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Diffusivities of Mono-, Di-, and Triethanolamines in Aqueous Solutions

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Diffusivities of mono-, di-, and triethanolamines in aqueous solutions were measured at 25 °C and atmospheric pressure as a function of ethanolamine concentration by means of a diaphragm cell technique. Experimental results were compared with those of Thomas and Furzer and with the Stokes–Einstein relation.

Aqueous solutions of ethanolamines, such as MEA (monoethanolamine), DEA (diethanolamine), or TEA (triethanolamine), are frequently used for the removal of acidic gases. Therefore, a knowledge of the diffusivities of these ethanolamines in the aqueous solutions of various concentrations is important in the rational design of absorption equipment. Thomas and Furzer (*6*) have measured the diffusivities of MEA, DEA, and TEA in aqueous solutions by the Gouy method up to high concentrations and found that the diffusivities of MEA and TEA follow the Stokes–Einstein relation; i.e., the product $D\mu$ is constant at constant temperature, whereas the diffusivity of DEA shows large deviation from the Stokes–Einstein relation. They have explained that this large deviation is due to the increase in molecular weight of DEA in the solution through association and hydration. However, on the basis of the experimental results that all of the three ethanolamines are molecularly associated in aqueous solution, Ibrahim and Kuloor (*2*) have pointed out that the anomalous behavior in the case of DEA cannot be solely attributed to association. In this paper, new data for the diffusivities of MEA, DEA, and TEA in aqueous solutions are reported and compared with the data of Thomas and Furzer (*6*) and with the Stokes–Einstein relation.

Experimental Section

The diffusivities of MEA, DEA, and TEA in aqueous solutions were measured by the diaphragm cell technique described by Stokes (*3*,*5*). The diaphragm cell used in the present work consisted of two compartments of ~50-cm³ volume separated by a No. 4 sintered glass diaphragm (porosity ~15 μm) of 3-mm thickness. Each compartment was provided with two capillary tubes with stopcocks.

For each diffusion run, two aqueous solutions of the same ethanolamine, one denser than the other, were prepared. The upper compartment of the cell was filled with the less dense solution, and the lower compartment with the more dense solution. The cell was kept in a water bath maintained at 25 °C. The solution in each compartment was stirred by means of a magnetic stirring bar at a constant rate of 100 rpm, and diffusion of ethanolamine was allowed to proceed for ~72 h.

The diffusivity D of ethanolamine in the solution was calculated from eq 1, where β is the cell constant, t is the time of the diffusion period, C and C' are the ethanolamine concentrations in the lower and upper compartments, respectively, and the subscripts i and f denote the initial and final values, respectively.

$$D = \ln\left[(C_i - C'_i)/(C_f - C'_f)\right]/\beta t \qquad (1)$$

The cell constant β was obtained by calibrating with 0.1 kmol/m³ aqueous potassium chloride solution diffusing into pure water at 25 °C.

Aqueous solutions of ethanolamines were prepared from distilled water and ethanolamines of reagent grade. The determination of ethanolamines in the solutions was made by titrating the liquid sample with standard hydrochloric acid and with bromphenol blue as an indicator.

Table I. Diffusivities of MEA, DEA, and TEA in Aqueous Solutions at 25 °C and 1 atm

ethanolamine	concn of ethanolamine, C kmol/m³	no. of measurement	diffusivity, $10^{10}D$, m²/s	D/D_w	μ/μ_w
MEA	0		(11.6)		
	0.0472	4	11.5	0.991	1.00
	0.0947	2	11.6	1.000	1.01
	0.562	1	10.6	0.914	1.08
	1.07	1	9.84	0.848	1.21
	1.98	2	9.10	0.784	1.45
	2.97	1	8.38	0.722	1.78
DEA	0		(8.20)		
	0.0508	3	8.08	0.985	1.02
	0.107	3	7.96	0.971	1.03
	0.490	1	6.74	0.822	1.18
	0.987	2	6.48	0.790	1.43
	1.04	1	6.17	0.752	1.46
	1.68	1	5.22	0.637	1.87
	2.21	1	4.86	0.593	2.30
	3.01	2	4.31	0.526	3.45
	3.29	2	4.01	0.489	3.97
TEA	0		(7.70)		
	0.0541	2	7.59	0.986	1.02
	0.0994	1	7.72	1.003	1.04
	0.494	2	6.64	0.849	1.23
	0.983	3	5.75	0.747	1.58
	2.04	2	4.16	0.540	2.84
	2.94	2	2.95	0.383	5.15
	3.50	2	2.46	0.319	7.58

The viscosities of aqueous ethanolamine solutions were measured with the standard Ostwald viscometer.

All of the measurements were carried out at atmospheric pressure and at 25 °C.

Results and Discussion

The measured values of the diffusivities D of MEA, DEA, and TEA in aqueous solutions are listed in Table I, together with the values of the viscosity ratio μ/μ_w of the solutions, as a function of ethanolamine concentration C. Many of the D values reported are the arithmetic means of 2–4 measurements. The standard deviation of the measured values of D for each of the ethanolamines was ca. ±3% of the mean values. In Table I the values of the diffusivities D_w for three ethanolamines at infinite dilution, which were determined by extrapolating the diffusivity data to zero ethanolamine concentration, are also given.

