Equilibria of CO_2 in Solutions of Diethanolamine in Aqueous Ethylene Glycol at 298 K

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New experimental data are presented for the equilibria of CO_2 in solutions of diethanolamine (DEA) in aqueous ethylene glycol (ETG) solvents at 298 K. The results show that at equilibrium the CO_2 loading, α_{CO_2}, decreases with increasing amounts of ETG in the solvent. Equilibrium constants for the equilibrium model of Kent and Eisenberg are obtained by fitting the constants on the experimental vapor pressures of CO_2, and the results are compared with experimental and literature data. The equilibrium constant K_{ov} for the overall reaction between CO_2 and DEA in aqueous ETG solvents at 298 K decreases with increasing amounts of ETG in the solvent.

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 (*2*).

The chemical method is restricted to gas-liquid systems in which the mass transfer can be described as an absorption of a gas-phase component into a liquid in which an irreversible reaction occurs with a liquid-phase component. Actually the reaction between CO_2 and DEA is not irreversible, and therefore the influence of the reversibility of the reaction on the mass-transfer rate has to be checked. Versteeg and van Swaaij (*3*) studied this and concluded for the reaction between CO_2 and DEA that the reversibility of this reaction should be taken into account especially in organic solvents like ethanol and 1-butanol in which the equilibrium constants for the reaction are relatively low. As also the amount of organic material in the solvent increases with the addition of ETG, equilibrium studies have to be incorporated in the development of this viscous reaction system.

Data on the equilibrium constants for the reaction between CO_2 and DEA in water are reported in literature for a wide range of concentrations and temperatures and are summarized by Lal et al. (*4*). However, in literature no information can be found on equilibrium constants in solutions of DEA in aqueous ETG. Therefore, a set of experiments has been executed to determine the equilibrium constants for the reaction between CO_2 and DEA in aqueous ETG at 298 K over the complete composition range. The results will be used in a numerical model for mass transfer with an equilibrium reaction, developed by Versteeg et al. (*5*), in order to estimate the effects of the reversibility on the determination of kinetic and mass-transfer parameters when absorption experiments are executed with this viscous reaction system.

2. Reaction Equilibria of CO_2

The system of CO_2 and DEA in aqueous solutions can be described by the reaction equilibria

$$DEAH^+ + H_2O \overset{K_1}{\rightleftharpoons} DEA + H_3O^+ \tag{1}$$

$$DEACO_2^- + H_2O \overset{K_2}{\rightleftharpoons} DEA + HCO_3^- \tag{2}$$

$$CO_2 + 2H_2O \overset{K_3}{\rightleftharpoons} HCO_3^- + H_3O^+ \tag{3}$$

$$2H_2O \overset{K_4}{\rightleftharpoons} OH^- + H_3O^+ \tag{4}$$

$$HCO_3^- + H_2O \overset{K_5}{\rightleftharpoons} H_3O^+ + CO_3^{2-} \tag{5}$$

At low amine conversions most of the chemically combined CO_2 exists as carbamate. Due to carbamate hydrolyses to bicarbonate, carbonate, and free amine according to reactions 2 and 5, at higher amine conversions more CO_2 can react than according to the stoichiometric amount of the overall reaction

$$CO_2 + 2DEA \overset{K_{ov}}{\rightleftharpoons} DEACO_2^- + DEAH^+ \tag{6}$$

with

$$K_{ov} = K_3/K_1K_2 \tag{7}$$

The set of equations 1-5 can be solved together with the electric charge balance and the mass balances for CO_2, DEA, and H_2O, so the partial concentrations of all components can be calculated if the equilibrium constants K_{1-5} and the total CO_2, DEA, and H_2O concentrations are known.

Extended with the specific reaction equilibria for H_2S, this setup is normally used to calculate the equilibrium vapor pressures of H_2S and CO_2 above amine solutions in acid gas treating processes. The equilibrium vapor pressures of the acid gases are then related to the liquid-phase concentrations of the gases by Henry's law, which equals for CO_2

$$P_{CO_2,G} = c_{CO_2,L}/He_{CO_2} \tag{8}$$

In order to obtain values for the equilibrium constants $K_{1...n}$, Kent and Eisenberg (*6*) proposed an experimental method to relate the reaction equilibria (1, ..., n) with the experimental vapor pressure data of H_2S-CO_2-amine systems. Their method accommodates all nonidealities of the liquid-phase solutions in the equilibrium constants K_1 and K_2 by fitting these two constants on the experimental vapor pressure data. Furthermore, they assumed all other equilibrium constants K_3, K_4, and K_5 to be really constant and equal to the values at infinite dilution. As no information is available on the effects of nonidealities on the thermodynamic properties in the viscous reaction system used in the present study, the method of Kent and Eisenberg (*6*) has been applied in order to obtain values for the equilibrium constants of the reaction between CO_2 and DEA in aqueous ETG at 298 K. As the water concentration $c_{H_2O,L}$ for the different aqueous ETG solvents used in our experiments ranged between 55 and 1 mol/L, we corrected all equilibrium constants for the water concentration by dividing K_1, K_2, and K_5 by $c_{H_2O,L}$ and K_3 and K_4 by $c_{H_2O,L}^2$.

