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Densities, Viscosities, and Liquid Diffusivities in Aqueous Piperazine and Aqueous (Piperazine + *N*-Methyldiethanolamine) Solutions

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Densities and viscosities of aqueous solutions containing both piperazine (PZ) and *N*-methyldiethanolamine (MDEA) have been determined at a temperature range from (293.15 to 323.15) K. The concentrations of MDEA have been kept constant at (1, 2, 3, and 4) mol·dm^{-3} with the concentration of PZ varying from (0 to 1) mol·dm^{-3}. Liquid diffusivities of aqueous PZ solutions have been determined using the Taylor dispersion technique over a temperature range from (293.15 to 368.15) K and concentrations from (0 to 1.5) mol·dm^{-3}. At infinite dilution, the method proposed by Othmer & Thakar can be used to estimate the liquid diffusivities, and a modified Stokes−Einstein relation can be used to predict the diffusivities at higher concentrations. Liquid diffusivities of both PZ and MDEA have been determined in aqueous solutions containing 4.0 mol·dm^{-3} MDEA and (0, 0.5, and 1.0) mol·dm^{-3} PZ at a temperature range from (298.15 to 368.15) K. The liquid diffusivities can be estimated by a modified Stokes−Einstein relation.

Introduction

Aqueous solutions of (alkanol)amines are frequently used for the removal of acid gases, such as CO_2 and H_2S, from a variety of gas streams.[1] Recently, the technique of adding small amounts of piperazine (PZ) to an aqueous solution of *N*-methyldiethanolamine (MDEA) has found widespread application in the bulk removal of CO_2. The success of this so-called "activated MDEA solvent" is based on the relatively high rate of reaction of PZ with CO_2 and the relatively low enthalpy of reaction of MDEA with CO_2, thereby leading to higher absorption rates in the absorber column, while a lower heat of regeneration is required in the stripper section. In these solvents, the concentration of MDEA is usually kept at about (3 to 4) mol·dm^{-3}, and typically a maximum PZ concentration of about 1.0 mol·dm^{-3} is applied.[2–9]

Accurate design of gas−liquid contactors requires knowledge of the mass transfer coefficients and diffusion coefficients. As the mass transfer coefficients are related to the diffusion coefficients, knowledge of the diffusion coefficients is necessary to make the design of this equipment more reliable. They are also essential for a correct and accurate interpretation of many (laboratory scale) absorption rate experiments such as, e.g., the experiments aimed at the determination of the intrinsic kinetics in a gas−liquid process. In the past, several studies have reported experimental diffusivities of carbon dioxide and various (alkanol)amines in systems relevant for acid gas absorption.[10,11] In this work, densities, viscosities, and diffusivities are presented to extend the existing experimental database of absorbent properties.

Table 1. Dimensions of the Experimental Setup and Flow Conditions

length of the coil	L	14.92 m
inner radius of the coil	R	$5.14 \cdot 10^{-4}$ m
radius of the coil	R_C	0.1 m
injection volume	V_{inj}	$(2.5 \text{ to } 4.1) \cdot 10^{-8}$ m^3
liquid flow velocity	u	$(2 \text{ to } 6) \cdot 10^{-3}$ m·s^{-1}

Densities and viscosities of aqueous solutions containing (PZ + MDEA) are reported at various temperatures and concentrations. Liquid diffusivities in aqueous PZ solutions and aqueous (PZ + MDEA) solutions are reported at various concentrations and temperatures. The liquid diffusivities have been determined using the Taylor dispersion technique.

Experimental

Chemicals. The amine solutions were prepared by dissolving known amounts of piperazine, systematic (IUPAC) name 1,4-diazacyclohyexane [110-85-0] (purity 99 %, Aldrich), and/or MDEA, IUPAC 2,2′-(methylamino)diethanol [105-59-9] (purity 98 %, Aldrich) in double-distilled water. The actual amine concentrations in the prepared solution were measured (at $T =$ 293 K) by means of a volumetric titration with 1.0 mol·dm^{-3} HCl. The experimentally determined PZ and MDEA concentrations showed an uncertainty of 1.0 % of the concentrations as determined by the weight ratios of the components. The methanol [67-56-1] (purity 99 %, Aldrich) solutions in water, used in validation experiments, were prepared in a similar manner. The helium gas [7440-59-7] used was supplied by Hoekloos.

Densities and Viscosities. The densities were determined with a commercial density meter (DMA 58, Anton Paar GmbH), in which the temperature could be controlled to within ± 0.05 K. The viscosities were measured using an Ubbelohde viscometer having a suitable viscosity range, submerged in a thermostat bath for temperature control within ± 0.1 K.