Figures 1–3 compare the present data on the diffusivities of the three ethanolamines with the data of Thomas and Furzer (*6*). As can be seen in these figures, the present data are considerably higher than the Thomas–Furzer data. The values of D_w are 5.5, 24.2, and 13.2% higher than the values obtained by Thomas and Furzer for MEA, DEA, and TEA, respectively.

Table II shows the comparison of the experimental D_w values for the three ethanolamines with those predicted by the Wilke and Chang (*7*), Scheibel (*4*), and Hayduk and Laudie (*1*) cor-

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Table II. Comparison of Experimental and Predicted Diffusivities of Ethanolamines in Aqueous Solutions at 25 °C and Infinite Dilution

		predicted diffusivities					
		Wilke-Chang (7)		Scheibel (4)		Hayduk-Laudie (1)	
ethanolamine	exptl $10^{10}D$, m²/s	$10^{10}D$, m²/s	dev,[a] %	$10^{10}D$, m²/s	dev,[a] %	$10^{10}D$, m²/s	dev,[a] %
MEA	11.6	12.8	+10.3	12.0	+3.4	12.4	+6.9
DEA	8.2	9.25	+12.8	8.63	+5.2	8.96	+9.3
TEA	7.7	7.46	−3.1	7.06	−8.3	7.26	−5.7

[a] % deviation = $100(D_{\text{calcd}} - D_{\text{exptl}})/D_{\text{exptl}}$.

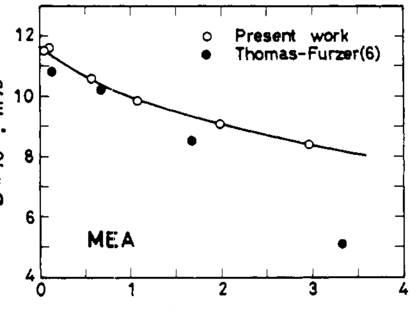

Figure 1. Diffusivity of MEA in aqueous solutions at 25 °C and 1 atm.

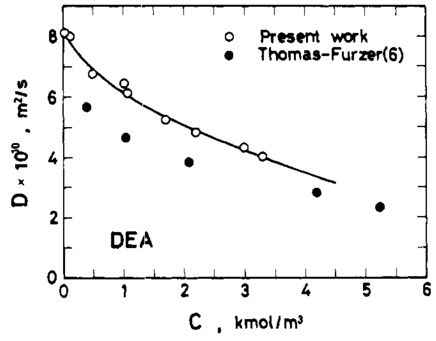

Figure 2. Diffusivity of DEA in aqueous solutions at 25 °C and 1 atm.

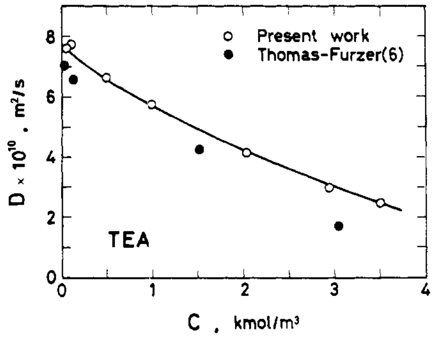

Figure 3. Diffusivity of TEA in aqueous solutions at 25 °C and 1 atm.

relations. The molar volumes of the ethanolamines were estimated by the LeBas incremental method. All of the correlations tested predict diffusivities within ±13% of the experimental values.

In Figure 4 all of the measured values of the diffusivities of the three ethanolamines in aqueous solutions are shown as a log-log plot of the diffusivity ratio D/D_w against the solution viscosity ratio μ/μ_w. The broken line in this figure represents the well-known Stokes–Einstein relation

$$D/D_w = (\mu/\mu_w)^{-1} \quad (2)$$

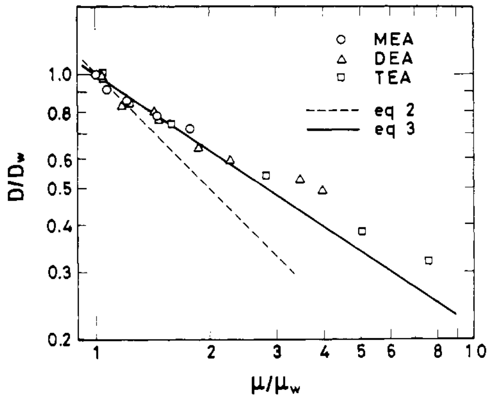

Figure 4. Effect of solution viscosity on diffusivities of ethanolamines in aqueous solutions.

As can be seen in the figure, this relation is not satisfactory for the present systems and predicts diffusivities that are too low when the solution viscosities are high. The present diffusivity data are considerably well correlated by a solid line with a slope of −²/₃ representing eq 3, the average deviation being 5.9%,

$$D/D_w = (\mu/\mu_w)^{-2/3} \quad (3)$$

although the data points at high values of μ/μ_w fall somewhat above the solid line.

Glossary

C	concentration of ethanolamine in aqueous solution, kmol/m³
C_i, C_f	initial and final concentrations of ethanolamine in lower compartment of diaphragm cell, kmol/m³
C'_i, C'_f	initial and final concentrations of ethanolamine in upper compartment of diaphragm cell, kmol/m³
D, D_w	liquid-phase diffusivities of ethanolamine in aqueous solution and at infinite dilution, m²/s
t	diffusion time, s
β	cell constant, 1/m²
μ, μ_w	viscosities of aqueous ethanolamine solution and of water, Pa s

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