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ARTICLE *in* JOURNAL OF CHEMICAL & ENGINEERING DATA · APRIL 1994

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Viscosity of Aqueous Solutions of *N*-Methyldiethanolamine and of Diethanolamine

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The viscosity of aqueous solutions of methyldiethanolamine (MDEA) and of diethanolamine (DEA) have been measured at five temperatures in the range 25–80 °C throughout the whole concentration range. The viscosity has been correlated as a function of composition for use in industrial calculations.

Introduction

Aqueous solutions of alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), *N*-methyldiethanolamine (MDEA), di-2-propanolamine (DIPA), and bis[2-(hydroxyamino)ethyl] ether (DGA) are good solvents for the removal of acid gases such as CO₂ and H₂S from the gas streams of many processes in the natural gas, petroleum, ammonia synthesis, and some chemical industries (1). The equilibrium solubility of the acid gases in alkanolamines and other chemical and physical solvents is essential in the design and operation of processes involving the respective solvents, and has been determined over a wide range of temperatures and partial pressures (1, 2).

Diethanolamine has a rapid rate of reaction with CO₂ with an enthalpy of reaction of 67 kJ/mol, and has a higher capacity for the acid gases than monoethanolamine (3). *N*-Methyldiethanolamine has a lower enthalpy of reaction with CO₂ and has been used for the selective removal of H₂S (4, 5). It has a higher capacity to absorb CO₂ than MEA and DEA. Recently many studies have been done on the absorption and desorption of acid gases into aqueous MDEA, DEA, and their blends (6–10). Viscosity data for both MDEA and DEA solutions are needed for the analysis of the absorption and desorption processes.

The present study presents the viscosities of the binary aqueous solutions of MDEA and of DEA at 25, 40, 60, 70, and 80 °C throughout the whole concentration range for industrial application. The results are represented by concentration polynomials and the deviation of the viscosity from a mole fraction average is correlated by a Redlich–Kister-type equation.

Experimental Section

Binary aqueous solutions of *N*-methyldiethanolamine and of diethanolamine were prepared from doubly distilled water by mass. Both *N*-methyldiethanolamine and diethanolamine were obtained from Aldrich Chemical Co. with a purity of 99%. They were used without further purification.

Because of the wide range of viscosities for both MDEA and DEA solutions, several Schott Geräte Type 24 501 capillary viscometers of various sizes were used. Distilled water (11) and Cannon Certified Standard Viscosity Liquids N35 and N350 were used for calibration. The equation for

Table 1. Viscosities of Aqueous MDEA Solutions

$x(\text{MDEA})$	$\eta/(\text{mPa}\cdot\text{s})$				
	25 °C	40 °C	60 °C	70 °C	80 °C
0.0000	0.8903	0.6531	0.4666	0.4049	0.3554
0.0079	1.059	0.756	0.532	0.451	0.399
0.0176	1.301	0.902	0.624	0.522	0.456
0.0364	1.901	1.260	0.838	0.685	0.588
0.0612	3.057	1.893	1.128	1.026	0.852
0.0923	5.172	2.995	1.650	1.443	1.156
0.1322	9.172	5.219	2.487	2.082	1.629
0.1859	17.02	8.843	4.174	3.080	2.347
0.2526	32.11	14.32	6.203	4.436	3.264
0.3021	43.51	18.62	7.742	5.407	3.925
0.3658	56.06	23.58	9.530	6.566	4.695
0.5026	74.16	31.33	12.33	8.413	5.980
0.5653	81.05	33.63	13.18	8.951	6.344
0.6960	82.37	35.36	14.09	9.614	6.840
0.8989	78.87	34.89	14.36	9.926	7.111
1.0000	77.19	34.11	14.30	9.849	7.115

