

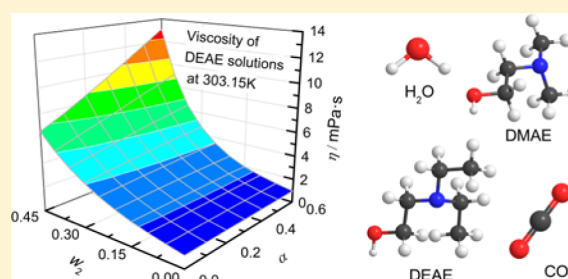


Density and Viscosity of Partially Carbonated Aqueous Tertiary Alkanolamine Solutions at Temperatures between (298.15 and 353.15) K

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ABSTRACT: The density and viscosity of partially carbonated aqueous solutions of either 2-dimethylaminoethanol or 2-diethylaminoethanol were measured over a temperature range of (298.15 to 353.15) K with alkanolamine mass fractions of 0.15 to 0.45. Correlations were developed to represent the density and viscosity of these solutions as a function of amine concentration, CO₂ loading, and temperature. For the density, the correlation represents the experimental data to within ± 0.2 %, while the viscosity data were correlated to within ± 4 %. The data and models reported in this paper will help facilitate a better understanding of the performance of these amines in CO₂ capture processes, especially in relation to mass transfer and hydrodynamic calculations.



INTRODUCTION

Amine-based absorption processes are the dominant mature technology for postcombustion CO₂ capture (PCC) and a leading contender for application in carbon capture and storage (CCS) processes designed to mitigate global warming.¹ Alkanolamines, such as monoethanolamine (MEA), diethanolamine (DEA), *N*-methyldiethanolamine (MDEA), and 2-amino-2-methyl-1-propanol (AMP), have been widely applied to remove acid gases in industrial processes over the past 80 years.^{2,3} However, these solvents are not ideal choices for large-scale CCS projects because of their comparatively rapid degradation and high energy requirements for regeneration.⁴ It is therefore essential to develop new solvents for separating dilute CO₂ from flue gases and process streams as efficiently and effectively as possible. The tertiary amines 2-dimethylaminoethanol (DMAE) and 2-diethylaminoethanol (DEAE) exhibit a moderate energy requirement, good chemical stability, and high CO₂ loading capacity, and have been identified as possible alternative solvents for CO₂ capture processes.^{5,6} It is thus necessary to quantify a range of important physical properties that influence the performance of such solvents in absorbers and strippers. In particular, the density and viscosity, which are the topic of this article, are required in thermal-hydraulic design calculations, especially in relation to mass transfer and pressure drop in packed columns.⁷ Other physical properties of interest include heat capacity, surface tension, and diffusion coefficients.

The density and viscosity of binary solutions of amines and water have been extensively studied and results over comprehensive ranges of compositions and temperatures have been reported in the literature.^{8–12} However, few literature data are available for the density and viscosity of CO₂-loaded aqueous amine systems; the systems that have been studied

under CO₂-loading include MEA, DEA, MDEA, AMP, and piperazine (PZ).^{13–20} Thus, further measurements of these properties are required for newly proposed solvent systems for CCS applications such as DMAE and DEAE. The density and viscosity of unloaded aqueous DMAE and DEAE solutions are available in the literature,^{9–12} but the influence of CO₂ dissolution has not been reported. Therefore, this study focused on the effect of CO₂-loading on the density and viscosity of aqueous DMAE and DEAE solutions, and we report both experimental measurements and empirical correlations developed for these properties. The present paper also includes some measurements on the well-studied aqueous MEA system under CO₂-loading, and these serve to validate the experimental approaches followed.

EXPERIMENTAL SECTION

Solvent Preparation and CO₂ Loading Analysis. The sources and chemical purities of the samples used in this work are detailed in Table 1; purities are as specified by the supplier, and no further purification was carried out. Unloaded solutions were prepared in 100 g batches by adding deionized water obtained from the Ultrapure Water System to the weighed quantities of amine on an analytical balance (PA413, Ohaus Pioneer) with resolution of 1 mg. The solutions were degassed in a water-filled ultrasonic bath (FB15049, Fisher Scientific). The estimated expanded uncertainty of the mass fraction of amine is 0.0002 at 95 % confidence. The CO₂-loaded solutions were prepared by bubbling pure CO₂ through the solution in a gas washing bottle for a period of (3 to 6) h, which was found

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Table 1. Description of Chemical Samples, in Which α Denotes Mole Fraction

chemical name	source	purity ^a
MEA ^b	VWR	$\alpha \geq 0.99$
DMAE ^c	Fisher Scientific	$\alpha \geq 0.99$
DEAE ^d	Fisher Scientific	$\alpha \geq 0.99$
carbon dioxide	BOC	$\alpha \geq 0.9999$
water ^e	Sigma-Aldrich	Electrical resistivity >18 M Ω -cm at $T = 298$ K
water ^f	Millipore Direct-Q UV3 apparatus	Electrical resistivity >18 M Ω -cm at $T = 298$ K

^aSpecified by the supplier. ^bMEA = monoethanolamine. ^cDMAE = 2-dimethylaminoethanol. ^dDEAE = 2-diethylaminoethanol. ^eFor densimeter calibration. ^fFor solution preparation.

to be sufficient to attain saturation. The saturated solutions were sampled and analyzed in a PerkinElmer Clarus 500 gas chromatograph (GC) system to determine the actual CO₂ loading and then sealed in bottles and stored in a cupboard at $T \approx 293$ K until needed. The GC was calibrated and operated as described previously.²¹ Partially loaded solutions were prepared when required by blending saturated solution with unloaded solution; the samples were then transferred smoothly using a pipe and mixed gently to avoid bubble formations. The same GC analysis method was applied to check the CO₂ loading of the dilute solutions.

