within ±0.02 K by a constant-temperature circulator. Each reported value of the surface tension was the average of at least three measurements with a maximum deviation from the average of ±0.4%.

Results and Discussion

The density, viscosity, and surface tension data for aqueous MDEA, DEA, and DEA + MDEA are tabulated in Tables 1–3, respectively. The density of the aqueous MDEA, DEA, and DEA + MDEA solutions is plotted versus temperature in Figures 1–3, respectively. The aqueous MDEA density data of Al–Ghawas et al. (*1*) and Li and Shen (*2*) are also plotted in Figure 1 for comparison. The densities of aqueous DEA reported by Oyevaar et al. (*3*) are plotted in Figure 2 for comparison. The densities measured in this work are in agreement with those of these researchers.

The dynamic viscosity of aqueous MDEA, DEA, and DEA + MDEA is plotted versus temperature in Figures 4–6, respectively. The viscosity results of aqueous MDEA reported by Al-Ghawas et al. (*1*) and Versteeg and van Swaaij (*4*) are also plotted in Figure 4 for comparison. The dynamic viscosity data for aqueous DEA of Littel et al. (*6*), Oyevaar et al. (*3*), and Sada et al. (*5*) are plotted in Figure 5 for comparison. In Figure 6, it is evident that the dynamic viscosity data of the 50 mass % DEA + MDEA are almost identical for the different molar ratios and may be taken to be equal to the data for 50 mass % MDEA with little error. The dynamic viscosity results for aqueous MDEA and DEA measured in this work are in agreement with the data of the researchers referenced above, with the exception of the values for 20 and 30 mass % DEA at 25 °C reported by Oyevaar et al. (*3*) and Sada et al. (*5*), which are slightly lower than the smooth curve drawn through the data of the present study.

The surface tension of aqueous solutions of MDEA, DEA, and DEA + MDEA is plotted versus temperature in Figures

Table 2. Density, Viscosity, and Surface Tension of Aqueous DEA Solutions

mass % DEA	T/°C	ρ/(g cm^{-3})	η/(mPa s)	σ/(mN m^{-1})
10	20	1.0101	1.427	63.90
10	40	1.0034	0.898	61.74
10	60	0.9941	0.624	60.05
10	80	0.9830	0.465	56.84
10	100	0.9698	0.322	
20	20	1.0220	2.171	65.27
20	40	1.0142	1.304	63.31
20	60	1.0052	0.848	62.04
20	80	0.9931	0.606	58.99
20	100	0.9804	0.448	
30	20	1.0342	3.615	61.94
30	40	1.0272	1.996	60.17
30	60	1.0170	1.239	58.02
30	80	1.0037	0.824	55.27
30	100	0.9901	0.608	

Table 3. Density, Viscosity, and Surface Tension of Aqueous 50 mass % Solutions of DEA + MDEA

mass ratio of DEA to MDEA	T/°C	ρ/(g cm^{-3})	η/(mPa s)	σ/(mN m^{-1})
0.0441	20	1.0465	11.65	51.36
0.0441	40	1.0341	5.171	48.02
0.0441	60	1.0200	2.707	41.68
0.0441	80	1.0052	1.591	37.91
0.0441	100	0.9896	1.018	
0.2206	20	1.0489	11.77	52.05
0.2206	40	1.0363	5.178	48.37
0.2206	60	1.0227	2.698	42.63
0.2206	80	1.0081	1.598	38.81
0.2206	100	0.9912	1.049	
0.4413	20	1.0509	12.02	52.71
0.4413	40	1.0383	5.211	49.10
0.4413	60	1.0249	2.805	43.89
0.4413	80	1.0106	1.609	40.47
0.4413	100	0.9946	1.059	
0.5883	20	1.0517	11.989	52.93
0.5883	40	1.0395	5.237	49.78
0.5883	60	1.0262	2.793	44.81
0.5883	80	1.0121	1.614	42.42
0.5883	100	0.9969	1.068	

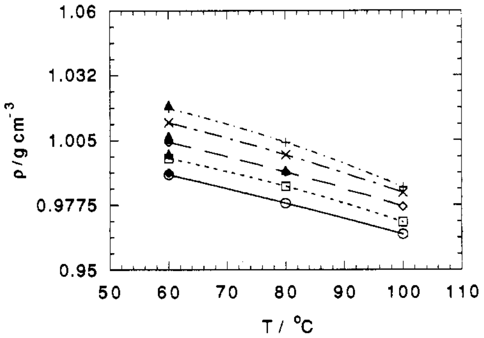

Figure 1. Density of aqueous solutions of MDEA: ○, 10 mass % MDEA; □, 20 mass % MDEA; ◇, 30 mass % MDEA; ×, 40 mass % MDEA; +, 50 mass % MDEA; ◆, Al-Ghawas et al. (*1*); ▲, Li and Shen (*2*).

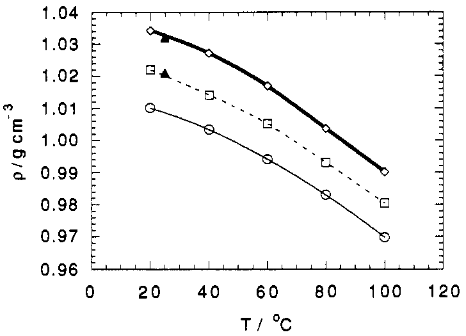

Figure 2. Density of aqueous solutions of DEA: O, 10 mass % DEA; □, 20 mass % DEA; ◇, 30 mass % DEA; ▲, Oyevaar et al. (*3*).