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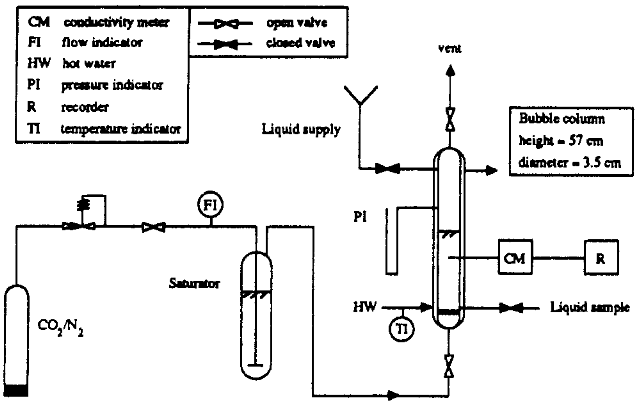

Figure 1. Experimental setup for the equilibrium experiments.

3. Experimental Section

3.1. Experimental Installation. The equilibrium experiments are performed in a glass bubble column with a total volume of 0.5×10^{-3} m^3. The column is thermostated at 298 K (±0.2 K) and operates at atmospheric pressures. A schematic flow sheet of the experimental setup is presented in Figure 1.

Before each experiment the column is filled with a batch ($\pm 0.2 \times 10^{-3}$ m^3) of a freshly prepared solution of DEA in aqueous ETG. This solution is contacted continuously with a N_2/CO_2 gas mixture from a pressurized gas bottle. A needle valve and a rotameter are used to control and measure the gas flow ($\pm 2 \times 10^{-5}$ m^3/s). The bubble column is equipped with a gas distributor made of sintered glass to achieve a good dispersion of the gas phase. In order to prevent evaporation losses from the solution in the column, a saturator, which contains an aqueous ETG solution of the same ETG concentration as of the DEA solution in the column, is installed in front of the column.

During an experiment CO_2 is absorbed from the gas mixture into the DEA solution until equilibrium between both phases is reached. During absorption the ion concentration in the liquid phase will increase. Therefore, the electrical conductivity of the DEA solution is monitored continuously on a recorder and used to determine whether equilibrium is reached. Then the equilibria of the reactions 1-5 have been established and the vapor pressure of CO_2 in the gas mixture is in equilibrium with the liquid-phase concentration of CO_2 according to Henry's law; see eq 8. Equilibrium at different DEA conversions can be achieved by using different N_2/CO_2 gas mixtures.

3.2. Experimental Procedure. The time to reach equilibrium varies from 4 to 20 h, depending on the composition of the DEA solution. At equilibrium two liquid samples are taken to determine the total DEA and CO_2 concentrations in the solution. The DEA concentration is determined with a standard acid-base titration and the amount of CO_2 by means of the method used by Blauwhoff et al. (*7*). The volume fractions of CO_2 in the N_2/CO_2 mixtures are determined with a gas chromatograph.

The DEA solutions for the equilibrium experiments are prepared from commercial grade aqueous DEA solutions of 80 vol % with a purity of ≥98% as supplied by BASF and commercial grade ETG with a purity of ≥99% as supplied by Wolbert. Various N_2/CO_2 gas mixtures with CO_2 volume fractions ranging from 0.02 to 0.15 with a purity of ≥99.5% as supplied by Hoek Loos are used.

Concentrated DEA solutions are added to already prepared aqueous ETG solvents containing decreasing amounts of distilled water: the ETG content of these solvents is 0, 20, 40, 60, 80, and 100 mass %. The ETG concentrations of the solvent are corrected for the additional amount of water added with the amine. The physicochemical properties of this viscous reaction system such as densities of the solutions and solubilities of CO_2 are obtained from the relations presented by Oyevaar et al. (*2*).

4. Results and Discussion

4.1. Experimental Results. Equilibrium experiments for each ETG solvent have been executed with four different N_2/CO_2 gas mixtures and for solutions with DEA concentrations between 800 and 2500 mol/m^3. The results are presented in Table I and show a decrease in the CO_2 loading α_{CO_2} with increasing ETG contents. The reproducibility of the experiments is within 5%.