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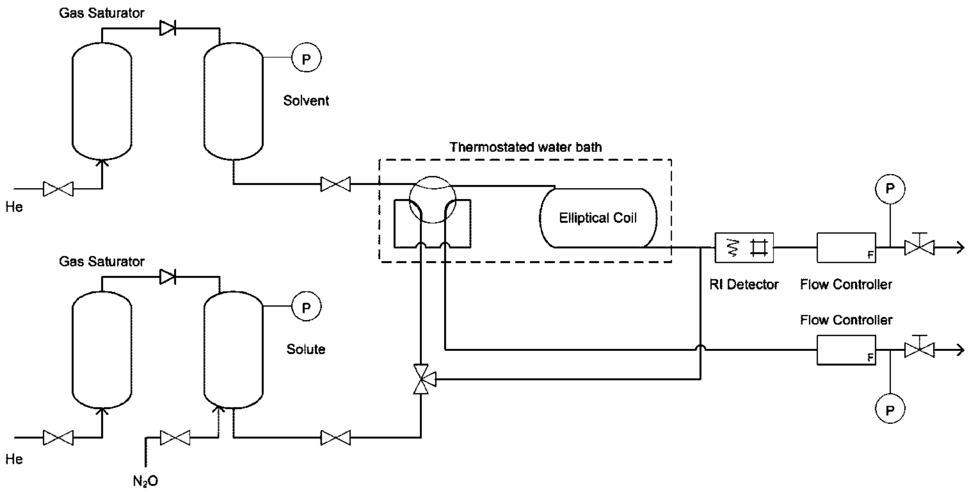

Figure 1. Schematic representation of the Taylor dispersion setup.

Table 2. Density, ρ, and Viscosity, μ, of Aqueous Solutions Containing (1.0, 2.0, 3.0, or 4.0) mol·dm^{-3} MDEA and (0, 0.25, 0.50, 0.75, or 1.0) mol·dm^{-3} PZ

	c_{MDEA} / mol·dm^{-3}	c_{PZ} / mol·dm^{-3}	ρ / kg·m^{-3}	μ / mPa·s
$T = 293.15$ K	1.0	0	1008.67	1.576
	1.0	0.25	1010.12	1.779
	1.0	0.50	1011.41	2.003
	1.0	0.75	1013.04	2.280
	1.0	1.00	1014.45	2.630
	2.0	0	1020.10	2.680
	2.0	0.25	1021.69	3.082
	2.0	0.50	1023.48	3.566
	2.0	0.75	1024.98	4.087
	2.0	1.00	1026.53	4.728
	3.0	0	1032.14	4.786
	3.0	0.25	1032.91	5.559
	3.0	0.50	1034.37	6.529
	3.0	0.75	1035.94	7.966
	3.0	1.00	1037.24	9.100
	4.0	0	1042.47	9.553
	4.0	0.25	1043.56	10.89
	4.0	0.50	1044.73	13.06
	4.0	0.75	1046.36	16.25
	4.0	1.00	1047.85	19.65
$T = 298.15$ K	1.0	0	1007.14	1.390
	1.0	0.25	1008.48	1.534
	1.0	0.50	1009.76	1.719
	1.0	0.75	1011.29	1.960
	1.0	1.00	1012.61	2.194
	2.0	0	1018.87	2.288
	2.0	0.25	1019.68	2.599
	2.0	0.50	1021.31	2.992
	2.0	0.75	1022.67	3.426
	2.0	1.00	1024.20	3.905
	3.0	0	1028.97	3.948
	3.0	0.25	1030.42	4.580
	3.0	0.50	1031.82	5.329
	3.0	0.75	1037.8	6.431
	3.0	1.00	1034.86	7.230
	4.0	0	1039.68	7.782
	4.0	0.25	1040.58	8.642
	4.0	0.50	1041.71	10.15
	4.0	0.75	1043.27	12.77
	4.0	1.00	1044.61	15.06
$T = 303.15$ K	1.0	0	1005.56	1.224
	1.0	0.25	1006.80	1.341
	1.0	0.50	1007.88	1.498
	1.0 20	0.75	1009.42	1.680
	1.0	1.00	1010.68	1.866
	2.0	0	1016.09	1.971
	2.0	0.25	1017.47	2.235
	2.0	0.50	1019.05	2.532
	2.0	0.75	1020.36	2.901
	2.0	1.00	1021.83	3.265
$T = 303.15$ K	3.0	0	1026.49	3.317
	3.0	0.25	1027.76	3.900
	3.0	0.50	1029.26	4.385
	3.0	0.75	1307.50	6.650
	3.0	1.00	1031.96	5.882
	4.0	0	1036.64	6.212
	4.0	0.25	1038.36	6.991
	4.0	0.50	1039.27	8.118
	4.0	0.75	1040.64	9.796
	4.0	1.00	1041.92	11.74
$T = 313.15$ K	1.0	0	1001.56	0.987
	1.0	0.25	1003.41	1.053
	1.0	0.50	1003.81	1.164
	1.0	0.75	1005.05	1.296
	1.0	1.00	1006.22	1.444
	2.0	0	1011.33	1.497
	2.0	0.25	1012.71	1.675
	2.0	0.50	1014.11	1.777
	2.0	0.75	1015.21	2.121
	2.0	1.00	1016.31	2.378
	3.0	0	1020.97	2.415
	3.0	0.25	1022.22	2.749
	3.0	0.50	1023.46	3.118
	3.0	0.75	1025.05	3.645
	3.0	1.00	1025.86	4.043
	4.0	0	1030.46	4.292
	4.0	0.25	1030.98	4.785
	4.0	0.5	1031.89	5.426
	4.0	0.75	1033.11	6.46
	4.0	1	1034.12	7.558
$T = 323.15$ K	1.0	0	996.91	0.793
	1.0	0.25	997.60	0.856
	1.0	0.50	999.05	0.932
	1.0	0.75	1000.24	1.043
	1.0	1.00	1001.25	1.127
	2.0	0	1006.20	1.182
	2.0	0.25	1007.42	1.311
	2.0	0.50	1008.71	1.474
	2.0	0.75	1009.59	1.618
	2.0	1.00	1010.68	1.798
	3.0	0	1015.02	1.838
	3.0	0.25	1016.11	2.057
	3.0	0.50	1017.31	2.311
	3.0	0.75	1018.71	2.648
	3.0	1.00	1019.45	2.913
	4.0	0	1024.04	3.149
	4.0	0.25	1024.21	3.398
	4.0	0.50	1025.01	3.843
	4.0	0.75	1026.05	4.421
	4.0	1.00	1026.91	5.198

