J. Chem. Eng. Data 1989, 34, 77–82

Density, Viscosity, Solubility, and Diffusivity of CO_2 and N_2O in Solutions of Diethanolamine in Aqueous Ethylene Glycol at 298 K

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New experimental data are presented for the solubilities of CO_2 and N_2O in aqueous ethylene glycol (ETG) at 298 K measured over the complete composition range. The results show that the N_2O analogy can be applied for the estimation of the solubilities of CO_2 in solutions of alkanolamines in aqueous ETG at 298 K. Results are reported on the densities, the viscosities, and the solubilities of N_2O in solutions of diethanolamine (DEA) in aqueous ETG at 298 K, and where comparisons are possible, the agreement with previously determined data is satisfactory. Literature data on the diffusivities of CO_2 in aqueous ETG at 298 K are summarized. All physicochemical properties are fitted by empirical correlations, which are useful for the evaluation of these properties in mass-transfer experiments with solutions of DEA in aqueous ETG at 298 K.

1. Introduction

In our laboratory we investigate new reaction systems for the determination of interfacial areas by the chemical method in gas–liquid contactors. Recently (*1*), a viscous reaction system has been developed, which is based on the reaction between CO_2 and diethanolamine (DEA) in aqueous ethylene glycol (ETG). By changing both DEA and ETG concentrations the viscosity of the liquid phase at 298 K could be varied between 0.9 and 40 cP. Literature data on densities, viscosities, and solubilities of CO_2 in solutions of DEA in aqueous ETG are insufficient or not available, and therefore, a comprehensive set of experiments has been executed to determine these physicochemical properties.

The solubility of CO_2 in alkanolamine solutions cannot be determined directly because of the chemical reaction taking place. In view of the similarities of CO_2 and N_2O with regard to configuration, molecular volume and electronic structure, the solubility of CO_2 is often estimated by the N_2O analogy:

$$\text{(solubility of CO}_2\text{ in amine solution)} = C_1\text{(solubility of N}_2\text{O in amine solution)} \quad (1)$$

The value of the constant C_1 can be found by determination of the ratio of the solubilities of CO_2 and N_2O in the pure solvent without amines:

$$C_1 = \frac{\text{(solubility of CO}_2\text{ in pure solvent)}}{\text{(solubility of N}_2\text{O in pure solvent)}} \quad (2)$$

Laddha et al. (*2*) showed that the N_2O analogy is valid for the solubilities of CO_2 in aqueous solutions of alcohols, which are nonreacting and which have a structure analogous to that of MEA and DEA. Recently, Diaz et al. (*3*) reported that the analogy is also valid for the diffusivities of CO_2 in these aqueous alcohol solutions. These results indicate that the N_2O analogy can be applied for the estimation of the solubilities and the diffusivities of CO_2 in aqueous alkanolamine solutions. Comprehensive data and semiempirical correlations on the solubilities and diffusivities of CO_2 and N_2O in aqueous alkanolamine solutions are given by Versteeg and van Swaaij (*4*).

In this study new experimental results on the solubilities of CO_2 and N_2O in aqueous ETG at 298 K will be presented. It is shown that the N_2O analogy holds over the whole range of water and ETG mass percentages from 0 to 100 mass %. Additionally, new data will be presented on the density, the viscosity, and the solubility of N_2O for solutions of DEA in aqueous ETG at 298 K, and these new data will be compared with literature data when these are available. The available literature data on the diffusivity of CO_2 in aqueous ETG at 298 K will be summarized. Finally, all physicochemical properties will be fitted with empirical correlations, which are useful for the evaluation of mass-transfer experiments with this viscous reaction system.

2. Experimental Section

2.1. Density and Viscosity. Densities were measured by means of calibrated pycnometer bottles of 10 mL and viscosities by means of calibrated Ubelohde capillary viscometers. The measurements were performed in a constant temperature bath at 298 (±0.1) K. The experimental errors were estimated to be equal to $\pm1 \times 10^{-6}$ kg/m^3 and $\pm1 \times 10^{-4}$ N s/m^2, respectively.

Analytical grade DEA with a purity of ≥97% and ETG with a purity of ≥99%, supplied by Janssen Chimica, were used in the density and viscosity measurements. Diethanolamine was added to already prepared solvents of aqueous ETG containing decreasing amounts of distilled water: the ETG mass percentages of these solvents amounted to 0, 20, 40, 60, 80, and 100 mass %. Because of the hygroscopic nature of ETG, special care was taken to prevent excessive exposure of the glycol solutions to air.