Several composition variables are used in this work and, for simplicity, the components are numbered as follows: 1 \equiv water, 2 \equiv amine, 3 \equiv CO₂. Amine mass fraction is defined on a CO₂-free basis as $w_2 = m_2/(m_1 + m_2)$, where m_i is the mass of component i . The CO₂ loading α is defined as n_3/n_2 , and the equivalent CO₂ molality is $b_3 = n_3/(m_1 + m_2) = \alpha w_2/M_2$, where n_i is the amount and M_i is the molar mass of substance i . We also make use of the mole fractions x_1 and x_2 of water and amine in CO₂-free solutions.

The uncertainty of the CO₂ loading from the composition measurement was about 0.02α . We found that, if handled and stored carefully as described above, CO₂-loaded samples remained stable and without loss of dissolved gas for periods of up to 1 week. This was verified by repeated composition measurements. Experiments were carried out in glass apparatus and so, when substantial degassing did occur (at high temperatures and CO₂ loading, as discussed below), it could usually be observed and the experiment was then abandoned. Nevertheless, measurements were usually possible with increasing temperature up to almost the saturation temperature at the given CO₂ loading. In some cases during the viscosity

measurements, minor changes in CO₂ loading were found when comparing the composition before and after the measurements. In these cases, the average value of α was ascribed to the measurements in question. In view of this, the overall expanded uncertainty of α was finally taken to be the larger of 0.02 and 0.04α at 95 % confidence. Given the low uncertainty of w_2 , the relative uncertainty of b_3 is practically the same as that of α .

Density Measurement. Density ρ was measured with an Anton Paar DMA 5000 M vibrating-tube densimeter calibrated at $T = 293.15$ K with ambient air and ultrapure water. The temperature was measured with the built-in platinum resistance thermometer, which was calibrated by the manufacturer. The calibration of the thermometer was verified in this work by inserting a second calibrated platinum resistance thermometer into the thermowell in the densimeter block; differences were within ± 0.01 K. The expanded uncertainty of the temperature was estimated to be 0.02 K at 95 % confidence. The estimated expanded uncertainties of density for the measurements on CO₂-free liquids was $0.00002 \text{ g}\cdot\text{cm}^{-3}$ at 95 % confidence, including the effects of calibration uncertainty, repeatability, and the temperature uncertainty. For carbonated solutions, where the uncertainty of the CO₂-loading must also be considered, the combined estimated expanded uncertainty of density is $0.0001 \text{ g}\cdot\text{cm}^{-3}$. Measurements were generally carried out at temperatures between (298.15 and 353.15) K. However, gas bubbles were observed to form in some solutions at high CO₂ loading and high temperature, and meaningful measurements at those state points were not possible.

Viscosity Measurement. Kinematic viscosity was measured with certified glass U-tube capillary viscometers (PSL) with capillaries sizes O and A for samples in the ranges of (0.3 to 1) $\text{mm}^2\cdot\text{s}^{-1}$ and (0.9 to 3) $\text{mm}^2\cdot\text{s}^{-1}$, respectively. The capillary viscometer was immersed in an oil bath thermostat (Julabo 18 V) where the temperature was regulated within ± 0.01 K and measured with a calibrated secondary-standard platinum resistance thermometer (Fluke model S615) operating with a digital readout (Fluke 1502A) having a resolution of 0.001 K. The estimated expanded uncertainty of the temperature was 0.02 K and the combined expanded relative uncertainty of the viscosity measurements on CO₂-loaded solutions was 2 %, both at 95 % confidence. Measurements were carried out between (298.15 and 353.15) K but, as with the density measurements, degassing prevented measurements with higher CO₂ loadings toward the upper end of this temperature range.

Table 2. Density ρ of MEA Solutions with Amine Mass Fraction $w_2 = 0.3000$ (on a CO₂-Free Basis) at a Pressure of 0.1 MPa, Temperature T , CO₂ Loading α and Equivalent CO₂ Molality b_3 ^a

α	T/K :	298.15	299.15	301.15	303.15	313.15	323.15	333.15	343.15	353.15
	$b_3/(\text{mol}\cdot\text{kg}^{-1})$	$\rho/(\text{g}\cdot\text{cm}^{-3})$								
0.00	0.00	1.01044	1.01001	1.00911	1.00820	1.00332	0.99790	0.99221	0.98583	0.97922
0.14	0.69	1.04176	1.04133	1.04044	1.03954	1.03474	1.02953	1.02393	1.01795	1.01144
0.25	1.23	1.06668	1.06614	1.06514	1.06406	1.05886	1.05328	1.04769	1.04182	1.03547
0.38	1.87	1.09332	1.09289	1.09199	1.09107	1.08619	1.08103	1.07551	1.06966	1.06349
0.49	2.41	1.11707	1.11659	1.11564	1.11468	1.10969	1.10441			

^aExpanded uncertainties at 95 % confidence are $U(T) = 0.02$ K, $U(\rho) = 0.0001 \text{ g}\cdot\text{cm}^{-3}$, $U(w_2) = 0.0002$ and, for $\alpha > 0$, $U(\alpha) = 0.02$ and $U(b_3) = 0.1 \text{ mol}\cdot\text{kg}^{-1}$.

Table 3. Viscosity η of MEA Solutions with Amine Mass Fraction $w_2 = 0.3000$ (on a CO_2 -Free Basis) at a Pressure of 0.1 MPa, Temperature T , CO_2 Loading α and Equivalent CO_2 Molality b_3^a

α	T/K :	298.15	303.15	313.15	323.15	333.15	343.15	353.15
	$b_3/(\text{mol}\cdot\text{kg}^{-1})$	$\eta/(\text{mPa}\cdot\text{s})$						
0	0.00	2.54	2.19	1.68	1.33	1.07	0.89	0.76
0.14	0.69	2.79	2.42	1.87	1.49	1.21	1.01	0.86
0.25	1.23	2.97	2.54	1.95	1.56	1.27	1.06	0.89
0.38	1.87	3.29	2.82	2.17	1.73	1.41		
0.49	2.41	3.72	3.25	2.52	2.01			

^aExpanded uncertainties at 95 % confidence are $U(T) = 0.02$ K, $U(\eta) = 0.02\eta$, $U(w_2) = 0.0002$ and, for $\alpha > 0$, $U(\alpha) = 0.02$ and $U(b_3) = 0.1$ mol $\cdot\text{kg}^{-1}$.

