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Effect of Hydrogen Sulfide Loading on the Density and Viscosity of Aqueous Solutions of Methyldiethanolamine

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The change in the density and viscosity of aqueous methyldiethanolamine on the addition of hydrogen sulfide was investigated in this study. At 25 °C densities and viscosities were measured for loadings up to 0.5 mol of H_2S per 1 mol of amine for amine concentrations up to 50 mass %. Solution densities and viscosities were measured at 40 °C for an amine concentration of 50 mass % and for H_2S loadings up to 0.5. It was found that the solution density increases with H_2S loading whereas the viscosity decreases as the H_2S loading increases.

Introduction

Aqueous alkanolamine solutions are commonly used to remove acid gases such as carbon dioxide and hydrogen sulfide from natural gas. Liquid densities and viscosities are needed both to interpret laboratory data for kinetic rates constants (Rinker et al., 1995a) and diffusion coefficients (Tamini et al., 1994) and to predict mass-transfer characteristics of gas/liquid contacting devices. We have previously reported density and viscosity data for unloaded aqueous amine solutions (Rinker et al., 1995b). In the work described here we present data on the effect of H_2S-loading on the density and viscosity of aqueous solutions of methyldiethanolamine (MDEA). MDEA is a tertiary amine that is widely used in the gas-processing industry and has proven to be an effective chemical solvent for selective absorption of H_2S in the presence of CO_2.

Experimental Section

The aqueous amine solutions were prepared with deionized water. The MDEA was obtained from Union Carbide Corporation with a purity greater >99 mass %. The composition of each solution was measured by titration with HCl to an equivalence point of pH equal to 4.5 (Al-Ghawas et al., 1989). All solutions were found to be within ±0.2 mass % of the nominal concentration.

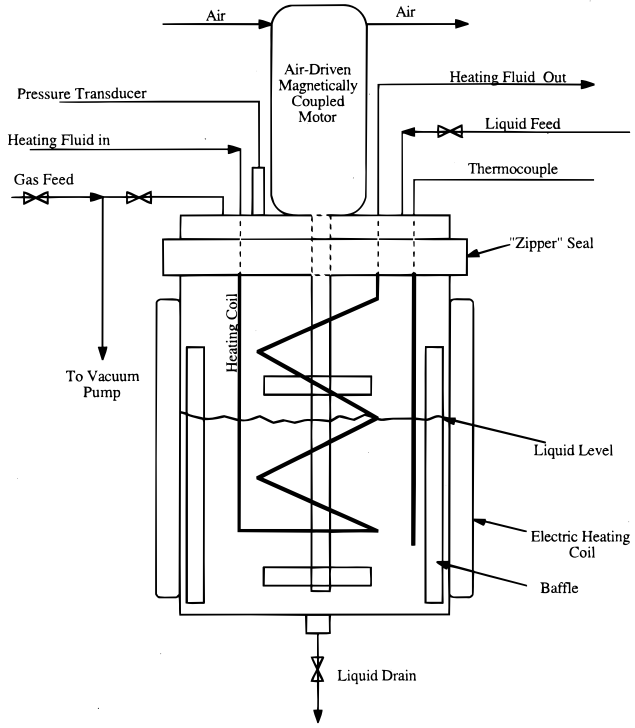

Figure 1. Schematic drawing of the modified zipperclave reactor.