the kinematic viscosity is

$$\nu = k_1 t - k_2/t \quad (1)$$

where t is the efflux time and k_1 and k_2 are the viscometer constants. The second term, k_2/t , represents the correction due to kinetic energy and can generally be neglected. The viscometers were immersed into a thermostated Tamson Holland water bath during the measurements. The water bath temperatures were controlled to ± 0.01 °C, and were read with a digital thermometer from Guildline Instruments Ltd. (model 9535/120). The Schott Geräte capillary viscometers were fitted with fiber optic sensors of the type described by Gardner and Senanayake (12). The sensors were used to automatically start and stop an electronic timer which measures the efflux time of a known volume of liquid passing through a precision capillary. The timer was accurate to 0.01 s. For each measurement, an average efflux time was taken over at least six runs. The overall average percent deviation of the means was estimated to be ± 0.045 . The absolute viscosities were obtained by multiplying the measured kinematic viscosities with the densities of the same solutions also measured in this laboratory (13). The propagation of errors for the measurements results in an overall accuracy of the absolute viscosity value of $\pm 0.1\%$.

Results and Discussion

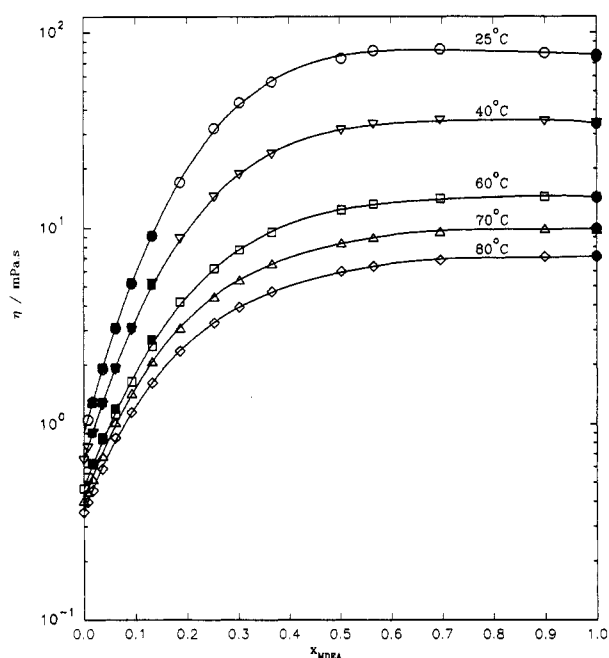
Experimentally measured viscosities of the binary aqueous solutions of MDEA and of DEA, respectively, at 25, 40, 60, 70, and 80 °C throughout the whole concentration range are listed in Tables 1 and 2. In addition to the solutions of various concentrations and the five temperatures, the viscosity of

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Table 2. Viscosities of Aqueous DEA Solutions^a

$x(\text{DEA})$	$\eta / (\text{mPa}\cdot\text{s})$				
	25 °C	40 °C	60 °C	70 °C	80 °C
0.0000	0.8903	0.6531	0.4666	0.4049	0.3554
0.0093	1.051	0.755	0.532	0.451	0.398
0.0188	1.255	0.878	0.609	0.513	0.448
0.0414	1.875	1.250	0.835	0.685	0.588
0.0690	3.240	1.884	1.245	1.029	0.866
0.1028	5.486	3.008	1.855	1.482	1.213
0.1469	10.34	5.522	2.959	2.269	1.801
0.2054	21.44	10.42	4.939	3.654	2.800
0.2884	48.78	21.56	8.975	6.342	4.611
0.4026	112.5	44.04	16.37	10.99	7.726
0.6059	262.4	95.06	32.02	20.23	13.44
0.8012	420.3	143.9	45.70	28.30	18.37
0.9438	524.1	175.3	54.35	33.24	21.37
1.0000	566.3	188.2	57.69	35.09	22.43