Equilibrium experiments have also been performed in a pure ETG solvent, but the results could not be interpreted with the model due to numerical problems at the low water concentrations: they are therefore omitted. However, the results on α_{CO_2} in a pure ETG solvent are in line with the results on α_{CO_2} in the other ETG solvents as given in Table I.

4.2. Parameter Estimation. 4.2.1. Parameter Estimation Setup. For the reaction equilibria (1-5) we assume that K_3, K_4, and K_5 are true constants and we evaluate K_1 and K_2 for the different ETG solvents by fitting them on the experimental vapor pressure data of CO_2. For this parameter estimation we have used the RKPES computer program developed by Klaus and Rippin (*8*), which applies the maximum likelihood approach. For a single response model it reduces to a minimization of the sums of the squares of the residuals according to the Marquardt algorithm.

Kent and Eisenberg (*6*) present relations for the equilibrium constants K_{1-5} for the CO_2-DEA system in water. After correction for the water concentration these relations result in the values given in Table II. As no information is available on the values of K_3, K_4, and K_5 in ETG solvents, we have used for the parameter estimations the values of K_3, K_4, and K_5 in water as given in Table II.

4.2.2. Parameter Estimation Results. The optimal values for K_1 and K_2 as obtained with the parameter estimations are presented in Table III. Comparison with the equilibrium constants in water from Kent and Eisenberg (*6*) (see Table II) shows that the optimal values of K_1 and K_2 from this study are both 25% lower than the literature data. This is probably caused by the corrections as applied in this study for the water concentration. In contrast to the optimal values for K_1, which are practically constant, the optimal values for K_2 increase about a factor 10 with an increase in the ETG content from 0 to 80 mass %.

For all equilibrium experiments the vapor pressures of CO_2 calculated on the basis of the reaction equilibria (1-5) and the optimal values for K_1 and K_2 are given also in Table I. Parity plots of the calculated and the experimental vapor pressures of CO_2 for each ETG composition are shown in Figure 2. These plots given an indication of the reliability of the obtained values for K_1 and K_2, if the other concentrations are assumed to be exact. It can be seen that the agreement between the calculated and the experimental data is rather good and that almost all calculated values for $P_{CO_2,G}$ are within 20% of the experimental values.

4.3. Comparison with Literature Data. Comparison with literature data is only possible for vapor pressures of CO_2 above solutions of DEA in pure water at 298 K. In Figure 3 it is shown that the vapor pressures of CO_2, as calculated with the equilibrium constants from Table III, agree very well with the data presented by Kent and Eisenberg (*6*), even for high vapor pressures of CO_2 outside the pressure range applied in this work.

The equilibrium constant K_{ov} for the overall reaction (*6*) at 298 K can be calculated from the optimal values for K_1 and K_2 and from K_3. The calculated values for K_{ov}, not corrected for

Table I. Experimental Data and Calculated Vapor Pressures of CO_2 Above Solutions of DEA in Aqueous ETG at 298 K