The aqueous solutions of MDEA were loaded with H_2S using the modified Zipperclave reactor shown in Figure 1. Approximately 300 g of aqueous amine solution was drawn into the reactor, and the exact mass was determined from the difference in weight of the reservoir from which it was drawn. The reactor pressure was then pulled down to the vapor pressure of the aqueous amine solution by a vacuum while stirring the gas and liquid phases in the reactor with an air-driven packless magnetic motor. Once an equilibrium vapor pressure was reached, the pressure was measured with a calibrated Omega pressure transducer. The vacuum and stirrer were shut off, and a fixed amount of pure H_2S was injected quickly into the chamber. The pressures at the beginning and end of this injection were measured and recorded. The stirrer was then restarted, and the pressure in the reactor was monitored until it reached a steady value. The final pressure was measured and recorded. The temperature in the reactor was maintained to within 0.2 °C by a heating/cooling coil inside the reactor chamber. Samples of the loaded solution were then drained out the bottom of the reactor. The loading of the solution was calculated from the following equation:

$$L_{\mathrm{H_2S}} = \frac{(P_i - P_f)\left(1028.15 - \frac{m_l}{\rho}\right)M_{\mathrm{MDEA}}}{(1000)(w_{\mathrm{MDEA}})m_l RT} \qquad (1)$$

where P_i is the pressure at the end of the gas injection (atm), P_f is the final equilibrium pressure (atm), 1028.15 is the volume of the reactor in cm^3, m_l is the mass of liquid in the reactor (g), ρ is the density of the solution (g/cm^3), M_{MDEA} is the molecular weight of MDEA (g/gmol), and w_{MDEA} is the mass fraction of MDEA in the solution.

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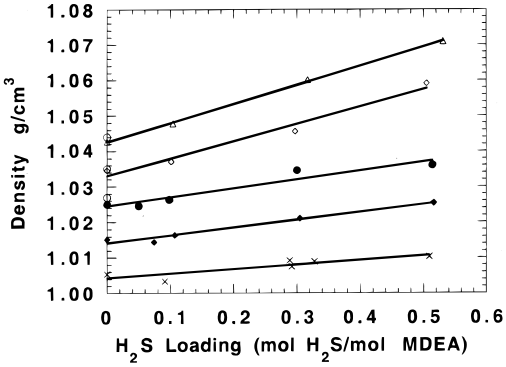

Figure 2. Density of aqueous MDEA solutions as a function of H_2S loading at 25 °C: ○, Weiland et al. (1998); ×, 10 mass % MDEA; +, 20 mass % MDEA; ●, 30 mass % MDEA; ◇, 40 mass % MDEA; △, 50 mass % MDEA.

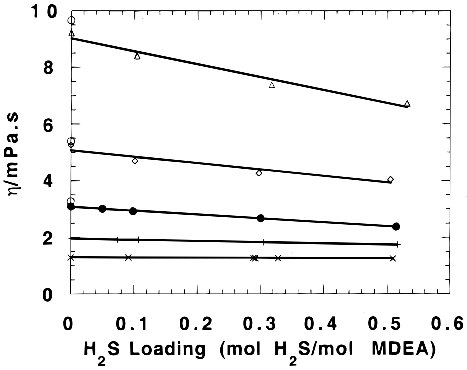

Figure 3. Viscosity of aqueous MDEA solutions as a function of H_2S loading at 25 °C: ○, Weiland et al. (1998); ×, 10 mass % MDEA; +, 20 mass % MDEA; ●, 30 mass % MDEA; ◇, 40 mass % MDEA; △, 50 mass % MDEA.

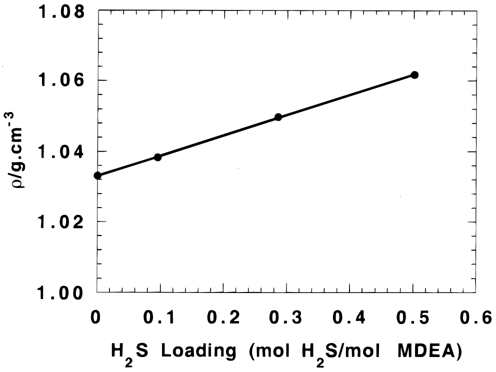

Figure 4. Density of 50 wt % MDEA at 40 °C versus H_2S loading.