2.2. Solubility. Solubilities were measured in a glass vessel with a total volume of 1.05×10^{-3} m^3, as used by Versteeg and van Swaaij (*4*). The vessel was thermostated at 298 (±0.2) K and could be operated at pressures between 0.0 and 0.1 MPa. In each experiment the vessel was filled with a carefully determined volume $\pm4.0 \times 10^{-3}$ m^3) of solution. First the solution was degassed by means of evacuation of the vessel and the contents were held under vacuum until air bubbles ceased to evolve from the liquid. After the solution has been degassed the vessel was closed and left alone until the vapor–liquid equilibrium was established. The pressure within the vessel was followed by means of a pressure transducer. The vapor–liquid equilibrium pressure was recorded, and then either pure CO_2 or N_2O was fed to the vessel until an arbitrary initial pressure was reached. The vessel was closed again, the initial pressure was recorded, and liquid agitation by means of a magnetic stirrer was started. When again the gas–liquid equilibrium pressure was reached and recorded, the solubility could be calculated from the initial and equilibrium pressure on the basis of Henry's law according to

$$m = \frac{He}{RT} = \frac{P_{G,init} - P_{G,eq}}{P_{G,eq}} \frac{V_G}{V_L} \quad (3)$$

In eq 3 m is a kind of dimensionless solubility defined as the

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0021-9568/89/1734-0077$01.50/0

Table I. Densities and Viscosities for Solutions of DEA in Aqueous ETG at 298 K

ETG%	$c_{DEA,L}$, mol/kg	$10^{-3}\rho_L$, kg/m^3	$10^3\mu_L$, N s/m^2
0	0	0.997	0.89
	0.120	1.000	0.92
	0.201	0.999	0.93
	0.471		1.03
	0.671	1.008	
	0.738	1.006	1.12
	0.942	1.012	
	1.141	1.014	
	1.992	1.021	1.74
	2.347	1.028	2.17
	2.853	1.032	2.72
20	0	1.022	1.35
	0.113	1.024	1.41
	0.166	1.025	1.43
	0.452		1.58
	0.700		1.75
	0.964	1.032	1.89
	1.162	1.035	2.04
	1.444	1.037	2.28
	2.293		3.13
	2.849	1.053	3.64
40	0	1.050	2.23
	0.078	1.051	2.30
	0.204	1.052	2.41
	0.472	1.054	2.64
	0.681	1.056	2.85
	0.905	1.056	3.10
	1.111	1.059	3.34
	1.356	1.060	3.63
	1.768	1.064	4.37
	2.244	1.066	5.41
	2.788	1.070	6.46
60	0	1.076	3.94
	0.081	1.079	4.06
	0.186	1.076	4.19
	0.455	1.079	4.60
	0.683	1.078	5.00
	0.866	1.080	5.36
	1.135	1.079	5.94
	1.746	1.082	7.58
	2.192	1.083	9.08
	2.627	1.086	11.08
80	0	1.095	8.14
	0.087	1.097	
	0.148	1.096	8.67
	0.413		9.51
	0.668	1.096	10.32
	0.866	1.099	
	1.103	1.097	12.62
	1.228	1.099	12.76
	1.689	1.099	14.96
	2.222	1.099	18.42
	2.795	1.099	23.06
100	0	1.113	17.00
	0.079	1.112	17.27
	0.163	1.112	17.72
	0.741	1.111	20.95
	1.241	1.111	25.16
	1.694		28.03
	2.474	1.099	37.15

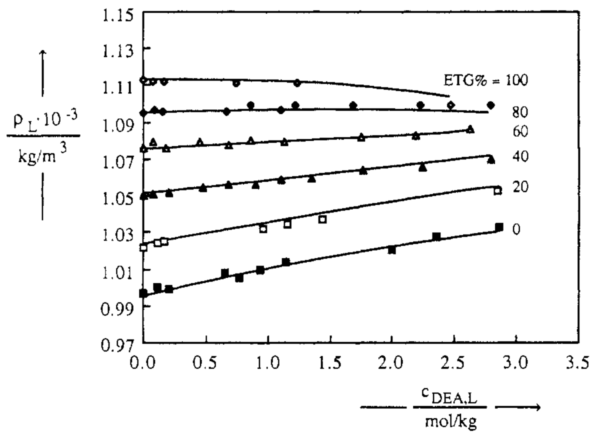

Figure 1. Densities for solutions of DEA in aqueous ETG at 298 K versus DEA concentration.