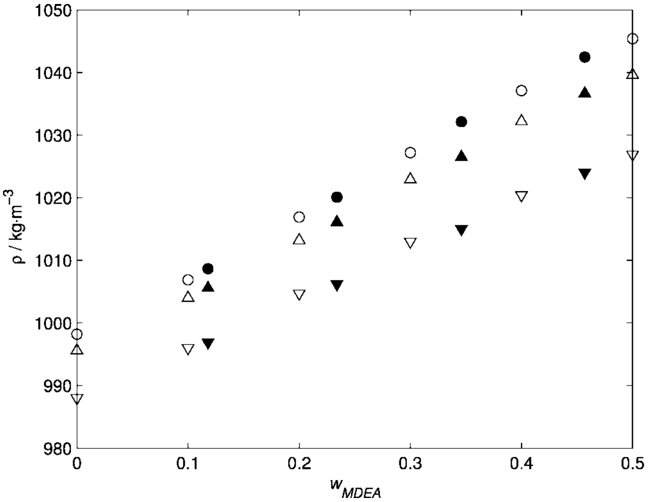

Figure 2. Density of (MDEA + H_2O), ρ, as a function of MDEA mass fraction, w_{MDEA}. At 293.15 K: •, this work; ○, Al-Ghawas et al.[18] At 303.15 K: ▲, this work; Δ, Al-Ghawas et al.[18] At 323.15 K: ▼, this work; ▽, Al-Ghawas et al.[18]

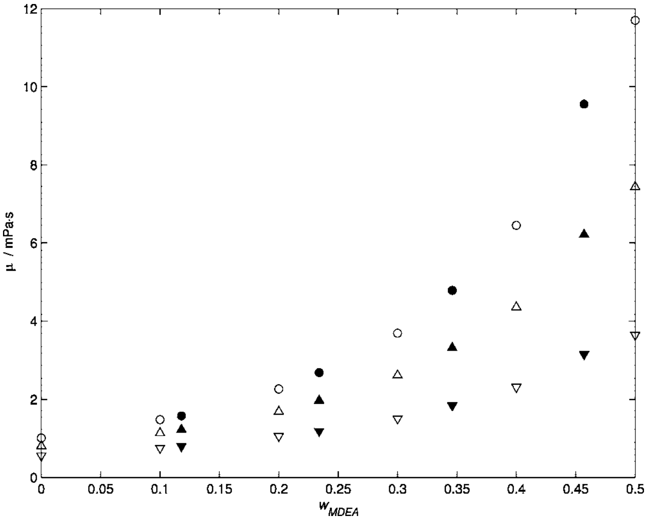

Figure 3. Viscosity of (MDEA + H_2O), μ, as a function of MDEA mass fraction w_{MDEA}. At 293.15 K: ●, this work; ○, Al-Ghawas et al.[18] At 303.15 K: ▲, this work; Δ, Al-Ghawas et al.[18] At 323.15 K: ▼, this work; ▽, Al-Ghawas et al.[18]

Table 3. Diffusion Coefficient, $D_{methanol}$, of Methanol in Water at 308.15 K as a Function of Mole Fraction, $x_{methanol}$

$x_{methanol}$	$D_{methanol}/10^{-9}\cdot m^2\cdot s^{-1}$
0.00	1.89
0.01	1.81
0.10	1.51
0.20	1.31
0.30	1.26
0.40	1.18
0.50	1.27
0.60	1.36
0.80	1.91
1.00	2.62

Table 4. Diffusion Coefficient at Infinite Dilution, $D_{0,\,methanol}$, of Methanol in Water As a Function of Temperature T