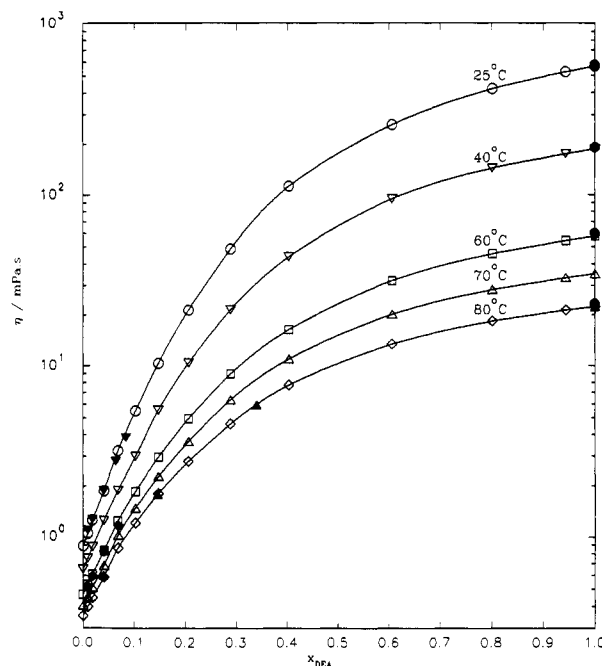
^a η of pure DEA at 30 °C, 383.8 mPa·s.**Figure 1.** Viscosity of binary aqueous MDEA solutions at various temperatures as a function of mole fraction: (●) DiGuilio et al. (14); (■) Al-Ghawas et al. (15).

pure DEA liquid at 30 °C has been measured. Its value is given in the footnote of Table 2. The viscosity of pure DEA at 25 °C was measured by immersing the viscometer containing the pure DEA into the water bath at a temperature higher than its melting point, 27–30 °C. The water bath was then slowly cooled to 25 °C, and the viscosity was measured. The DEA liquid at 25 °C was probably in a metastable state.

Table 3. Coefficients of the Polynomial $\ln \eta = \ln \eta_0 + \sum_1^m a_k x^k$ for the Binary Solutions of MDEA and of DEA at Various Temperatures

$t/^\circ\text{C}$	amine	a_1	a_2	a_3	a_4	a_5	a_6	σ^b
25	MDEA	2.27021E+1 ^a	-4.22796E+1	3.46898E+1	-1.06501E+1			1.79E-2
	DEA	1.99609E+1	-2.36986E+1	7.79090	7.19233	-4.69444		2.09E-2
40	MDEA	1.99406E+1	-3.82725E+1	3.32888E+1	-1.10070E+1			1.95E-2
	DEA	1.60553E+1	-6.14446	-5.06698E+1	1.11447E+2	-9.41950E+1	2.91726E+1	1.21E-2
60	MDEA	1.64896E+1	-3.10387E+1	2.67285E+1	-8.76094			1.83E-2
	DEA	1.56535E+1	-2.46212E+1	2.42608E+1	-1.42902E+1	3.81503		1.32E-2
70	MDEA	1.69350E+1	-4.13009E+1	5.67079E+1	-4.15075E+1	1.23593E+1		2.23E-2
	DEA	1.44965E+1	-2.14949E+1	1.67335E+1	-5.27816			2.21E-2
80	MDEA	1.59736E+1	-4.05720E+1	5.89011E+1	-4.54208E+1	1.41180E+1		1.74E-2
	DEA	1.38062E+1	-2.14742E+1	1.76726E+1	-5.86633			2.03E-2

^a 2.27021E+1 = 2.27021 $\times 10^1$. ^b σ = standard deviation = $[\sum (y^{\text{obs}} - y^{\text{cal}})^2 / (n - k)]^{1/2}$, where n = number of points and k = number of parameters (coefficients).

**Figure 2.** Viscosity of binary aqueous DEA solutions at various temperatures as a function of mole fraction: (●) DiGuilio et al. (14); (▲) Leibush and Shorina (16); (◆) Littell et al. (17); (▼) Glasscock (18).

Viscosities of pure MDEA measured in this work agree well with those of DiGuilio et al. (14). Al-Ghawas et al. (15) measured densities and viscosities of pure MDEA and aqueous MDEA solutions up to 50 mass %. Their viscosity values are slightly higher except for pure MDEA at 25 °C. This could be due to the higher density values they reported.