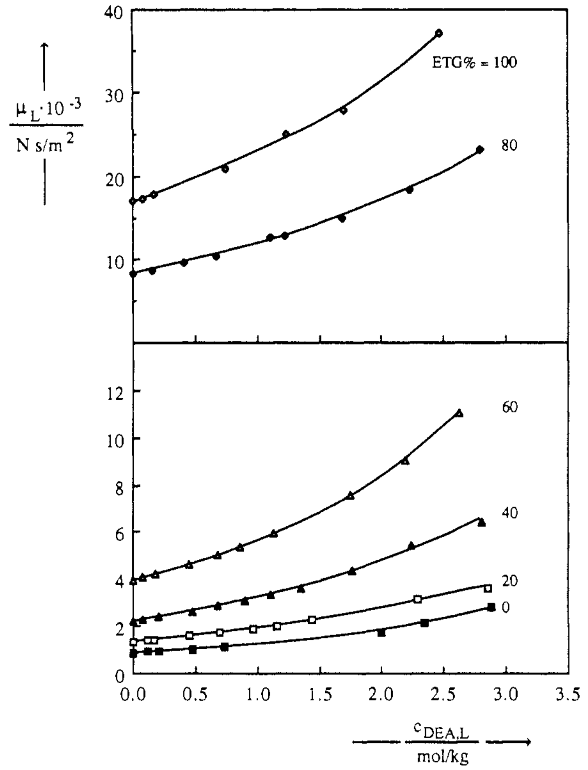

Figure 2. Viscosities for solutions of DEA in aqueous ETG at 298 K versus DEA concentration.

ratio of the liquid-phase concentration to the gas-phase concentration of the solute gas at equilibrium conditions.

In the lower viscosity range, where the ETG content is below 60 mass %, the reproducibility between the experiments was within 3%, while in the higher viscosity range it was within 5%. At these higher viscosities it was impossible to create a vortex in the vessel. Together with the lower mass-transfer coefficients at higher viscosities this caused extremely low absorption rates and consequently long times to reach equilibrium (1–3 days). It was very difficult to determine the gas–liquid equilibrium pressure due to these extremely low absorption rates; the experimental errors are therefore larger for the experiments with solutions in the higher viscosity range.

In the solubility experiments commercial grade aqueous DEA solutions of 80 vol % with a purity of ≥98%, supplied by BASF, and commercial grade ETG with a purity of ≥99%, supplied by Wolbert, were used. Also CO_2 with a purity of ≥99.5% and N_2O with a purity of ≥99.7%, supplied by Hoek Loos, were used. Concentrated DEA solutions were added to already prepared solvents of aqueous ETG containing decreasing amounts of distilled water: the ETG mass percentages of these solvents amounted to 0, 20, 40, 60, 80, and 100 mass %. The glycol mass percentages of the solvent were corrected for the additional amount of water added with the amine. The DEA concentration of each experimental solution was determined with a standard acid–base titration by means of the method described by Blauwhoff et al. (*5*).

3. Results and Discussion

3.1. Density and Viscosity. The results of the density and the viscosity determinations are presented in Table I. The data

Table II. Empirical Correlations on the Densities and Viscosities for Solutions of DEA in Aqueous ETG at 298 K[a]

ETG%		
0, 20, 40, 60, 80, 100	$\rho_L = 0.9958 + (1.555 \times 10^{-2})x - (1.141 \times 10^{-3})x^2 + (1.534 \times 10^{-3})y - (3.627 \times 10^{-6})y^2 - (2.959 \times 10^{-4})xy + (7.290 \times 10^{-5})x^2y + (1.656 \times 10^{-6})xy^2 - (8.725 \times 10^{-7})x^2y^2$	(4)
0	$\ln \mu_L = -0.1135 + (2.572 \times 10^{-1})x + (4.694 \times 10^{-2})x^2$	(5)
20, 40, 60	$\ln \mu_L = -0.1439 + (3.800 \times 10^{-1})x - (2.928 \times 10^{-2})x^2 + (2.039 \times 10^{-2})y + (8.120 \times 10^{-5})y^2 - (2.181 \times 10^{-4})xy + (1.310 \times 10^{-3})x^2y - (8.946 \times 10^{-6})xy^2 - (7.595 \times 10^{-6})x^2y^2$	(6)
80, 100	$\ln \mu_L = -0.8344 - (3.671 \times 10^{-1})x + (2.561 \times 10^{-1})x^2 + (3.697 \times 10^{-2})y - (3.378 \times 10^{-6})y^2 + (1.941 \times 10^{-2})xy - (6.080 \times 10^{-3})x^2y - (1.286 \times 10^{-4})xy^2 + (3.633 \times 10^{-5})x^2y^2$	(7)

[a] $x = c_{DEA,L}$ in mol/kg and y = ETG% in mass percentage; ρ_L in 10^{-3} kg/m³ and μ_L in 10^{-3} N s/m².