T/K	$D_{0,methanol}/10^{-9}\cdot m^2\cdot s^{-1}$
298.15	1.55
313.15	2.39
333.15	3.58
353.15	4.68
363.15	5.39

Diffusivities and the Taylor Dispersion Technique. The diffusivities were determined using the Taylor dispersion technique. A square pulse of a solute solution was injected into a solvent solution showing laminar flow through a capillary tube. The solute contained the same components as the solvent, but with a slightly higher concentration of the component of which diffusivities were to be determined (an addition of approximately 0.05 $mol\cdot dm^{-3}$). As an example, for measurements of liquid diffusivity of PZ in aqueous PZ solution at about 1.0 $mol\cdot dm^{-3}$, the solvent solution would contain 1.00 $mol\cdot dm^{-3}$ PZ. The solute solution would contain 1.05 $mol\cdot dm^{-3}$ PZ, and a square pulse of this solution would be injected into the flowing solvent solution. The combined action of axial convection and radial and axial molecular diffusion will eventually change the shape of the solute pulse (the excess amount of $c_{PZ} \approx 0.05$ $mol\cdot dm^{-3}$ injected) into a Gaussian shaped curve. The theory and mathematical description of such measurements have been described in detail by Taylor[12,13] and Aris.[14] The mathematical description of a measurement is described by

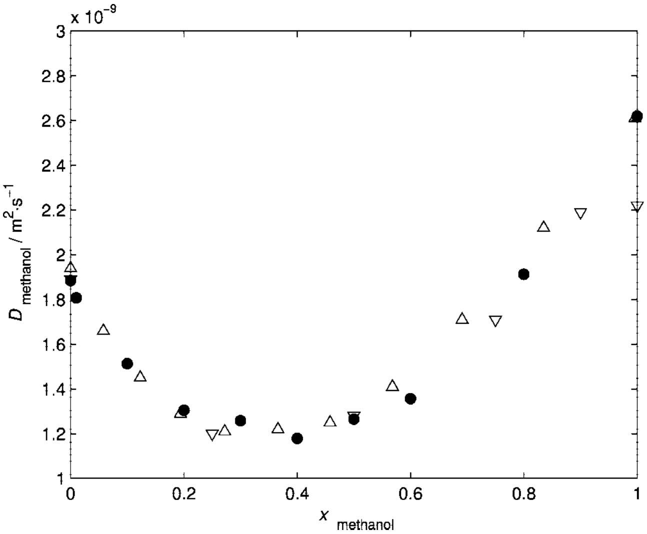

Figure 4. Diffusion coefficient, $D_{methanol}$, of methanol in water at 308.15 K as a function of mole fraction, $x_{methanol}$. ●, this work; Δ, van de Ven-Lucassen et al.;[19] ▽, Lee & Li.[20]

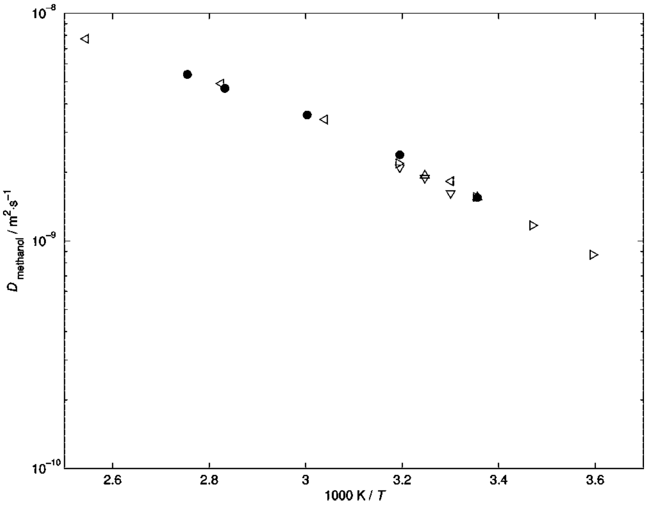

Figure 5. Diffusion coefficient at infinite dilution, $D_{0,\,methanol}$, of methanol in water as a function of temperature T. ●, this work; Δ, van de Ven-Lucassen et al.;[19] ▽, Lee & Li;[20] open triangle pointing right, Easteal & Woolf;[16] open triangle pointing left, Matthews & Akgerman.[21]

$$c_{\mathrm{m}} = \frac{N_{\mathrm{inj,A}}}{2\pi R^2 \sqrt{\pi K_{\mathrm{A}} t}} \exp\left(-\frac{(L-ut)^2}{4K_{\mathrm{A}}t}\right) \tag{1}$$