RESULTS AND DISCUSSION

Experimental Data. The measurement systems were first validated by studying partially carbonated MEA solutions, which serve as a benchmark amine solvent that is commercialized for CO_2 absorption. The MEA solutions had an amine mass fraction $w_2 = 0.3$ (on a CO_2 -free basis) and the measured densities and viscosities are reported Tables 2 and 3. Figure 1 shows the present results for the dynamic viscosity of

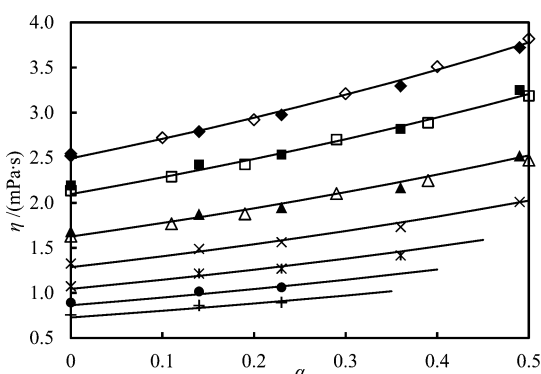


Figure 1. Viscosity of 30 mass % MEA solution. This work: \blacklozenge , $T = 298$ K; \blacksquare , $T = 303$ K; \blacktriangle , $T = 313$ K; \times , $T = 323$ K; $*$, $T = 333$ K; \bullet , $T = 343$ K; $+$, $T = 353$ K. Literature data: \diamond , $T = 298$ K;¹³ \square , $T = 303$ K;¹⁸ \triangle , $T = 313$ K;¹⁸ lines, Weiland's correlations.¹³

MEA solutions together with those of Weiland et al.¹³ at $T = 298.15$ K and Hartono et al.¹⁸ at $T = (303.15$ and $313.15)$ K. It can be seen that the viscosity is significantly increased by the dissolution of CO_2 and that all the measured data agree well with the correlation of Weiland et al.¹³

Measurements were made for DMAE and DEAE solutions at various amine concentrations, CO_2 loadings, and temperatures. The results are listed in Tables 4 to 7. As tertiary amines, both DMAE and DEAE solutions exhibit a higher viscosity compared to that for MEA at the same conditions and the CO_2 loading has a more significant influence on viscosity at a high amine concentration, especially in the DEAE solutions with $w_2 = 0.45$.

The densities of the pure liquid components were also measured in this work and the results are reported and compared with literature values in Table 8. For water, the agreement is within 0.002 % in comparison with the equation of state of Pruss and Wagner.²² For the amines, the agreement with literature^{10,12,23} is less good with relative differences of up to 0.2 %.

Correlations. For simplicity of application, we have correlated the densities of the three pure liquids studied as functions of temperature in a nondimensional form as follows:

$$\rho/(\text{g}\cdot\text{cm}^{-3}) = a + b(T/T_0) + c(T/T_0)^2 \quad (1)$$

where $T_0 = 298.15$ K. It was found, by means of trials with polynomials of higher and lower order, that the three terms in eq 1 were necessary and sufficient. The parameters a , b , and c determined for each liquid are given in Table 9. Here and

Table 4. Density ρ of Aqueous DMAE Solutions at a Pressure of 0.1 MPa, Temperature T , CO_2 -Free Amine Mass Fraction w_2 , CO_2 Loading α and Equivalent CO_2 Molality b_3^a

w_2	α	T/K :	298.15	299.15	301.15	303.15	313.15	323.15	333.15	343.15	353.15
		$b_3/(\text{mol}\cdot\text{kg}^{-1})$	$\rho/(\text{g}\cdot\text{cm}^{-3})$								
0.1500	0.00	0.00	0.99233			0.99035	0.98586	0.98082	0.97514	0.96893	0.96224
	0.47	0.79	1.02683			1.02625	1.02107	1.01539	1.00930	1.00283	
	0.82	1.38	1.05293			1.05061	1.04601				
0.3000	0.00	0.00	0.98800	0.98742	0.98626	0.98508	0.97892	0.97234	0.96536	0.95798	0.95022
	0.26	0.88	1.02680	1.02617	1.02490	1.02362	1.01697	1.01000	1.00273	0.99521	
	0.43	1.45	1.05132	1.05068	1.04940	1.04810	1.04139	1.03440	1.02718		
0.4500	0.00	0.00	0.98040			0.97675	0.96932	0.96169	0.95366	0.94533	0.93672
	0.09	0.45	0.99985			0.99608	0.98840	0.98051	0.97239	0.96404	0.95538
	0.15	0.76	1.01395			1.01013	1.00239	0.99447	0.98638	0.97808	0.96955
	0.23	1.16	1.03042			1.02660	1.01881	1.01089	1.00283	0.99459	0.98613
	0.33	1.67	1.05479			1.05096	1.04320	1.03536	1.02740		
	0.44	2.22	1.07704			1.07327	1.06567	1.05801	1.05025		
	0.48	2.42	1.08603			1.08232	1.07482	1.06724			

^aExpanded uncertainties at 95 % confidence are $U(T) = 0.02$ K, $U(\rho) = 0.0001$ g $\cdot\text{cm}^{-3}$, $U(w_2) = 0.0002$ and, for $\alpha > 0$, $U(\alpha) = \text{Max}(0.02, 0.04\alpha)$ and $U(b_3)/b_3 = U(\alpha)/\alpha$.