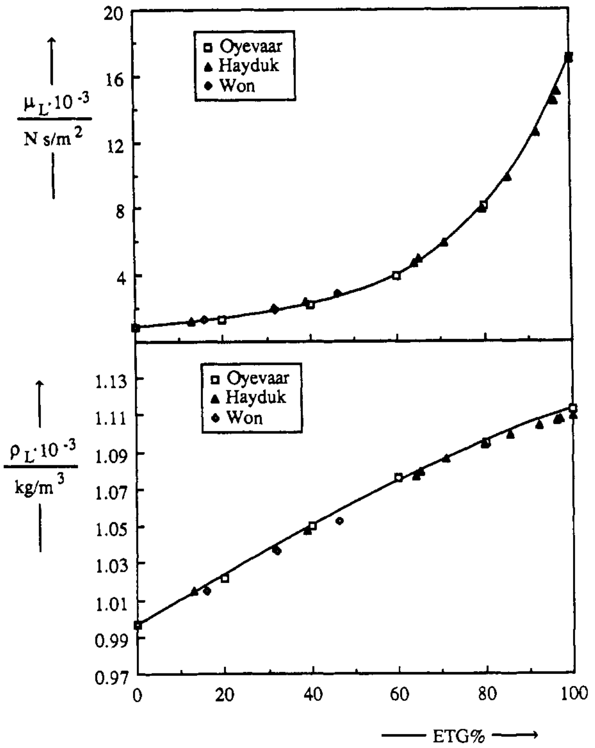

Figure 3. Comparison between literature data and experimental densities and viscosities for aqueous ETG at 298 K versus ETG mass percentage.

are plotted in Figures 1 and 2, respectively, with empirical correlation equations, which represented by the full lines; the equations themselves are given in Table II. These empirical correlations are fitted on the experimental data by means of a least-squares method. All density data could be fitted very well over the whole range of DEA concentrations and ETG mass percentages with one single correlation (r = 0.998).

However, all viscosity data could not be fitted with one single correlation. This is caused by the larger variation of the viscosities with both the DEA concentration and the ETG mass percentage in comparison with the variation in the densities. The viscosity data could only be described satisfactorily with three separate correlations: (1) one correlation for the viscosities of solutions of DEA in pure water (r = 0.9991); (2) one for the viscosities of solutions of DEA in aqueous ETG solvents with an ETG content of 20, 40, and 60 mass % (r = 0.9998); and (3) the last one for the viscosities of solutions of DEA in aqueous ETG solvents with an ETG content of 80 and 100 mass % (r = 0.9999). A closer look at the last two correlations reveals that the viscosities for solutions of DEA in ETG solvents with an ETG content of 60 mass % are equally well described by the correlations of eq 6 and 7. So we recommend the use of these two correlations within their appropriate validity range of 20–60 and 60–100 mass %, respectively, for the calculation of the viscosities for solutions of DEA in aqueous ETG with ETG contents between 20 and 100 mass %.

Table III. Literature Data on the Densities and Viscosities for Aqueous ETG at 298 K

ref	ETG%	$10^{-3}\rho_L$, kg/m³	$10^3\mu_L$, N s/m²
6	0	0.9971	0.894
	12.9	1.0144	1.22
	31.5	1.0379	1.97
	38.8	1.0477	2.36
	63.8	1.0771	4.73
	65.2	1.0796	4.96
	70.8	1.0860	5.94
	79.7	1.0943	7.93
	85.8	1.0994	9.90
	92.3	1.1044	12.56
	96.4	1.1073	14.49
	97.1	1.1078	15.05
	99.9	1.1097	16.94
	100.0	1.1098	17.01
7	0	0.997	0.895
	15.9	1.015	1.32
	32.0	1.036	1.95
	46.3	1.053	2.90

Table IV. Literature Data on the Viscosities for Aqueous DEA at 298 K

ref	$c_{DEA,L}$, mol/kg	$10^3\mu_L$, N s/m²
9	0.496	1.095
	0.972	1.264
	1.885	1.870
	2.725	2.805
8	0.896	1.236
	1.318	1.464
	1.701	1.733
	2.152	2.122
	2.506	2.430

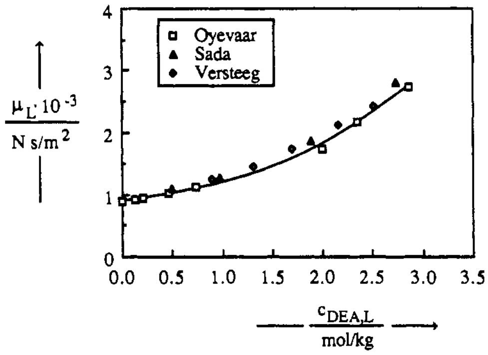

Figure 4. Comparison between literature data and experimental viscosities for aqueous DEA at 298 K versus DEA concentration.