$$K_{\mathrm{A}} = \frac{u^2R^2}{48D_{\mathrm{A}}} + D_{\mathrm{A}} \tag{2}$$

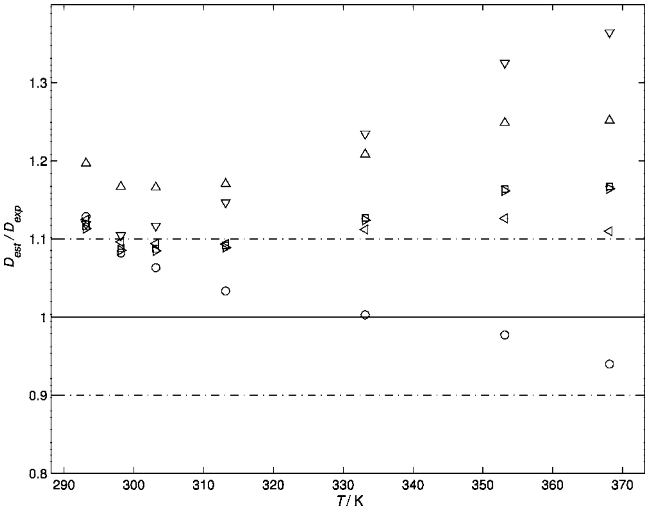

Figure 6. Comparison between the experimental diffusion coefficient at infinite dilution and the estimated value according to the estimation methods applied. ○, Othmer−Thakar;[22] Δ, Wilke−Chang;[23] ▽, Hayduk-Minas;[24] open triangle pointing right, Scheibel;[25] open triangle pointing left, Hayduk−Laudie;[26] □, modified Wilke−Chang.[26]

Table 5. Diffusion of PZ in Aqueous PZ Solutions

$\frac{T}{\mathrm{K}}$	$\frac{c_{\mathrm{ref,PZ}}}{\mathrm{mol \cdot dm^{-3}}}$	$\frac{D_{\mathrm{PZ}}}{10^{-9} \cdot \mathrm{m^2 \cdot s^{-1}}}$
293.15	$0.8 \cdot 10^{-3}$	0.757
	0.284	0.660
	0.602	0.617
	0.907	0.560
	1.46	0.511
298.15	$0.8 \cdot 10^{-3}$	0.889
	0.285	0.762
	0.602	0.714
	0.908	0.666
	1.46	0.607
303.15	$0.9 \cdot 10^{-3}$	1.01
	0.285	0.870
	0.602	0.799
	0.908	0.754
	1.46	0.715
313.15	$1.0 \cdot 10^{-3}$	1.27
	0.285	1.11
	0.603	1.05
	0.910	0.972
	1.46	0.948
333.15	$1.2 \cdot 10^{-3}$	1.83
	0.285	1.66
	0.604	1.59
	0.913	1.52
	1.47	1.41
353.15	$1.4 \cdot 10^{-3}$	2.47
	0.287	2.36
	0.605	2.24
	0.915	2.15
	1.47	2.01
368.15	$1.6 \cdot 10^{-3}$	3.06
	0.287	2.89
	0.606	2.82
	0.917	2.60
	1.48	2.59

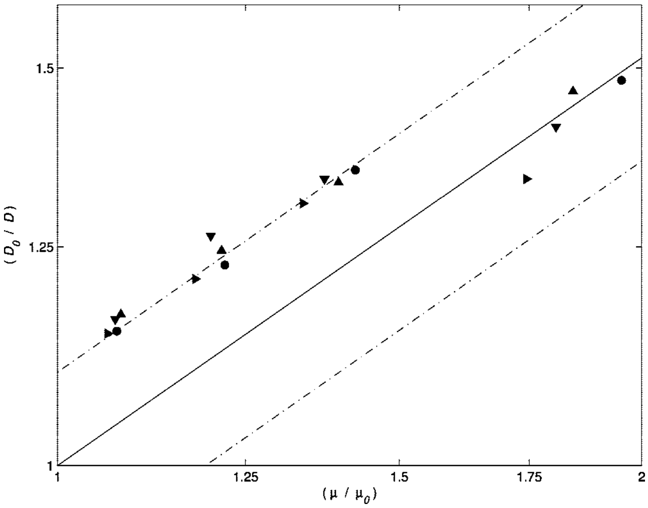

Figure 7. Stokes−Einstein plot for the diffusion coefficient of PZ in aqueous PZ solutions: •, 293 K; ▲, 298.15 K; ▼, 303.15 K; solid triangle pointing right, 313.15 K. The solid line represents eq 7, and the dashed lines represent ±10 %.