Table 5. Viscosity η of Aqueous DMAE Solutions at a Pressure of 0.1 MPa, Temperature T , CO₂-Free Amine Mass Fraction w_2 , CO₂ Loading α and Equivalent CO₂ Molality b_3 ^a

w_2	α	T/K:	303.15	313.15	323.15	333.15	343.15	353.15
		$b_3/(\text{mol}\cdot\text{kg}^{-1})$	$\eta/(\text{mPa}\cdot\text{s})$					
0.1500	0.00	0.00	1.45	1.14	0.91	0.74	0.62	0.53
	0.47	0.79	1.46	1.16	0.94	0.78		
	0.83	1.40	1.47	1.18				
0.3000	0.00	0.00	2.95	2.08	1.56	1.22	0.98	0.84
	0.26	0.88	3.03	2.23	1.69	1.34	1.08	
	0.43	1.45	3.20	2.39	1.85	1.38		
0.4500	0.00	0.00	5.19	3.52	2.51	1.86	1.43	1.16
	0.08	0.40	5.80	3.95	2.84	2.12	1.63	1.30
	0.15	0.76	6.10	4.17	2.98	2.23	1.73	1.37
	0.23	1.16	6.62	4.55	3.27	2.44	1.90	1.51
	0.34	1.72	7.29	5.01	3.62	2.71		
	0.40	2.02	7.72	5.32	3.85	2.90		
	0.48	2.42	8.43	5.85	4.28	3.22		

^aExpanded uncertainties at 95 % confidence are $U(T) = 0.02$ K, $U(\eta) = 0.02\eta$, $U(w_2) = 0.0002$ and, for $\alpha > 0$, $U(\alpha) = \text{Max}(0.02, 0.04\cdot\alpha)$ and $U(b_3)/b_3 = U(\alpha)/\alpha$.

Table 6. Density ρ of Aqueous DEAE Solutions at a Pressure of 0.1 MPa, Temperature T , CO₂-Free Amine Mass Fraction w_2 , CO₂ Loading α and Equivalent CO₂ Molality b_3 ^a

w_2	α	T/K:	298.15	303.15	313.15	323.15	333.15	343.15	353.15
		$b_3/(\text{mol}\cdot\text{kg}^{-1})$	$\rho/(\text{g}\cdot\text{cm}^{-3})$						
0.1500	0.00	0.00	0.99303	0.99095	0.98624	0.98089	0.97493	0.96849	0.96155
	0.52	0.67	1.02276	1.02037	1.01508	1.00920	1.00283	0.99607	0.98895
	0.83	1.06	1.03968	1.03767	1.03321	1.02822	1.02272		
0.3000	0.00	0.00	0.98696	0.98379	0.97715	0.97011	0.96269	0.95488	0.94671
	0.26	0.67	1.01782	1.01430	1.00696	0.99924	0.99146	0.98340	0.97513
	0.49	1.25	1.04450	1.04094	1.03352	1.02580	1.01793	1.01013	
	0.61	1.56	1.06058	1.05733	1.05052	1.04349	1.03607		
	0.82	2.10	1.07848	1.07517	1.06853				
0.4500	0.00	0.00	0.97572	0.97187	0.96392	0.95568	0.94712	0.93827	0.92911
	0.26	1.00	1.01821	1.01394	1.00531	0.99658	0.98774	0.97876	0.96960
	0.33	1.27	1.03069	1.02633	1.01764	1.00889	1.00009	0.99117	
	0.42	1.61	1.04517	1.04083	1.03214	1.02346	1.01475	1.00597	
	0.48	1.84	1.05540	1.05107	1.04246	1.03386	1.02526	1.01659	
	0.58	2.23	1.07185	1.06768	1.05934	1.05105	1.04275		
	0.68	2.61	1.08727	1.08345	1.07574	1.06800			
	0.81	3.11	1.11062	1.10731					

^aExpanded uncertainties at 95 % confidence are $U(T) = 0.02$ K, $U(\rho) = 0.0001$ g·cm⁻³, $U(w_2) = 0.0002$ and, for $\alpha > 0$, $U(\alpha) = \text{Max}(0.02, 0.04\cdot\alpha)$ and $U(b_3)/b_3 = U(\alpha)/\alpha$.

below, we measure the goodness of fit by means of the average absolute relative deviation $\Delta_{\text{AAD},X}$ defined for a property X by the relation

$$\Delta_{\text{AAD},X} = \frac{1}{N} \sum_{i=1}^N \frac{|X_{\text{exp},i} - X_{\text{cal},i}|}{X_{\text{exp},i}} \quad (2)$$

Here, $X_{\text{exp},i}$ is the i th experimental datum, $X_{\text{cal},i}$ is the value calculated from the correlation at the same state point, and N is the total number of points. We also give the maximum absolute relative deviation $\Delta_{\text{MAD},X}$ defined for property X by

$$\Delta_{\text{MAD},X} = \max \left(\frac{|X_{\text{exp},i} - X_{\text{cal},i}|}{X_{\text{exp},i}} \right) \quad (3)$$

These statistics are also reported in Table 9 and indicate that eq 1 provided a very good representation of the pure-component densities.