The density and the viscosity data from the present study for aqueous ETG are plotted in Figure 3 in which they are compared with data for aqueous ETG as earlier reported by Hayduk and Malik (*6*) and Won et al. (*7*). These literature data on densities and viscosities for aqueous ETG at 298 K are given in Table III. It can be concluded from Figure 3 that the data from the present work agree very well with the literature data over the whole range of ETG concentrations.

The viscosities for aqueous DEA without ETG are compared in Figure 4 with data presented by Versteeg et al. (*8*) and Sada

Table V. Solubilities of CO_2 and N_2O in Solutions of DEA in Aqueous ETG at 298 K

ETG%	$c_{H_2O,L}$, mol/kg	$c_{DEA,L}$, mol/kg	m_{N_2O}	m_{CO_2}	m_{CO_2}/m_{N_2O}
0	55.56	0	0.590	0.791	1.34
0	54.27	0.194	0.585		
0	52.94	0.393	0.585		
0	52.57	0.449	0.580		
0	52.57	0.449	0.580		
0	50.71	0.731	0.574		
0	49.33	0.941	0.573		
0	48.52	1.064	0.561		
0	46.09	1.437	0.543		
0	44.28	1.717	0.525		
0	39.08	2.530	0.512		
20	44.44	0	0.515	0.729	1.42
19.76	42.31	0.446	0.473		
19.48	40.06	0.916	0.478		
18.99	36.06	1.639	0.460		
18.94	36.29	1.706	0.462		
40	33.33	0	0.460	0.646	1.40
39.52	31.92	0.455	0.467		
39.04	30.62	0.875	0.451		
38.02	28.21	1.650	0.461		
36.50	25.26	2.595	0.445		
60	22.22	0	0.451	0.614	1.36
59.28	21.52	0.471	0.451		
58.06	20.92	0.871	0.450		
57.12	19.75	1.649	0.444		
54.91	18.31	2.593	0.441		
80	11.11	0	0.537	0.696	1.30
79.11	11.11	0.442	0.531		
78.15	11.11	0.883	0.522		
76.13	11.13	1.688	0.532		
73.48	11.14	2.563	0.507		
100	0	0	0.734	0.945	1.29
99.00	0.59	0.406	0.683		
98.95	0.62	0.426	0.688		
98.02	1.13	0.775	0.660		
97.76	1.27	0.869	0.683		
96.96	1.68	1.148	0.677		
95.87	2.19	1.501	0.646		
95.17	2.50	1.713	0.609		
93.07	3.36	2.299	0.609		

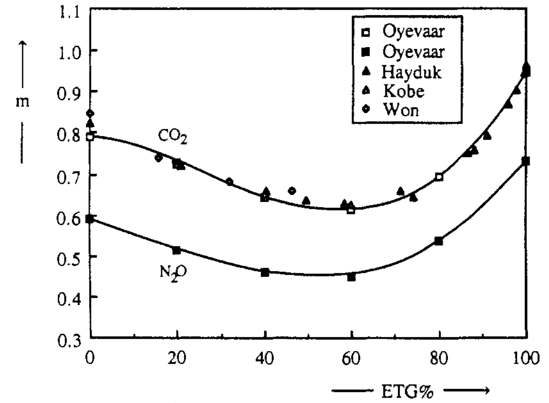

Figure 5. Comparison between literature data and experimental solubilities of CO_2 and N_2O in aqueous ETG at 298 K versus ETG mass percentage.

et al. (*9*). These literature data on viscosities for aqueous DEA at 298 K are presented in Table IV. It can be seen that a rather good agreement between the data from the present work and those from literature exists, except for the three highest DEA concentrations for which the viscosities from the present work are slightly lower.

3.2. Solubility. 3.2.1. Solubilities of CO_2 and N_2O in Aqueous ETG. The results for the solubilities of CO_2 and N_2O in aqueous ETG at 298 K are given in Table V. The solubilities of CO_2 and N_2O in aqueous ETG are plotted in Figure 5 together with empirical correlation equations ($r = 0.996$ and $r = 0.998$, respectively), which are presented by the full lines; the equations themselves are given in Table VI. The solubilities of CO_2 in aqueous ETG are also compared in Figure 5 with literature data on the solubilities of CO_2 in aqueous ETG by Hayduk and Malik (*6*), Won et al. (*7*), and Kobe and Mason (*10*). These literature data are given in Table VII. It can be concluded from Figure 5 that the solubilities for CO_2 from the present study agree with the solubilities are reported in literature.

It can also be seen from Figure 5 that the solubilities of CO_2 and N_2O have the same kind of dependence on the ETG concentration. Both solubilities initially decrease with increasing ETG mass percentage and have a typical minimum around an ETG content of 60 mass %. For pure ETG the solubilities of CO_2 and N_2O at 298 K are both larger than for pure water at 298 K. A similar behavior with such a typical minimum has been observed by Takahashi et al. (*11*) for the solubility of CO_2 in various mixed solvents.