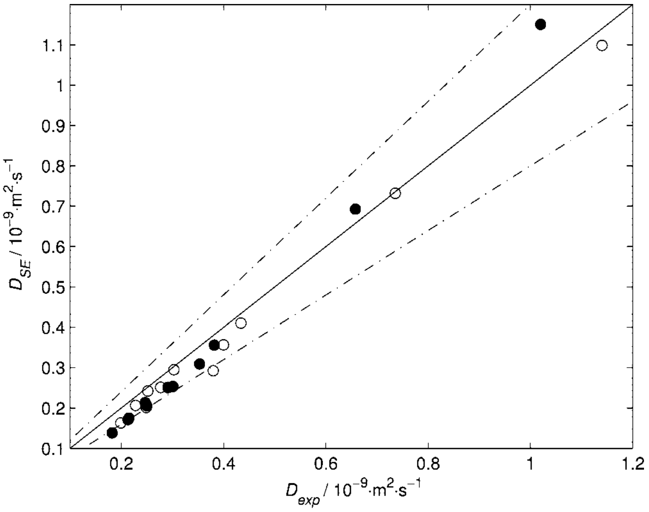

Figure 8. Comparison between the experimentally determined diffusion coefficients, D_{exp}, and the values estimated with the Stokes−Einstein equation, D_{SE}: •, PZ; ○, MDEA. The dashed lines represents ± 20 %.

where c_{m} is the measured Gaussian concentration profile; $N_{\mathrm{inj,A}}$ is the excess amount of mole amine injected; t is the time; and D_{A} is the binary diffusion coefficient. The subscript A refers to the amine. The other parameters are defined in Table 1. $N_{\mathrm{inj,A}}$, u, and D_{A} are the independent parameters used to curve fit eqs 1 and 2 to the experimentally recorded results. Since the concentration of the solute pulse decreases because of dispersion while the solute pulse is traversing with the solvent through the tubing, an average concentration value has to be determined. Alizadeh et al.[15] referred to this as the reference concentration c_{ref} given by

$$c_{\mathrm{ref}} = c_{\mathrm{solv}} + \frac{N_{\mathrm{inj,A}}\left(\frac{5}{16} - \frac{1}{8\sqrt{\pi}}\right)}{\pi R^2 \sqrt{2K_{\mathrm{A}}t'}} \tag{3}$$

where c_{solv} is the solvent concentration and t' is the time at which the measurement ends.

The experimental setup used is shown schematically in Figure 1. Two vessels containing the solute solution and solvent solution were kept under a constant 5 bar pressure of saturated helium to create a constant flow of the solute solution and the solvent solution. Introduction of a square solute pulse was done by switching an air

Table 6. Diffusion Coefficients of PZ and MDEA in Aqueous (PZ + MDEA) Solutions

$\frac{T}{\mathrm{K}}$	$\frac{c_{\mathrm{MDEA}}}{\mathrm{kmol \cdot m^{-3}}}$	$\frac{c_{\mathrm{ref,PZ}}}{\mathrm{kmol \cdot m^{-3}}}$	$\frac{D_{\mathrm{PZ}}}{10^{-9} \cdot \mathrm{m^2 \cdot s^{-1}}}$	$\frac{c_{\mathrm{PZ}}}{\mathrm{kmol \cdot m^{-3}}}$	$\frac{c_{\mathrm{ref,MDEA}}}{\mathrm{kmol \cdot m^{-3}}}$	$\frac{D_{\mathrm{MDEA}}}{10^{-9} \cdot \mathrm{m^2 \cdot s^{-1}}}$
298.15	4.0	$0.6 \cdot 10^{-3}$	0.252	0	3.99	0.250
	4.0	0.504	0.228	0.5	3.96	0.215
	4.0	1.00	0.199	1.0	4.02	0.182
303.15	4.0	$0.6 \cdot 10^{-3}$	0.303	0	3.99	0.291
	4.0	0.504	0.277	0.5	3.96	0.247
	4.0	1.01	0.249	1.0	4.02	0.213
313.15	4.0	$0.7 \cdot 10^{-3}$	0.434	0	3.99	0.382
	4.0	0.506	0.400	0.5	3.96	0.353
	4.0	1.01	0.380	1.0	4.02	0.301
333.15	4.0	$1.0 \cdot 10^{-3}$	0.736	0	4.00	0.658
	4.0	0.509	0.716	0.5	3.98	0.610
	4.0	1.01	0.662	1.0	4.03	0.538
353.15	4.0	$1.2 \cdot 10^{-3}$	1.14	0	4.01	1.02
	4.0	0.516	1.10	0.5	3.99	0.964
	4.0	1.02	1.12	1.0	4.04	0.886
368.15	4.0	$1.3 \cdot 10^{-3}$	1.48	0	4.02	1.34
	4.0	0.519	1.46	0.5	3.99	1.27
	4.0	1.02	1.47	1.0	4.05	1.16

actuated six-way valve back and forth within a few seconds. The capillary was a coiled elliptical tube (stainless steel) and was placed in a water bath for temperature control. The flow velocity was controlled with mass flow controllers (Rosemount Flowmega 5881), located behind the refractive index (RI) detector (Varian 350 RI) and the six-way pulse valve to obtain a constant pulsation-free solute and solvent solution flow throughout the measurement. To avoid bubble formation inside the tubing and a disturbance of the laminar fluid flow profile, especially at higher temperatures, pressure reducers were located behind the RI detector and the six-way pulse valve. These reducers pressurized the fluids inside the tubing to 4 bar. The influence of the pressure on the diffusion coefficients could be neglected for the pressure applied.[16,17] Prior to each experiment, both the solute and the solvent solution were degassed by applying a vacuum for a while, and further the RI detector was calibrated. The RI detector showed a linear response to concentration changes of the amines investigated. A computer was connected to the setup for control and data acquisition. The output signal from the RI detector was recorded as a function of time and used to determine the molecular diffusion coefficients as aforementioned. The dimensions of the experimental setup and the flow conditions are given in Table 1.