ETG %, mass %	$10^{-3}c_{H_2O,L}$, mol/m^3	$10^{-3}c_{DEA,L}$, mol/m^3	α_{CO_2}	$P_{CO_2,G}$(expt), kPa	$P_{CO_2,G}$(calc), kPa
0	50.27	1.015	0.509	1.844	1.37
0	48.55	1.360	0.490	1.844	1.47
0	45.71	1.930	0.481	1.844	1.85
0	43.51	2.369	0.463	1.844	1.72
0	50.34	1.001	0.619	4.974	4.38
0	48.66	1.338	0.576	4.974	4.07
0	43.89	2.294	0.537	4.974	5.03
0	49.48	1.172	0.679	9.968	10.3
0	48.75	1.319	0.661	9.968	10.2
0	46.16	1.840	0.604	9.968	9.03
0	50.42	0.984	0.736	14.80	13.7
0	48.57	1.356	0.683	14.80	13.5
0	45.37	1.997	0.631	14.80	14.3
0	43.01	2.463	0.618	14.80	17.2
19.52	42.25	0.865	0.550	2.370	2.01
18.62	37.43	2.150	0.467	2.370	1.91
19.27	40.78	1.255	0.579	4.923	4.24
18.64	37.51	2.129	0.532	4.923	4.59
19.25	40.64	1.290	0.664	9.968	10.7
19.21	40.42	1.351	0.652	9.968	10.2
18.96	39.06	1.713	0.616	9.968	9.83
18.94	38.96	1.740	0.629	9.968	11.6
18.68	37.70	2.077	0.602	9.968	11.0
18.65	37.58	2.11	0.599	9.968	10.9
19.48	42.01	0.928	0.722	9.968	11.6
18.95	39.01	1.725	0.662	14.80	16.5
18.63	37.47	2.139	0.624	14.80	14.9
39.00	32.68	0.914	0.524	2.370	2.49
38.05	30.81	1.646	0.474	2.370	2.72
37.36	29.63	2.117	0.448	2.370	2.54
38.70	32.06	1.156	0.549	4.923	3.97
37.37	29.66	2.107	0.520	4.923	5.59
38.42	31.50	1.376	0.626	9.968	9.71
37.98	30.68	1.700	0.616	9.968	11.6
39.03	32.73	0.893	0.712	14.80	11.8
38.42	31.51	1.373	0.677	14.80	15.4
37.97	30.68	1.701	0.634	14.80	13.8
37.77	28.74	2.476	0.607	14.80	17.2
58.60	22.73	0.878	0.468	2.370	1.98
57.79	22.16	1.316	0.448	2.370	2.19
56.98	21.64	1.720	0.441	2.370	2.45
58.59	22.73	0.882	0.550	4.923	4.53
57.79	22.16	1.316	0.510	4.923	4.47
56.98	21.64	1.719	0.507	4.923	5.56
57.66	22.07	1.385	0.579	9.917	10.2
57.00	21.65	1.710	0.564	9.917	11.1
55.90	21.01	2.206	0.547	9.917	12.0
58.56	22.71	0.896	0.667	14.42	14.3
57.69	22.09	1.371	0.598	14.42	12.4
57.00	21.66	1.707	0.596	14.42	16.0
55.93	21.03	2.192	0.553	14.42	12.9
78.10	12.17	0.905	0.422	2.370	1.71
76.45	12.16	1.571	0.420	2.370	2.53
74.34	12.15	2.295	0.403	2.370	2.71
76.45	12.16	1.569	0.477	4.923	4.38
74.41	12.15	2.273	0.481	4.923	6.07
76.34	12.16	1.609	0.560	9.917	9.68
75.47	12.15	1.920	0.543	9.917	9.81
78.27	12.17	0.832	0.673	14.42	12.2
76.40	12.16	1.590	0.608	14.42	14.8
75.50	12.15	1.913	0.595	14.42	16.0

Table II. Equilibrium Constants at 298 K for the CO_2–DEA System in Water According to Kent and Eisenberg (*6*)

K_1	8.14×10^{-12}	K_4	3.44×10^{-18}
K_2	4.02×10^{-3}	K_5	8.36×10^{-13}
K_3	8.29×10^{-9}		

the water concentration, are presented in Table IV and plotted in Figure 4. As expected, K_{ov} decreases with increasing ETG content and thus with increasing amount of organic material in the solvent. For water at 298 K K_{ov} equals 7.7 m^3/mol in comparison to a value of 4.56 m^3/mol for K_{ov} calculated from the relations of Kent and Eisenberg (*6*). As mentioned before, this difference may be caused by the corrections for the water concentration in this study.

5. Conclusions

The results from the present study on equilibria on CO_2 in solutions of DEA in aqueous ETG at 298 K lead to the following conclusions:

1. At equilibrium the CO_2 loading, α_{CO_2}, decreases with increasing ETG content.

Table III. Optimal Values for K_1 and K_2 at 298 K in the CO_2-DEA System in Aqueous ETG, as Obtained by Parameter Estimation

ETG%, mass %	K_1	K_2
0	6.1×10^{-12}	3.2×10^{-3}
20	5.3×10^{-12}	4.5×10^{-3}
40	5.9×10^{-12}	1.1×10^{-2}
60	5.7×10^{-12}	8.4×10^{-3}
80	3.8×10^{-12}	4.0×10^{-2}

Table IV. Equilibrium Constants K_{ov} for the Overall Reaction between CO_2 and DEA in Aqueous ETG at 298 K

ETG%, mass %	K_{ov}, m^3/mol	ETG%, mass %	K_{ov}, m^3/mol
0	7.7	60	3.1
20	6.3	80	1.0
40	2.3		