The ratios of the solubilities of CO_2 and N_2O at the different ETG mass percentages can be calculated from the experimental data and are also presented in Table V. They are plotted in Figure 6 together with a best fit correlation, which is given in Table VI. It is remarkable to see that where Laddha et al. (*2*) already found that the ratio is constant for ETG mass percentages up to 20%, the ratio remains practically constant over the whole range of ETG concentrations. Laddha et al. (*2*)

Table VI. Empirical Correlations on the Solubilities of CO_2 and N_2O in Solutions of DEA in Aqueous ETG at 298 K[a]

ETG–water	$m_{CO_2} = 0.792 - (1.82 \times 10^{-3})y - (9.71 \times 10^{-5})y^2 + (1.31 \times 10^{-6})y^3$	(8)
ETG–water	$m_{N_2O} = 0.590 - (3.66 \times 10^{-3})y - (1.86 \times 10^{-5})y^2 + (6.97 \times 10^{-7})y^3$	(9)
ETG–water	$m_{CO_2}/m_{N_2O} = C_1 = 1.340 + (6.58 \times 10^{-3})y - (1.57 \times 10^{-4})y^2 + (8.59 \times 10^{-7})y^3$	(10)
DEA–ETG–water	$m_{N_2O} = 0.687 - (1.40 \times 10^{-2})x - (2.69 \times 10^{-3})y - (8.16 \times 10^{-3})z + (1.18 \times 10^{-4})z^2 + (2.89 \times 10^{-7})y^3$	(11)

[a] $x = c_{DEA,L}$ in mol/kg, y = ETG% in mass percentage, and $z = c_{H_2O,L}$ in mol/kg.

Table VII. Literature Data on the Solubilities of CO_2 in Aqueous ETG at 298 K

ref	ETG%	m_{CO_2}	ref	ETG%	m_{CO_2}
6	0	0.825		97.9	0.903
	21.1	0.721		99.5	0.945
	40.5	0.660		99.9	0.962
	49.6	0.638		100.0	0.966
	58.6	0.630	*10*	20	0.726
	71.4	0.660		40	0.654
	74.1	0.643		60	0.627
	86.6	0.751	*7*	0	0.846
	88.2	0.760		15.9	0.739
	91.1	0.793		32.0	0.682
	96.0	0.871		46.3	0.660

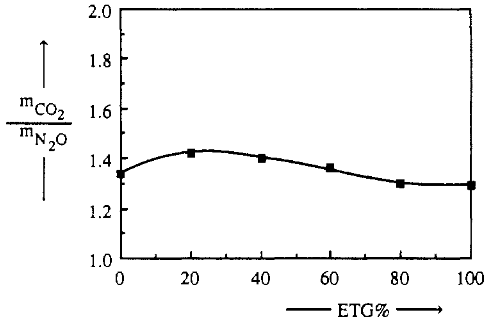

Figure 6. Ratio of solubilities of CO_2 and N_2O in aqueous ETG at 298 K versus ETG mass percentage.

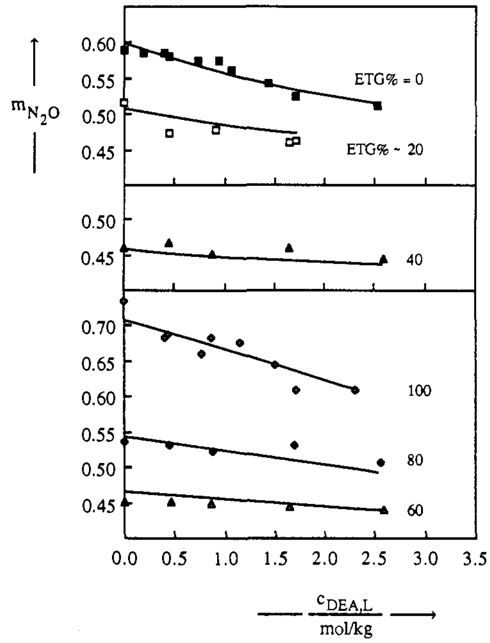

Figure 7. Solubilities of N_2O in solutions of DEA in aqueous ETG at 298 K versus DEA concentration.