A disturbance of the laminar fluid flow profile can occur due to the elliptic coiling of the tube. The varying path lengths traversed by the fluid at different radial positions inside the capillary tube and the secondary flows present in the flow can contribute additionally to the dispersion process. This topic has been extensively discussed by Alizadeh et al.[15] and Snijder et al.[11] To avoid this disturbance, the critical $(De)^2Sc$ was determined for each system. The dimensionless $(De)^2Sc$ number is defined as

$$De = Re\left(\frac{R_{\mathrm{C}}}{R}\right)^{-1/2} \tag{4}$$

$$Sc = \frac{\mu}{\rho D} \tag{5}$$

where Re is the well-known Reynolds number and μ and ρ are the solvent viscosity and density. The other parameters are defined in Table 1. The measurements had to be carried out at a value of $(De)^2Sc$ lower than the critical one.

Results and Discussion

Densities and Viscosities. Experimentally determined values of the densities and the viscosities as a function of both amine concentration and temperature are listed in Table 2. The experimental uncertainty is estimated to be 0.01 % (density) and 1 % (viscosity).

The experimental data from Table 2 for solutions containing no piperazine ($c_{\mathrm{PZ}} = 0$) are compared to the work of Al-Ghawas et al.,[18] who reported densities and viscosities of aqueous MDEA solutions for temperatures ranging from (288.15 to 333.15) K and mass fractions up to 50 %. A graphical comparison between the data of Al-Ghawas et al.[18] and the present data on aqueous MDEA solutions (where $c_{\mathrm{PZ}} = 0$) at (293.15, 303.15, and 323.15) K is given in Figures 2 and 3. The figures show that the present density and viscosity data on aqueous MDEA solutions are well in line with the experimental data reported by Al-Ghawas et al.[18]

Diffusivities. Validation. The diffusion coefficients of the binary system methanol−water were determined to validate the experimental setup. The critical $(De)^2Sc$ number was determined to be about 150 for this system. The experimentally obtained diffusion coefficients measured at different composition and temperature are listed in Tables 3 and 4, and a graphical comparison of the present data with literature data[19,20,16,21] is given in Figures 4 and 5. The experimental uncertainty is estimated to be 5 % at temperatures less than 333 K and 10 % at higher temperatures. It can be concluded that the newly obtained experimental diffusivity data are very well in line with the experimental data available in the literature.

Liquid Diffusivities in Aqueous PZ Solutions. Liquid diffusivities in aqueous PZ solution were measured over a concentration range of (0 to 1.4) $\mathrm{mol \cdot dm^{-3}}$ PZ and temperatures between (293.15 and 368.15) K. The results (averaged over at least three experiments) are listed in Table 5. The critical $(De)^2Sc$ was 150 for this system. The experimental uncertainty is estimated to be 5 % at temperatures less than 333 K and 10 % at higher temperatures.

As in the work of Snijder et al.,[11] all experimental diffusion coefficients were correlated using one equation accounting for the influence of both temperature and concentration. The resulting relation is given in eq 6, which was able to correlate all experimental data with an average deviation of less than 4 % (maximum deviation 9 %).

$$\ln(D/\mathrm{m^2 \cdot s^{-1}}) = -13.672 + \frac{-2160.9\ \mathrm{K}}{T} - 19.263 \cdot 10^{-5} \cdot (c_{\mathrm{PZ}}/\mathrm{mol \cdot dm^{-3}}) \quad (6)$$

Versteeg & Van Swaaij[10] suggested a modified Stokes−Einstein relation to estimate the amine diffusion coefficient from the solution's viscosity according to eq 7. Snijder et al.[11] showed in their work that this relation is able to predict the diffusion coefficients of various alkanolamines (MEA, DEA, MDEA, and DIPA) in aqueous solution over a wide range of temperatures and concentrations.

$$\frac{D}{D_0} = \left(\frac{\mu_0}{\mu}\right)^{0.6} \quad (7)$$

where μ_0 is the viscosity of pure water; μ is the viscosity of the solution; and D_0 is the diffusion coefficient at infinite dilution. Measuring viscosities is usually very straightforward, whereas the experimental determination of D_0 is a more laborious task. In the literature, several correlations have been proposed to estimate the diffusion coefficient at infinite dilution. In the present work, six of these estimation methods[22–26] are compared and evaluated on their ability to predict the diffusion coefficient of PZ at infinite dilution in water. An important parameter in all methods is the molar volume of PZ at the normal boiling point, which was estimated using the method of Le Bas.[27] This value (0.1052 $\mathrm{dm^3 \cdot mol^{-1}}$) was compared to the result obtained with an extrapolation relation given by Steele et al.[28] in their study on PZ's critical constants. As both methods yielded a similar value, the value of Le Bas[27] was found reliable to use in the diffusion coefficient estimations. The values calculated with the estimation methods are compared to the experimental diffusion coefficients at infinite dilution, taken from Table 5 at $c_{\mathrm{ref,\,PZ}}$ in the order of 10^{-3} $\mathrm{mol \cdot dm^{-3}}$, and the results are shown graphically in Figure 6.