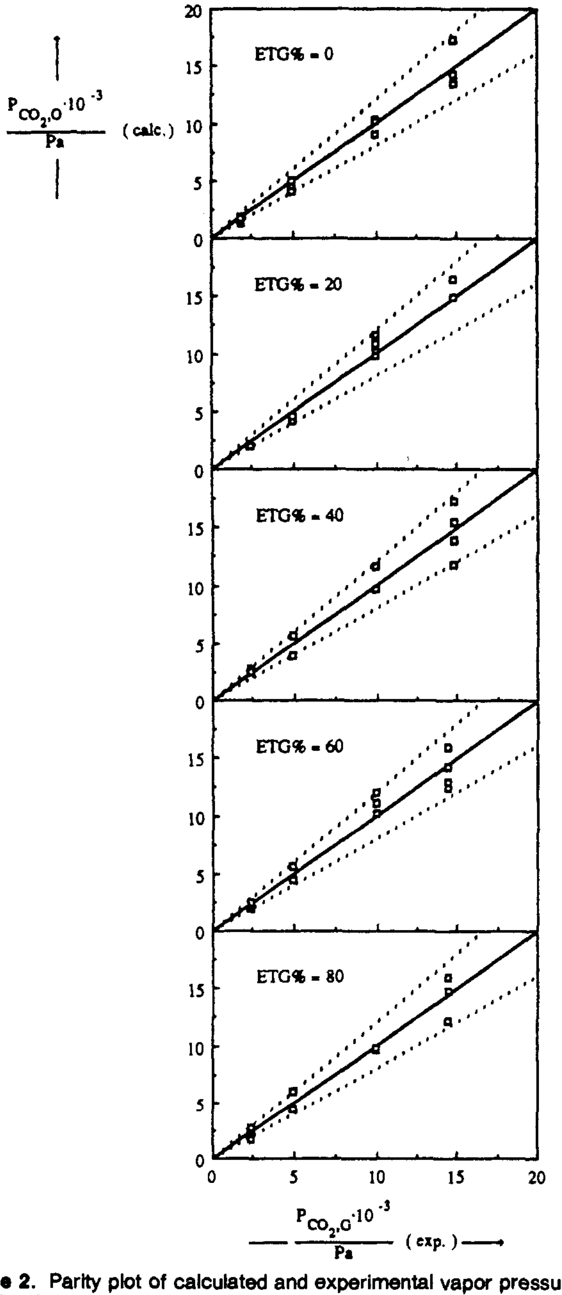

Figure 2. Parity plot of calculated and experimental vapor pressures of CO_2 above solutions of DEA in aqueous ETG at 298 K (···, 20% deviation boundaries).

2. Vapor pressures of CO_2 above solutions of DEA in aqueous ETG can be predicted with the method of Kent and Eisenberg (*6*) if the water concentration is taken into account.

3. The equilibrium constant K_{ov} for the overall reaction between CO_2 and DEA decreases with increasing ETG content.

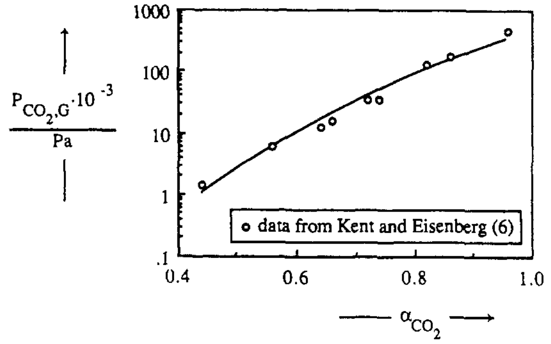

Figure 3. Comparison between literature data (O) and calculated vapor pressures of CO_2 (—) above solutions of DEA in water at 298 *K* (c_{DEA} = 2.0 mol/L).

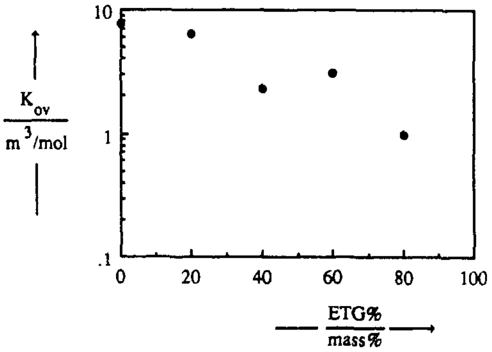

Figure 4. Overall equilibrium constants K_{ov} at 298 K versus ETG content in solutions of DEA in aqueous ETG.

Glossary

α_{CO_2}	CO_2 loading, mol of CO_2/mol of DEA
c	concentration, mol/m^3
He	Henry coefficient, mol/(m^3 Pa)
$K_{1...n}$	equilibrium constants, (mol/m^3)^x
P	pressure, Pa

Subscripts

G	gas
L	liquid
ov	overall

Abbreviations

DEA	diethanolamine
ETG	ethylene glycol
ETG%	ethylene glycol mass percentage

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

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Received for review September 16, 1988. Accepted July 10, 1989. The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Scientific Research (NWO).