Table VIII. Literature Data on the Solubilities of N_2O in Aqueous DEA Solutions at 298 K

ref	$c_{DEA,L}$, mol/kg	m_{N_2O}	ref	$c_{DEA,L}$, mol/kg	m_{N_2O}
12	0.448	0.595	*8*	1.378	0.564
	1.984	0.565		1.398	0.559
	2.257	0.556		1.532	0.573
	2.302	0.531		2.236	0.542
	2.980	0.535		2.330	0.553

used aqueous ETG and other aqueous solutions of alcohols, which had a structure somewhat similar to that of MEA and DEA, to prove the validity of the N_2O analogy. In the present study the ratio of the solubilities of CO_2 and N_2O in aqueous ETG at 298 K shows only a maximum variation between 1.42 and 1.29 over the whole composition range. It can therefore be concluded that the N_2O analogy can be applied for the estimation of solubilities of CO_2 in solutions of DEA in aqueous ETG at 298 K. Once again this investigation demonstrates the applicability of the N_2O analogy for the estimation of physicochemical properties of CO_2 in reacting solvents.

3.2.2. Solubilities of N_2O in Solutions of DEA in Aqueous ETG. The results for the solubilities of N_2O in solutions of DEA in aqueous ETG at 298 K are also given in Table V and are plotted in Figure 7. The solubilities of N_2O in these solutions could be fitted over the whole range of DEA concentrations and ETG percentages with one single correlation ($r = 0.989$). This correlation is given as eq 11 in Table VI and is represented by the full lines in Figure 7. It can be seen from Figure 7 that the correlation of eq 11, which had to contain the water concentration in order to obtain a good fit, predicts the solubilities of N_2O with an acceptable accuracy.

The solubilities of N_2O appear to be almost independent of the DEA concentration for glycol solvents of $36.5 \leq$ ETG% ≤ 60. This is in accordance with the observation that the solubilities of N_2O in aqueous ETG at these particular ETG mass percentages are also a weak function of the water and ETG concentrations; see Figure 5.

Comparison with literature data is only possible for solubilities of N_2O in solutions of DEA in water at 298 K. Solubility data of N_2O in these aqueous DEA solutions at 298 K by Versteeg et al. (*8*) and Sada et al. (*12*) are presented in Table VIII. The literature data are plotted in Figure 8, in which they are compared with the solubilities of N_2O in aqueous DEA at 298 K from the present work. The solubility data from the present study appear to be slightly lower than the literature data, especially at the higher DEA concentrations.

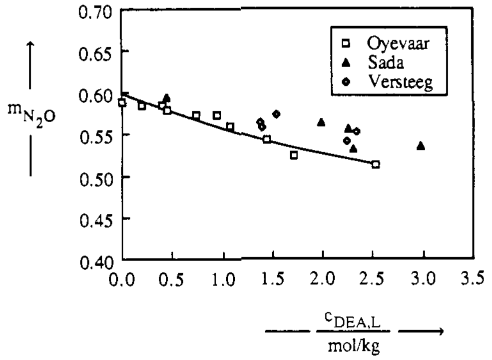

Figure 8. Comparison between literature data and experimental solubilities of N_2O in aqueous DEA at 298 K versus DEA concentration.

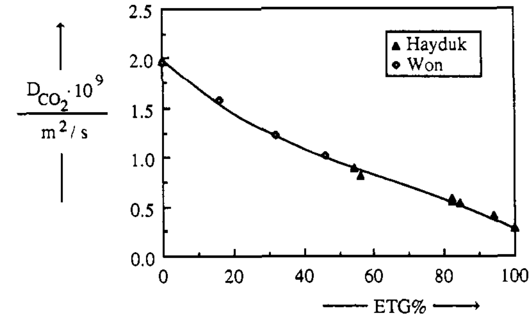

Figure 9. Literature data on diffusivities of CO_2 in aqueous ETG at 298 K versus ETG mass percentage.

Table IX. Literature Data on the Diffusivities of CO_2 in Aqueous ETG at 298 K

ref	ETG%	$10^9 D_{CO_2}$, m^2/s	ref	ETG%	$10^9 D_{CO_2}$, m^2/s
6	0	1.98		99.9	0.280
	54.4	0.894		99.9	0.283
	56.0	0.808		100.0	0.279
	82.2	0.554	*7*	0	1.96
	82.2	0.582		15.9	1.58
	84.7	0.549		32.0	1.22
	94.2	0.408		46.3	1.02

3.3. Diffusivity. Information on the liquid-phase diffusivities of CO_2 in the solutions of DEA in aqueous ETG is needed besides data on the densities, the viscosities, and the solubilities of CO_2 in these sollutions, because we need diffusivity data for the interpretation of mass-transfer experiments with the viscous reaction system. Experimental determination of liquid-phase diffusivities is rather time-consuming; in the present work the diffusivity of CO_2 was therefore estimated with the aid of literature data and a semiempirical Stokes–Einstein relation.