Figure 6 clearly illustrates that only the prediction method of Othmer & Thakar[22] is able to predict the piperazine diffusion coefficient at infinite dilution in water within 10 % over the complete temperature range. Also the Hayduk & Laudie[26] equation seems to be a suitable prediction method, although it consistently overpredicts the experimental value within about 10 %. Both the method of Scheibel[25] and the modified Wilke−Chang[26] relation provide satisfactory results up to a temperature of 313.15 K, but with increasing temperature, the agreement between prediction and experiment gradually deteriorates. In the study of Snijder et al.[11] on the diffusion of MEA, DEA, MDEA, and DIPA in aqueous solution, the method of Othmer & Thakar[22] was also found to give the best prediction results (together with the modified Wilke−Chang correlation).

Next, the applicability of the modified Stokes−Einstein relation (eq 7) was evaluated for the diffusion of PZ, using the experimental viscosity data reported by Derks et al.[29] and the experimental diffusion coefficients from Table 5. For this purpose, a double logarithmic plot of eq 7 is shown in Figure 7. Despite the fact there seems to be a small offset between some of the experimental data and the solid line representing eq 7, it may still be concluded that the modified Stokes−Einstein relation can be used for estimating PZ diffusivities in aqueous PZ systems (at concentrations < 1.5 $\mathrm{mol \cdot dm^{-3}}$) satisfactorily, as the deviation is always within about 10 %.

Liquid Diffusivities in Aqueous (PZ + MDEA) Solutions. Diffusivities in ternary (and multicomponent) systems have, in a large part, been determined by the use of interferometry at ambient temperatures. Among others, Miller[30,31] has conducted extensive work on this subject. Lately, the Taylor dispersion technique has also been used to determine diffusivities in ternary liquid systems.[32] In kinetic models describing aqueous solutions of (PZ + MDEA) as possible CO_2 absorbents, apparent diffusivities are used,[3,5,7,9] and multicomponent diffusion effects such as cross diffusion are thus neglected. The purpose of the present work is to determine diffusivities in the aqueous (PZ + MDEA) system to give insight into apparent diffusivities used in absorption models for these ternary systems.

The apparent diffusion coefficients of both PZ and MDEA in aqueous solutions containing 4.0 $\mathrm{mol \cdot dm^{-3}}$ MDEA and (0, 0.5, or 1.0) $\mathrm{mol \cdot dm^{-3}}$ PZ were measured at temperatures between (298.15 and 368.15) K. During measurements of PZ diffusivities in aqueous (PZ + MDEA) solutions, the concentration of MDEA was kept at a constant 4.0 $\mathrm{mol \cdot dm^{-3}}$ in both the solute and the solvent, e.g., no concentration gradient of MDEA in the fluid traversing through the capillary coil. The solute contained a slightly higher concentration of PZ than the solvent, e.g., an addition of approximately 0.05 $\mathrm{mol \cdot dm^{-3}}$. Cross diffusion effects present in ternary systems are neglected in these measurements. During measurements of MDEA diffusivities in aqueous (PZ + MDEA) solutions, the concentration of PZ was kept constant in both the solute and the solvent as described, whereas the solute contained a slightly higher concentration of MDEA (an addition of approximately 0.05 $\mathrm{mol \cdot dm^{-3}}$) than the solvent. The results (averaged over at least three experiments) are listed in Table 6. All experiments were carried out with $(De)^2Sc < 47$. The experimental uncertainty is estimated to be 10 %.

Similarly to the results obtained for the aqueous PZ system, the experimentally obtained results listed in Table 6 are compared to predictions made with the modified Stokes−Einstein equation (eq 7). The MDEA diffusion coefficient at infinite dilution was taken from the work of Snijder et al.[11] Due to a lack of viscosity data, this comparison is limited to the conditions of which the viscosity data are listed in this work and by Rinker et al.[33] Figure 8 shows that an agreement exists between the experimentally obtained PZ and MDEA diffusivities and the values obtained using the modified Stokes−Einstein equation.

Conclusion

Experimentally determined densities and viscosities in aqueous (PZ + MDEA) solutions are reported over a wide range of concentrations and temperatures. Results obtained for aqueous MDEA solutions where no PZ was added were found to be in good agreement with the experimental densities and viscosities reported in the literature.

Experimentally determined diffusivities in aqueous solutions containing PZ and (PZ + MDEA) are reported over a wide range of concentrations and temperatures. A modified Stokes−Einstein relation is able to predict the experimental diffusivities.

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