Viscosities of the aqueous DEA solutions measured in this work are in good agreement with those reported in the literature (16–18). For pure DEA, values obtained in the present work are in good agreement with those of DiGuilio et al. except at 80 °C.

Figures 1 and 2 are the plots of the viscosities of aqueous MDEA solutions and of aqueous DEA solutions, respectively, as a function of temperature and mole fraction. For convenience of interpolation, the viscosities at each temperature have been fitted by the following polynomial:

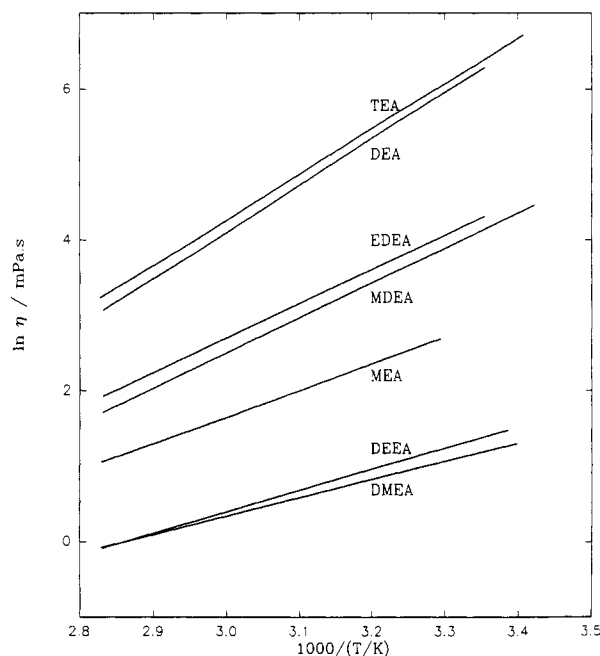
$$\ln \eta = \ln \eta_0 + \sum_1^m a_k x^k \quad (2)$$

where η is the viscosity of the binary solution, η_0 the viscosity of pure water, and x the mole fraction of the amines. a_k are the polynomial coefficients whose values are listed in Table 3.

Table 4. Activation Energies for Viscous Flow of Ethanolamines

amine	E /(kJ/mol)	temp range/°C
monoethanolamine (MEA)	29.22 ^b	30–80
diethanolamine (DEA)	51.49 ^a (51.51 ^b)	25–80
triethanolamine (TEA)	50.16 ^b	20–80
<i>N,N</i> -dimethylethanolamine (DMEA)	20.05 ^b	21–80
<i>N</i> -methyldiethanolamine (MDEA)	38.01 ^a (38.10 ^b) (39.17 ^c)	25–80
<i>N</i> -ethyldiethanolamine (EDEA)	38.62 ^b	19–80
<i>N,N</i> -diethylethanolamine (DEEA)	23.25 ^b	22–80

^a This work. ^b Data taken from ref 14. ^c Data taken from ref 15, temperature range 25–60 °C.