To relate the densities of the CO₂-free aqueous amine solutions to the excess molar volume V^E , the results were analyzed in terms of the relation

$$\rho = \frac{x_1 M_1 + x_2 M_2}{x_1 V_1 + x_2 V_2 + V^E} \quad (4)$$

where x_i is the mole fraction, M_i is the molar mass, and V_i is the molar volume of pure component i . The excess molar volume was correlated in a nondimensional form by means of the leading terms of a Redlich–Kister expansion^{20,24,25} as follows:

$$V^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_1 x_2 [A_0 + A_1(x_1 - x_2)] \quad (5)$$

It was found, by calculating V^E from the data and plotting it, that the two terms in eq 5 were necessary and sufficient. It was also apparent that, while A_1 was essentially constant, A_0 exhibited a linear dependence upon temperature which was represented as follows:

Table 7. Viscosity η of Aqueous DEAE Solutions at a Pressure of 0.1 MPa, Temperature T , CO₂-Free Amine Mass Fraction w_2 , CO₂ Loading α and Equivalent CO₂ Molality b_3 ^a

w_2	α	T/K:	303.15	313.15	323.15	333.15	343.15	353.15
		$b_3/(\text{mol}\cdot\text{kg}^{-1})$	$\eta/(\text{mPa}\cdot\text{s})$					
0.1500	0.00	0.00	1.53	1.18	0.93	0.76	0.63	0.54
	0.52	0.67	1.58	1.23	0.99	0.81	0.68	0.58
	0.82	1.05	1.61	1.26				
0.3000	0.00	0.00	2.90	2.07	1.55	1.20	0.96	0.80
	0.27	0.69	3.41	2.42	1.81	1.41	1.13	
	0.51	1.31	3.70	2.66	1.99	1.55	1.24	
	0.65	1.66	3.78	2.76	2.10	1.65	1.33	
	0.81	2.07	3.83	2.81				
0.4500	0.00	0.00	5.23	3.50	2.51	1.85	1.43	1.14
	0.21	0.81	7.11	4.73	3.33	2.48	1.92	
	0.30	1.15	7.84	5.22	3.67	2.72	2.09	
	0.40	1.54	8.79	5.78	4.05	3.00	2.31	
	0.43	1.65	9.14	6.01	4.18	3.06		
	0.56	2.15	10.32	6.79	4.76	3.50		
	0.61	2.34	10.91	7.18	5.00			
	0.80	3.07	11.80					

^aExpanded uncertainties at 95 % confidence are $U(T) = 0.02$ K, $U(\eta) = 0.02\eta$, $U(w_2) = 0.0002$, and, for $\alpha > 0$, $U(\alpha) = \text{Max}(0.02, 0.04\cdot\alpha)$ and $U(b_3) = U(\alpha)/\alpha$.

Table 8. Density ρ of Pure Water, DMAE, and DEAE at Pressure of 0.1 MPa and Temperature T ^a

T/K:	298.15	303.15	313.15	323.15	333.15	343.15	353.15	
component	$\rho/(\text{g}\cdot\text{cm}^{-3})$							source
water	0.99705	0.99564	0.99221	0.98802	0.98318	0.97776	0.97181	this work
	0.99705	0.99565	0.99222	0.98803	0.98320	0.97776	0.97179	ref 19
DMAE	0.88383	0.87957	0.87095	0.86220	0.85329	0.84420	0.83493	this work
	0.88358	0.87932	0.87069	0.86190	0.85297	0.84384	0.83452	ref 12
DEAE	0.88037	0.87575	0.86641	0.85695	0.84738	0.83774	0.82802	this work
		0.87640	0.86740	0.85830	0.84910	0.83860		ref 20
	0.87929	0.87459	0.86504		0.84649		0.82724	ref 10

^aExpanded uncertainties at 95 % confidence are $U(T) = 0.02$ K and $u(\rho) = 0.00002$ g·cm⁻³.

Table 9. Parameters for eq 1 for the Density of the Pure Amines Together with the Average Absolute Relative Deviations $\Delta_{\text{AAD},\rho}$ and the Maximum Absolute Relative Deviation $\Delta_{\text{MAD},\rho}$ ^a

substance	a	b	c	$\Delta_{\text{AAD},\rho}$	$\Delta_{\text{MAD},\rho}$
water	0.79484	0.48906	-0.28679	0.005 %	0.008 %
DMAE	1.06426	-0.10909	-0.07135	0.001 %	0.002 %
DEAE	1.11277	-0.18888	-0.04351	0.001 %	0.002 %

^aThe number of digits reported was chosen to avoid round-off errors.

$$A_0 = A_{0,0} + A_{0,1}(T/T_0) \quad (6)$$

The molar volumes of the pure components were calculated from the densities measured in this work, and the parameters in eqs 5 and 6 were then adjusted to best fit the measured solution

densities. The resulting values of $A_{0,0}$, $A_{0,1}$, and A_1 are given in Table 10 along with the corresponding values of $\Delta_{\text{AAD},\rho}$ and $\Delta_{\text{MAD},\rho}$ for the CO₂-free aqueous amine solutions. As evidenced by the very-low values of $\Delta_{\text{AAD},\rho}$ and $\Delta_{\text{MAD},\rho}$, this three-parameter model provides an excellent account of the experimental data. For both systems, A_0 is negative across the experimental temperature range. For aqueous solutions of DMAE, the asymmetry parameter A_1 is negative but small and of marginal statistical significance. For aqueous DEAE, this parameter is also negative but much greater in magnitude.

Plots of the densities of the CO₂-loaded amine solutions as functions of the CO₂-loading α showed that there exists a substantially linear dependence of ρ upon α . Furthermore, the derivative $(\partial\rho/\partial\alpha)_{T,w_2}$ was found to be essentially independent of T and proportional to the mass fraction w_2 of amine in the

Table 10. Parameters in eqs 5, 6 and 7 for the Density of CO₂-Free and CO₂-Loaded Aqueous Amine Solutions^a

amine	$A_{0,0}$	$A_{0,1}$	A_1	CO ₂ -free solutions		d	CO ₂ -loaded solutions	
				$\Delta_{\text{AAD},\rho}$	$\Delta_{\text{MAD},\rho}$		$\Delta_{\text{AAD},\rho}$	$\Delta_{\text{MAD},\rho}$
DMAE	-12.394	3.525	-0.5935	0.03 %	0.09 %	0.5003	0.05 %	0.17 %
DEAE	-7.872	6.838	-12.813	0.03 %	0.10 %	0.3790	0.06 %	0.21 %

^aThe number of digits reported was chosen to avoid round-off errors.