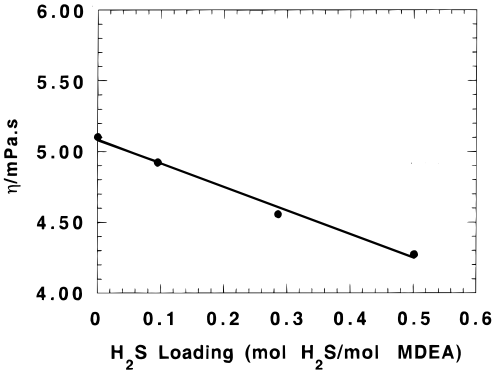

Figure 5. Viscosity of 50 wt % MDEA at 40 °C versus H_2S loading.

Table 1. Density and Viscosity of MDEA Solutions Loaded with H_2S

t/°C	mass % MDEA	H_2S loading (mol of H_2S/mol of MDEA)	ρ/g·cm^{-3}	η/mPa·s
25	10	0	1.0054	1.290
		0.091	1.0034	1.284
		0.289	1.0092	1.270
		0.292	1.0075	1.260
		0.328	1.0090	1.261
		0.509	1.0103	1.247
25	20	0	1.0152	1.941
		0.074	1.0145	1.914
		0.107	1.0164	1.910
		0.305	1.0210	1.821
25	30	0	1.0250	3.092
		0.050	1.0246	2.999
		0.098	1.0264	2.916
		0.300	1.0346	2.659
		0.514	1.0360	2.370
25	40	0	1.0346	5.253
		0.101	1.0370	4.701
		0.297	1.0456	4.264
		0.505	1.0590	4.037
25	50	0	1.0427	9.208
		0.104	1.0478	8.393
		0.317	1.0601	7.375
		0.531	1.0709	6.732
40	50	0	1.0331	5.105
		0.095	1.0383	4.923
		0.286	1.0497	4.556
		0.501	1.0617	4.274

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%.

The viscosity was measured using a Cannon-Fenske type viscometer (size 50). The viscometer was 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

$$v = Ct \tag{2}$$

where v 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, since the experimental times were generally much larger than 100 s. The constant C in eq 2 was determined for the Cannon-Fenske viscometer using water. Each reported measurement was the average of at least three runs. The dynamic viscosity was calculated by multiplying the kinematic viscosity by the corresponding density. The maximum error in the dynamic viscosity was deterministically estimated to be within ±0.3%.

Results

Measurements at 25 °C were carried out for H_2S loadings of 0.1, 0.3, and 0.5 (mol of H_2S/mol of MDEA) for MDEA concentrations of 10−50 wt %. Measurements at 40 °C were made for 50 wt % MDEA at H_2S loadings of 0.1, 0.3, and

0.5 mol of H_2S/mol of MDEA. These data are shown in Figures 2−5 and are listed in Table 1. As can be seen from the figures, the density of aqueous MDEA increases with increasing H_2S loading while the viscosity decreases with increasing H_2S loading.

Weiland et al. (1998) have measured the effect of CO_2 loading on the density and viscosity of aqueous MDEA solutions at 25 °C. Their measurements were for CO_2 loadings up to 0.50 mol of CO_2/mol MDEA. The no-loading measurements of density and viscosity by these authors are shown in Figures 2 and 3. It is seen that there is close agreement with the measurements of this work. Weiland et al. found that the density increased from 5 (30 mass % MDEA) to 8% (50 mass % MDEA) as the CO_2 loading increased from 0 to 0.5. For H_2S loading, the measurements of this work show an increase in density from 0.5% (10 mass % MDEA) to 3% (50 mass % MDEA) as the H_2S loading increases from 0 to 0.5. Weiland et al. found that the viscosity increased from 4% (30 mass % MDEA) to 33% (50 mass % MDEA) for CO_2 loading increasing from 0 to 0.5. For our work we find that as the H_2S loading increases from 0 to 0.5, the viscosity decreases 3% (10 mass % MDEA) to 2% (50 mass % MDEA).

Acknowledgment

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