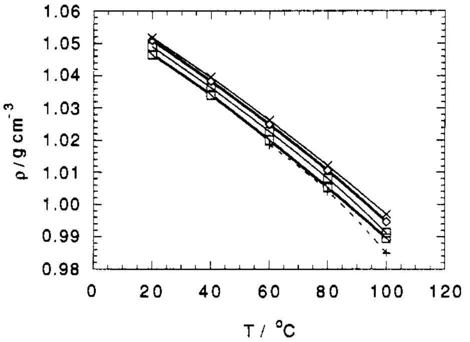

Figure 3. Density of aqueous 50 mass % solutions of DEA + MDEA: ▨, 0.0441 (g of DEA/g of MDEA); □, 0.2206; ◇, 0.4413; ×, 0.5883; +, 50 mass % MDEA.

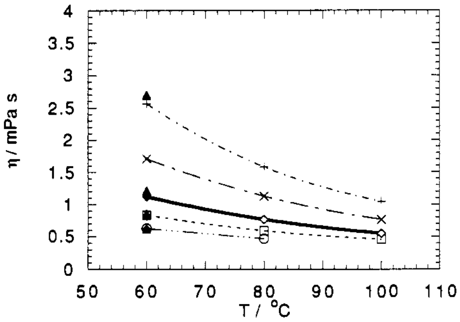

Figure 4. Viscosity of aqueous solutions of MDEA: O, 10 mass % MDEA; □, 20 mass % MDEA; ◇, 30 mass % MDEA; ×, 40 mass % MDEA; +, 50 mass % MDEA; ◆, Al-Ghawas et al. (*1*); ▲, Versteeg and van Swaaij (*4*).

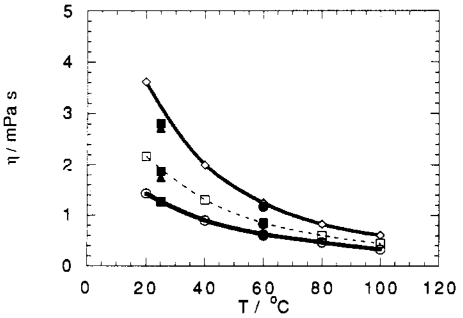

Figure 5. Viscosity of aqueous solutions of DEA: O, 10 mass % DEA; □, 20 mass % DEA; ◇, 30 mass % DEA; ▲, Oyevaar et al. (*3*); ●, Littel et al. (*6*); ■, Sada et al. (*5*).

7-9, respectively. The surface tension at 100 °C could not be measured with the apparatus used for these experiments because the evaporation rate of water at the gas–liquid interface was too high. The surface tension versus temperature plots of the amine solutions show the usual linear dependence on temperature. Note that, for the DEA solutions in Figure 8, the surface tension of 20 mass % DEA is higher than those of both 10 and 30 mass % DEA. It appears that there is a local maximum in the surface tension versus DEA concentration within the range 10–30 mass %. Also note in Figure 9 that the surface tension increases with increasing

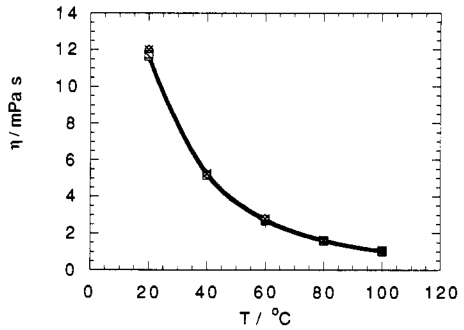

Figure 6. Viscosity of aqueous 50 mass % solutions of DEA + MDEA: ▨, 0.0441 (g of DEA/g of MDEA); □, 0.2206; ◇, 0.4413; ×, 0.5883; +, 50 mass % MDEA.

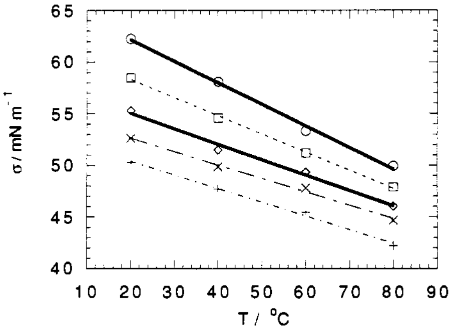

Figure 7. Surface tension of aqueous solutions of MDEA: O, 10 mass % MDEA; □, 20 mass % MDEA; ◇, 30 mass % MDEA; ×, 40 mass % MDEA; +, 50 mass % MDEA.

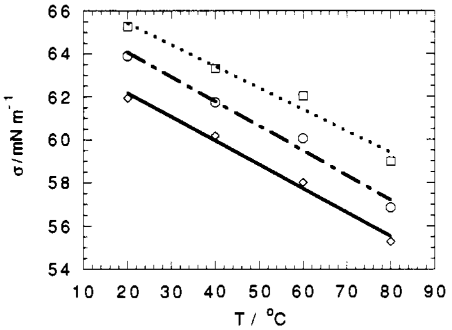

Figure 8. Surface tension of aqueous solutions of DEA: O, 10 mass % DEA; □, 20 mass % DEA; ◇, 30 mass % DEA.

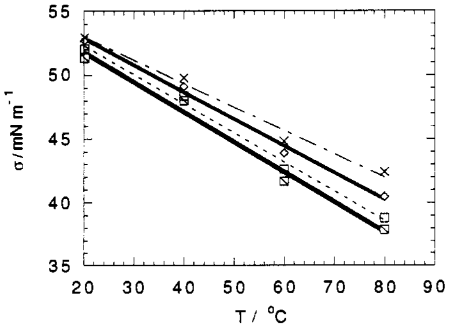

Figure 9. Surface tension of aqueous 50 mass % solutions of DEA + MDEA: ▨, 0.0441 (g of DEA/g of MDEA); □, 0.2206; ◇, 0.4413; ×, 0.5883.

DEA concentration, which is what one expects since DEA is a more polar molecule than MDEA.

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