CO₂-free solvent. Accordingly, the CO₂-loaded solution densities were correlated by means of the following simple one-parameter relation:

$$\rho(T, w_2, \alpha) = \rho_0(T, w_2)(1 + d\alpha w_2) \quad (7)$$

Here $\rho_0(T, w_2)$ is the density of the CO₂-free aqueous amine solution obtained from eq 4 with $x_2 = w_2[w_2 + (1 - w_2)(M_2/M_1)]^{-1}$, and d is an adjustable parameter. As shown in Figure 2,

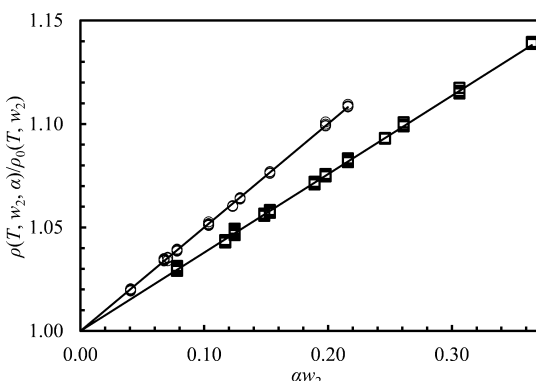


Figure 2. Ratio $\rho(T, w_2, \alpha)/\rho_0(T, w_2)$ of the density $\rho(T, w_2, \alpha)$ of CO₂-loaded aqueous amine solutions to the density $\rho_0(T, w_2)$ of the CO₂-free solution as a function of the product αw_2 of the CO₂-loading α and the amine mass fraction w_2 of the CO₂-free solution: O, DMAE; □, DEAE.

where we plot the density ratio $\rho(T, w_2, \alpha)/\rho_0(T, w_2)$ against αw_2 , this one-parameter model provided a remarkably good description of the measured density data. The parameters and goodness-of-fit measures obtained for the two systems are given in Table 10. We note that, from eq 7, the condition for the volume of solution to remain constant under dissolution of CO₂ at constant temperature and pressure is $d = M_3/M_2$. The fitted values of d exceed that ratio by about 2% for DMAE and by about 1% for DEAE, indicating that dissolution of CO₂ is in fact accompanied by a slight reduction in solution volume. The correlations of density are valid for $w_2 \leq 0.45$ and $298.15 \leq T/\text{K} \leq 353.15$, with CO₂ loading α up to saturation.

It is difficult to develop a generic model for the viscosity of partially carbonated amine solutions covering the wide ranges of amine mass fraction, CO₂-loading, and temperature encountered in CCS applications. For example, the correlation proposed by Weiland et al.¹³ for the MEA system works well only in the amine-mass-fraction range of 0.2 to 0.4, while that suggested by Hartono et al.¹⁸ for the same system performs satisfactorily only for w_2 between 0.3 and 0.4. This is primarily due to the complexity of the ionic species in partially carbonated solutions, where the CO₂ reacts with the amine to yield mainly carbamate and bicarbonate. The concentration of these species of course varies with temperature, amine mass fraction, and CO₂ loading and the arising complex molecular interactions, for example, hydrogen bonding, significantly enhance the viscosity.

In relation to the present work, we found that the data at fixed values of w_2 and α conformed well to a Vogel–Fulcher–Tammann equation. Thus, generalized correlations in the form

$$\ln \left[\frac{\eta(T, w_2, \alpha)}{\eta_w(T)} \right] = A(w_2, \alpha) + \frac{B(w_2, \alpha)}{T + C} \quad (8)$$

were developed, where $A(w_2, \alpha)$ and $B(w_2, \alpha)$ are composition-dependent functions to be determined, and C is taken as a constant. In eq 8, $\eta_w(T)$ is the viscosity of pure water at temperature T and was included as a divisor to ensure that correlation had the correct behavior in the limits $w_2 \rightarrow 0$ and $\alpha \rightarrow 0$. The viscosity of pure water was calculated from the IAPWS-95 recommended equation;²² the values may be represented to within $\pm 0.1\%$ in the present temperature range by means of the following expression:

$$\ln \left(\frac{\eta}{\text{mPa}\cdot\text{s}} \right) = -3.6957 + \frac{1.9011}{(T/T_0) - 0.4689} \quad (9)$$

Exploring the data for both water–amine–CO₂ systems, it is apparent that the coefficient B is simply proportional to w_2 and independent of α . Unfortunately, $A(w_2, \alpha)$ is not a simply linear function of its arguments and a satisfactory polynomial expansion appears to require at least six terms. The complexity of the composition dependence is illustrated in Figure 3 where

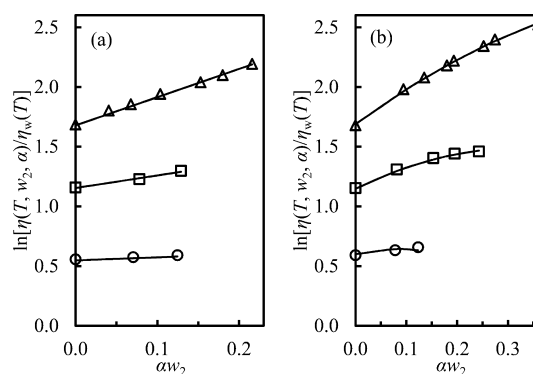


Figure 3. Natural logarithm of the ratio $\eta(T, w_2, \alpha)/\eta_w(T)$ of the viscosity $\eta(T, w_2, \alpha)$ of CO₂-loaded aqueous amine solutions to the viscosity $\eta_w(T)$ of pure water as a function of the product αw_2 of the CO₂-loading α and the amine mass fraction w_2 of the CO₂-free solution at temperature $T = 313.15$ K for (a) DMAE and (b) DEAE: O, $w_2 = 0.15$; □, $w_2 = 0.30$; △, $w_2 = 0.45$. Lines calculated from eq 10 for DMAE and eq 11 for DEAE.