**Figure 3.** Dynamic viscosity of pure ethanolamines as a function of temperature.

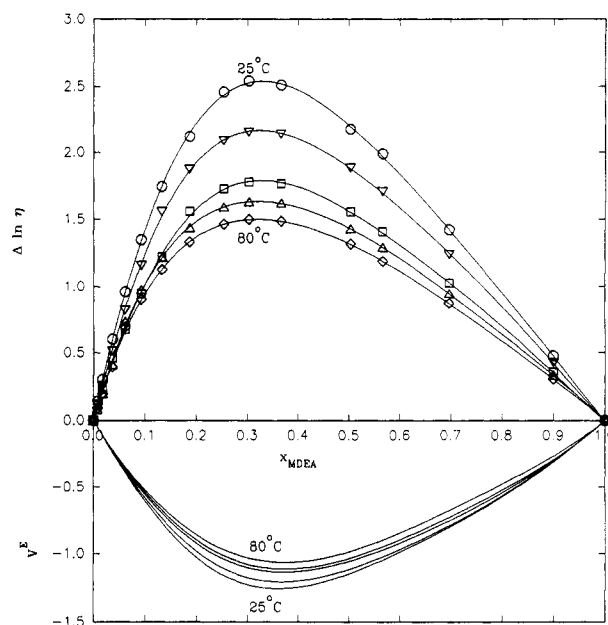
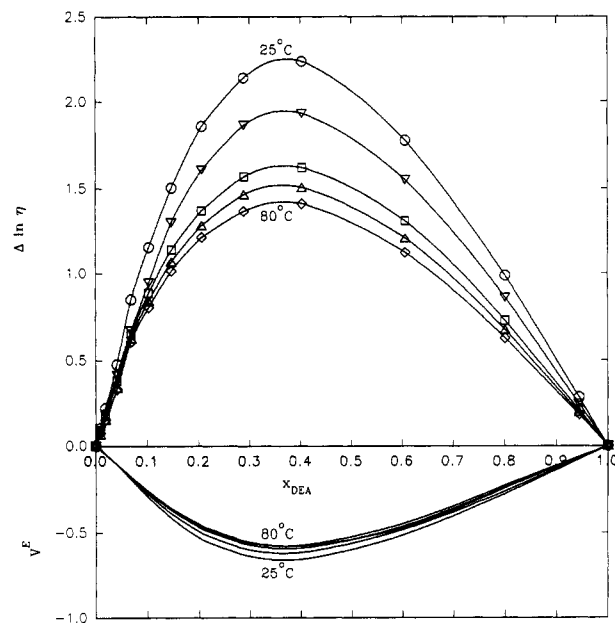
The viscosity of pure amines in certain temperature ranges can be represented by the Arrhenius equation:

$$\eta/(\text{mPa}\cdot\text{s}) = Ae^{E/RT} \quad (3)$$

where A is a system-specific constant, E the activation energy for viscous flow, R the gas constant, and T the temperature. Equation 3 has been applied to both MDEA and DEA. It represents quite well the viscosities of the pure MDEA and DEA in the temperature range between 25 and 80 °C. The activation energies obtained are listed in Table 4, together with values calculated from the data of DiGuilio et al. (14) and Al-Ghawas et al. (15). DEA has a higher activation energy for flow than MDEA. This could be due to the stronger hydrogen bonding from the "free" hydrogen in DEA than the methyl group in MDEA. From Table 4, *N*-ethyldiethanolamine (EDEA) shows a higher activation energy than MDEA probably due to the larger ethyl group than the methyl group in resisting flow. A similar trend can be seen if the activation energies of monoethanolamine (MEA), diethylethanolamine (DEEA), and *N,N*-dimethylethanolamine (DMEA) are compared. It would be of interest to know the flow behavior of *N*-methylethanolamine (MMEA). One would expect the value of the activation energy of MMEA to be between those of MEA and DEEA in the same temperature range.

Figure 3 shows the Arrhenius plot of $\ln \eta$ versus $1/T$ for the alkanolamines listed in Table 4.

Attempts have been made to describe the viscosities of the binary solutions in terms of composition and the viscosities

**Figure 4.** Excess logarithm of dynamic viscosity, $\Delta \ln \eta$, and excess molar volume, V^E , as a function of mole fraction for binary aqueous MDEA solutions.**Figure 5.** Excess logarithm of dynamic viscosity, $\Delta \ln \eta$, and excess molar volume, V^E , as a function of mole fraction for binary aqueous DEA solutions.

of the respective pure components and an interaction term. Grunberg and Nissan (19) have suggested the following equation:

$$\Delta \ln \eta = \ln \eta - x_1 \ln \eta_1 - x_2 \ln \eta_2 = x_1 x_2 D \quad (4)$$

where η , η_1 , and η_2 are the dynamic viscosities of the binary mixture and of the pure components 1 and 2, respectively. D is an interaction parameter. Plots of $\Delta \ln \eta$ versus mole fraction exhibit a similar type of curve as those of excess molar volumes. This is shown in Figures 4 and 5 for aqueous MDEA and DEA solutions, respectively. Values of D obtained for MDEA solutions are positive, varying from 17.7 to 5.2 at 25 °C and from 11.6 to 3.3 at 80 °C. For DEA solutions, it varies from 13.2 to 5.4 at 25 °C and from 8.7 to 3.5 at 80 °C. Positive values of D indicate a negative deviation from Raoult's law.