The available literature data on diffusivities of CO_2 in aqueous ETG at 298 K by Hayduk and Malik (*6*) and Won et al. (*7*) are summarized in Table IX. They are plotted in Figure 9, in which the full line represents the best fit correlation, which is given as

$$D_{CO_2} = 1.98 \times 10^{-9} - (3.17 \times 10^{-11})y + (3.00 \times 10^{-13})y^2 - (1.51 \times 10^{-15})y^3 \quad (12)$$

where y = ETG% in mass percentage and D_{CO_2} is in m^2/s. It can be concluded that this empirical correlation ($r = 0.999$) fits the literature data accurately.

Versteeg and van Swaaij (*4*) derived a modified Stokes–Einstein relation

$$(D_{N_2O}\mu_L^{0.8})_{\text{amine soln}} = \text{constant} = (D_{N_2O}\mu_L^{0.8})_{\text{water}} \quad (13)$$

for the diffusivities of N_2O in various aqueous alkanolamine solutions. The viscosities of these solutions ranged from 0.001 to 0.007 N s/m^2. It is assumed that this modified Stokes–Einstein relation can also be applied for the estimation of liquid-phase diffusivities at the higher viscosities up to 0.040 N s/m^2 for the solutions in the present study. If this assumption is justified, the diffusivities of CO_2 in solutions of DEA in aqueous ETG can be estimated from the correlation of eq 11 with the aid of the modified Stokes–Einstein relation

$$(D_{CO_2}\mu_L^{0.8})_{\text{amine soln}} = \text{constant} = (D_{CO_2}\mu_L^{0.8})_{\text{pure solvent}} \quad (14)$$

Without knowledge about the exact value of the constant in eq 14 the diffusivity of CO_2 in a solution of DEA in aqueous ETG can be estimated from the viscosity of this DEA solution and the viscosity and diffusivity of CO_2 in the pure ETG solvent with the same ETG mass percentage. The relevant data can be calculated from eq 5–7 and 12.

4. Conclusions

The results of the experimental work from the present study lead to the following conclusions:

1. The ratio of the solubilities of CO_2 and N_2O in aqueous ETG at 298 K remains practically constant over the whole composition range of mixtures of water and ETG.
2. The N_2O analogy can be applied for the estimation of the solubilities of CO_2 in solutions of alkanolamines in aqueous ETG at 298 K.
3. Empirical and semiempirical correlations, based on new experimental data and literature data, are derived for the physicochemical properties for solutions of aqueous ETG at 298 K and can be used for the estimation of these properties in mass-transfer experiments with this viscous reaction system.

Glossary

c	concentration, mol/m^3
C_1	constant, eq 2
D	diffusivity, m^2/s
He	Henry coefficient, mol/(m^3 Pa)
m	dimensionless solubility, $c_L = mc_G$, mol/mol
P	pressure, Pa
r	correlation coefficient
R	gas constant, 8.3144 J/(mol K)
T	temperature, K
V	volume, m^3
x	DEA concentration, mol/kg
y	ETG mass percentage
z	water concentration, mol/kg

Greek Symbols

μ	dynamic viscosity, N s/m^2
ρ	density, kg/m^3

Subscripts

amine	amine
eq	equilibrium
G	gas
init	initial
L	liquid
solvent	solvent

Abbreviations

DEA	diethanolamine
ETG	ethylene glycol
ETG%	ethylene glycol mass percentage
MEA	monoethanolamine

Registry No. ETG, 107-21-1; DEA, 111-42-2; CO_2, 124-38-9; N_2O, 10024-97-2.

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Received for review April 12, 1988. Revised September 6, 1988. Accepted September 29, 1988. The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid for the Netherlands Organization for the Advancement of Scientific Research (NWO).

Acidic Dissociation of Aqueous 4-Nitrocatechol

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Both primary and secondary acidic dissociation constants of aqueous 4-nitrocatechol (4-nitro-1,2-dihydroxybenzene) have been measured between 15 and 55 °C by pH potentiometry. The standard enthalpies and entropies of both dissociations are calculated from the temperature variations of the dissociation constants.

4-Nitro-1,2-dihydroxybenzene (4-nitrocatechol) is a weak diprotic acid. Several estimates of the acidic dissociation constant (*1–5*) have been reported, all in aqueous 0.1 M ionic strength media. Also, the enthalpy and entropy changes for the primary dissociation have been reported in aqueous 0.1 M ionic strength solution (*1*, *2*). However, we are unaware of measurements of the ΔH and ΔS parameters of the secondary dissociation. In the course of experiments to study acid–base tautomerism in 4-nitrocatechol, we required thermodynamic values (zero ionic strength aqueous media) of the two dissociation constants and the corresponding $\Delta H°$ and $\Delta S°$ parameters. Thus we made pH potentiometric measurements of dilute solutions of 4-nitrocatechol at several temperatures using pH potentiometry and report the results here.

0021-9568/89/1734-0082$01.50/0