we plot $\ln[\eta(T, w_2, \alpha)/\eta_w(T)]$ as a function of αw_2 for both amines systems at a constant temperature of 313.15 K. Tests with different composition variables (for example, mole fractions, mass fractions and molalities) did not appear to offer any improvement. To find a more efficient representation with fewer parameters, we made use of an evolutionary symbolic regression tool (Eureqa, Nutonian Inc.) to search for optimal mathematical structures in the general form of eq 8. The optimal structure found for the DMAE system was

$$\ln \left[\frac{\eta(T, w_2, \alpha)}{\eta_w(T)} \right] = a_1 w_2^2 + a_2 w_2^3 + a_3 \alpha w_2^3 + \frac{b_1}{(T/T_0) + C} \quad (10)$$

while, for the DEAE system, the optimal representation was

$$\ln \left[\frac{\eta(T, w_2, \alpha)}{\eta_w(T)} \right] = a_1 \sqrt{w_2} + a_2 \alpha w_2^2 + a_3 \alpha^2 w_2 + \frac{b_1 w_2}{(T/T_0) + C} \quad (11)$$

in both cases $T_0 = 298.15$ K as before. The optimal values of the parameters appearing in eqs 10 and 11 are given in Table

Table 11. Parameters in eqs 10 and 11 for the Viscosity of CO₂-Loaded Aqueous Amine Solutions^a

amine	a_1	a_2	a_3	b_1	C	$\Delta_{\text{AAD},\eta}$	$\Delta_{\text{MAD},\eta}$
DMAE	4.457	−6.990	11.68	0.864	−0.775	1.4 %	4.0 %
DEAE	0.2220	6.892	−0.931	0.942	−0.775	1.2 %	4.1 %

^aThe number of digits reported was chosen to avoid round-off errors.

11 along with the $\Delta_{\text{AAD},\eta}$ and $\Delta_{\text{MAD},\eta}$ statistics. As shown in Figures 4 and 5, eqs 10 and 11 provide a generally good

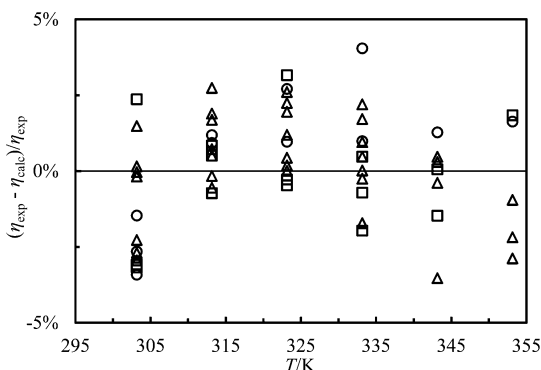


Figure 4. Deviations $(\eta_{\text{exp}} - \eta_{\text{calc}})/\eta_{\text{exp}}$ of experimental viscosities η_{exp} of CO₂-loaded aqueous DMAE solutions from values η_{calc} calculated from eq 10 with parameters from Table 11 as a function of temperature T : \circ , $w_2 = 0.15$; \square , $w_2 = 0.30$; \triangle , $w_2 = 0.45$.

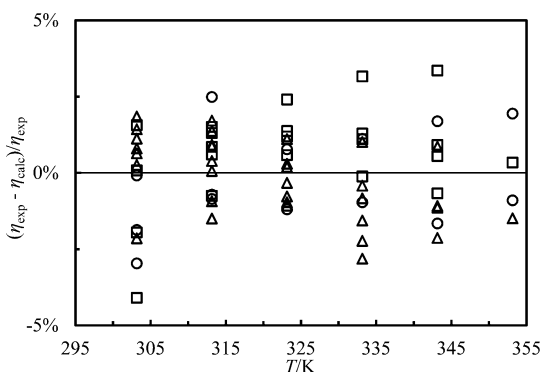


Figure 5. Deviations $(\eta_{\text{exp}} - \eta_{\text{calc}})/\eta_{\text{exp}}$ of experimental viscosities η_{exp} of CO₂-loaded aqueous MEAE solutions from values η_{calc} calculated from eq 11 with parameters from Table 11 as a function of temperature T : \circ , $w_2 = 0.15$; \square , $w_2 = 0.30$; \triangle , $w_2 = 0.45$.

account of the data, while not quite fitting it to within its estimated uncertainty. The correlations of viscosity are valid for $w_2 \leq 0.45$ and $303.15 \leq T/\text{K} \leq 353.15$, with CO₂ loading α up to saturation; given their empirical nature, the correlations should not be extrapolated outside these ranges.

CONCLUSIONS

Measurements have been made, and correlations have been developed, for the density and viscosity data of two amine-based solvents (DMAE and DEAE) over important ranges of CO₂ loading, temperature, and amine concentration. These results will facilitate improved process and plant design and, in particular, are useful for fluid dynamics calculations, gas–liquid mass transfer resistance, and the selection of pumps and packing in CO₂ scrubbing processes. Both the DMAE and DEAE solvents exhibited a higher viscosity than MEA solution at the same concentration and temperature. The effect of

dissolved CO₂ on the viscosity of DEAE solutions is significantly greater than for DMEA solutions. Correlations for the density of DMAE and DEAE solutions as functions of temperature, amine mass fraction, and CO₂ loading were obtained which are in satisfactory agreement with the experimental data ($\Delta_{\text{AAD},\rho} \leq 0.07\%$). Additionally, correlations for the viscosities of these two systems were obtained as functions of temperature, amine mass fraction, and CO₂ loading; these too are in satisfactory agreement with the experimental data ($\Delta_{\text{AAD},\rho} \leq 2\%$).