Table 5. Parameters a_j from Eq 6 for Binary Aqueous Solutions of MDEA and DEA

$t/$ °C	amine	a_0	a_1	a_2	a_3	a_4	a_5	a_6	a_7	σ
25	MDEA	1.40456E+2	-7.26352E+1	3.24342E+1	2.07052E+1	-1.67650E+3	9.72579E+2	2.14801E+3	-1.62590E+3	2.82E-1
	DEA	-4.05832E+2	-3.63969E+2	-2.37233E+2	2.63694E+2	1.01461E+3	-5.42449E+2	-8.57339E+2	5.78919E+2	1.09E-1
40	MDEA	5.55058E+1	-1.88181E+1	-5.14799E+1	-2.13470E+1	-1.04036E+2	5.44730E+1	1.51492E+2	-8.67739E+1	5.92E-2
	DEA	-1.07462E+2	-1.33205E+2	-1.92051E+1	5.50187E+1	4.46395E+1	2.11409E+1	-3.82328E+1		4.72E-2
60	MDEA	1.96654E+1	-3.22833	-1.59008E+1	-1.31725E+1	-1.88505E+1	3.40418	2.30952E+1		4.60E-2
	DEA	-2.11624E+1	-4.19502E+1	-1.25910E+1	2.41700E+1	1.27033E+1	-6.35058	-5.76035		1.64E-2
70	MDEA	1.31115E+1	-4.71085E+1	-1.41986E+1	-1.82955E+1	2.05386E+1	1.61493E+1	-2.12943E+1		2.10E-2
	DEA	-9.20546	-2.24537E+1	-1.24650E+1	4.60010	2.15205E+1	2.99978	-1.54493E+1		2.04E-2
80	MDEA	8.80467	-9.72209E-1	-6.09372	-3.46027					1.45E-2
	DEA	-3.49482	-1.27615E+1	-1.02006E+1	-5.47368E-1	1.76795E+1	3.26217	-1.20769E+1		1.38E-2

The viscosity deviation $\Delta\eta$ is defined by

$$\Delta\eta = \eta - x_1\eta_1 - x_2\eta_2 \quad (5)$$

It may be used to represent deviations from a rectilinear dependence of viscosity on mole fraction. $\Delta\eta$ values for MDEA solutions vary from negative to positive with amine concentration, indicating strong dispersion forces (20) at low concentrations and increasing strength of interaction at higher concentrations. $\Delta\eta$ values for DEA solutions are all negative throughout the whole concentration range except at 70 and 80 °C where the $\Delta\eta$ values become positive at $x_1 = 0.8$.

The viscosity deviations of the binary aqueous MDEA solutions and of binary aqueous DEA solutions at various temperatures have been calculated and fitted to a Redlich-Kister (21) type equation:

$$\Delta\eta/(\text{mPa}\cdot\text{s}) = x_1(1-x_1) \sum_1^{n'} a_j(1-2x_1)^{j-1} \quad (6)$$

The number of coefficients a_j is determined by the examination of the variation of the standard deviation with $j-1$. Table 5 lists the coefficients a_j for both MDEA and DEA solutions, together with the standard deviations.

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Received for review June 7, 1993. Revised October 29, 1993. Accepted November 22, 1993.* The financial support of the Natural Sciences and Engineering Research Council of Canada (Grant A5405) is gratefully acknowledged.

* Abstract published in *Advance ACS Abstracts*, February 1, 1994.