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Notes

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REFERENCES

- (1) IPCC Special Report on Carbon Dioxide Capture and Storage; Cambridge University Press: Cambridge, 2005.
- (2) Rochelle, G. T. Amine scrubbing for CO₂ capture. *Science* **2009**, 325, 1652–1654.
- (3) Kohl, A. L. and Nielsen, R. B. *Gas Purification*, 5th ed.; Gulf Publishing Co.: Houston, TX, 1997.
- (4) Zhang, J.; Qiao, Y.; Agar, D. W. Intensification of low temperature thermomorphic biphasic amine solvent regeneration for CO₂ capture. *Chem. Eng. Res. Des.* **2012**, 90, 743–749.
- (5) Vitse, F.; Bedell, S. A.; Baburao, B. Solvent and method for CO₂ capture from flue gas. CA Patent CA2811290, 2012.
- (6) Monteiro, J. G. M. S.; Pinto, D. D. D.; Zaidy, S. A. H.; Hartono, A.; Svendsen, H. F. VLE data and modelling of aqueous N,N-diethylethanolamine (DEEA) solutions. *Int. J. Greenhouse Gas Control* **2013**, 19, 432–440.
- (7) Mangers, R. J.; Ponter, A. B. Effect of viscosity on liquid film resistance to mass transfer in a packed column. *Ind. Eng. Chem. Process Des. Dev.* **1980**, 19, 530–537.
- (8) Maham, Y.; Liew, C. N.; Mather, A. E. Viscosities and excess properties of aqueous solutions of ethanolamines from 25 to 80 °C. *J. Solution Chem.* **2002**, 31, 743–756.
- (9) Maham, Y.; Teng, T. T.; Lebrette, L.; Mather, A. E. Volumetric properties of aqueous solutions of monoethanolamine, mono- and dimethylethanolamines at temperatures from 5 to 80 °C - I. *Thermochim. Acta* **2002**, 386, 111–118.
- (10) Lebrette, L.; Maham, Y.; Teng, T. T.; Hepler, L. G.; Mather, A. E. Volumetric properties of aqueous solutions of mono-, and diethylethanolamines at temperatures from 5 to 90 °C - II. *Thermochim. Acta* **2002**, 386 (2), 119–126.
- (11) Maham, Y.; Lebrette, L.; Mather, A. E. Viscosities and Excess Properties of Aqueous Solutions of Mono- and Diethylethanolamines at Temperatures between 298.15 and 353.15 K. *J. Chem. Eng. Data* **2002**, 47, 550–553.
- (12) Bernal-Garcia, J. M.; Hall, K. R.; Estrada-Baltazar, A.; Iglesias-Silva, G. A. Density and Viscosity of Aqueous Solutions of N,N-

dimethylethanolamine at $p = 0.1$ MPa from $T = (293.15 \text{ to } 363.15)$ K. *J. Chem. Thermodyn.* **2005**, *37*, 762–767.

(13) Weiland, R. H.; Dingman, J. C.; Cronin, D. B.; Browning, G. J. Density and Viscosity of Some Partially Carbonated Aqueous Alkanolamine Solutions and Their Blends. *J. Chem. Eng. Data* **1998**, *43*, 378–382.

(14) Amundsen, T. G.; Øi, L. E.; Eimer, D. A. Density and viscosity of monoethanolamine + water + carbon dioxide from $(25 \text{ to } 80)$ °C. *J. Chem. Eng. Data* **2009**, *54*, 3096–3100.

(15) Freeman, S. A.; Rochelle, G. T. Density and Viscosity of Aqueous (Piperazine + Carbon Dioxide) Solutions. *J. Chem. Eng. Data* **2011**, *56*, 574–581.

(16) Fu, D.; Chen, L.; Qin, L. Experiment and model for the viscosity of carbonated MDEA–MEA aqueous solutions. *Fluid Phase Equilib.* **2012**, *319*, 42–47.

(17) Fu, D.; Li, Z.; Liu, F. Experiments and model for the viscosity of carbonated 2-amino-2-methyl-1-propanol and piperazine aqueous solution. *J. Chem. Thermodyn.* **2014**, *68*, 20–24.

(18) Hartono, A.; Mba, O. E.; Svendsen, H. F. Physical properties of partially CO₂ loaded aqueous monoethanolamine (MEA). *J. Chem. Eng. Data* **2014**, *59*, 1808–1816.

(19) Han, J.; Jin, J.; Eimer, D. A.; Melaaen, M. C. Density of water (1) + diethanolamine (2) + CO₂ (3) and water (1) + N-methyldiethanolamine (2) + CO₂ (3) from $(298.15 \text{ to } 423.15)$ K. *J. Chem. Eng. Data* **2012**, *57*, 1843–1850.

(20) Pinto, D. D. D.; Monteiro, J. G. M. S.; Johnsen, B.; Svendsen, H. F.; Knuutila, H. Density measurements and modelling of loaded and unloaded aqueous solutions of MDEA (N-methyldiethanolamine), DMEA (N,N-dimethylethanolamine), DEEA (diethylethanolamine) and MAPA (N-methyl-1,3-diaminopropane). *Int. J. Greenhouse Gas Control* **2014**, *25*, 173–185.

(21) Tong, D.; Trusler, J. P. M.; Maitland, G. C.; Gibbins, J.; Fennell, P. S. Solubility of carbon dioxide in aqueous solution of monoethanolamine or 2-amino-2-methyl-1-propanol: Experimental measurements and modelling. *Int. J. Greenhouse Gas Control* **2012**, *6*, 37–47.

(22) Wagner, W.; Pruß, A. The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387–535.

(23) Kao, C. Z.; Li, M. H. Diffusion coefficients of aqueous N,N-diethylethanolamine, N,N-dimethylethanolamine, monoisopropanolamine, piperazine, and sulfolane solutions. *J. Chin. Inst. Chem. Eng.* **2006**, *37* (4), 341–353.

(24) Redlich, O.; Kister, A. T. Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.

(25) Li, M. H.; Lie, Y. C. Densities and Viscosities of Solutions of Monoethanolamine + N-Methyldiethanolamine + Water and Monoethanolamine + 2-Amino-2-methyl-1-propanol + Water. *J. Chem. Eng. Data* **1994**, *39*, 444–447.