Absorption of H_2S by an Aqueous Methyldiethanolamine Solution at 296 and 343 K

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An apparatus developed to measure absorption kinetics of acid gases by amine solutions is described as well as the experimental procedures dealing with either the initial kinetics or kinetics for loaded solutions. Data obtained for H_2S absorption into a 50 mass % methyldiethanolamine (MDEA) aqueous solution with various initial H_2S loadings are reported for the following conditions: H_2S loadings from 0 to 0.44 mol H_2S per mol MDEA and two temperatures, 296 and 343 K. The H_2S experimental absorption rates have been used together with a model, based on mass transfer and involving an instantaneous reversible reaction, to determine the MDEA diffusion coefficient.

Introduction

The removal of acid gases, such as H_2S and CO_2, from natural and industrial gases is a frequently encountered operation in the process industry. A common removal method is chemical absorption into an alkanolamine solution. Among the industrially important alkanolamines are the tertiary amines such as the *N*-methyldiethanolamine (MDEA). MDEA has been found to be an efficient chemical solvent for a selective absorption of H_2S from gas mixtures containing CO_2.

The following workers have measured the absorption kinetics of carbon dioxide and hydrogen sulfide in aqueous methyldiethanolamine solutions: Littel et al. (1992), Blauwhoff et al. (1984), Xu et al. (1992), Haimour et al. (1987), and Haimour and Sandall (1987).

The objective of this work was to study the absorption of H_2S into fresh and loaded MDEA aqueous solutions of initial MDEA composition of 50 mass %. At this concentration, for which no literature results are available, we measured H_2S absorption rates at 296 and 343 K, for H_2S loadings up to 0.44 mol of H_2S per mol of MDEA. These results were used to determine MDEA diffusion coefficients.

Experimental Apparatus

The reaction cell, shown in Figure 1, with a known interfacial area $A = (11.72 \pm 0.05) \times 10^{-4}$ m^2, is the same as that used by Pani et al. (1997). It is composed of a double-walled glass cylinder closed at both ends by two metallic flanges. The upper flange holds a SEDEME pressure transducer with a range from 0 to 2 bars and a tube for introducing the acid gases. The lower part of the cell is equipped with four vertical baffles, two concentric PTFE rings placed midway between the bottom and the top of the cell, and a Rushton turbine [diameter, D_{ag}, = $(4.25 \pm 0.02) \times 10^{-2}$ m], which is magnetically driven by an adjustable rotating field. The lower flange holds a special inlet closed by means of a septum that allows the introduction of a needle to feed the cell with the solvent and to load the solvent with H_2S. The total volume of the cell available for the gas and liquid phases is $(0.3504 \pm 0.0005) \times 10^{-3}$ m^3. A thermostatic liquid is circulated inside the double-walled glass cylinder to control the experimental temperature within ±0.05 K. The pressure transducer is thermostated at a temperature slightly higher than the experimental temperature (by about 2 K) to avoid any liquid condensate in its measuring chamber. The temperature is measured within ±0.05 K by means of a platinum probe going through the lower metallic flange as seen in Figure 1. The whole absorption cell is contained inside an air thermostat.

A microcomputer equipped with a “Strawberry Tree Computers” data acquisition card is used to record pressure as a function of time. The electrical signal from the pressure transducer is directly converted into pressure units (Pa) by the computer. Pressures are measured within ±200 Pa through the pressure transducer calibrated at each working temperature.

To work with loaded solutions, the equipment is fitted with a high-pressure reservoir, HPR (see Figure 1), containing the acid gas to be added to the absorption cell.

Experimental Procedure

Water and MDEA are degassed independently, and aqueous solutions are prepared under a vacuum. The respective masses of water and methyldiethanolamine are determined by differential weighings to within $\pm 10^{-2}$ g. This uncertainty on weighings leads to uncertainties in concentrations of less than ±0.05%.

The flask containing the degassed MDEA aqueous solution is connected to the absorption cell by means of a needle introduced through the septum situated at the bottom of the cell (see Figure 1a). The tube between the gas cylinder and the cell, the cell, and the tubing up to the Mohr’s clip, MC_1, are evacuated and then valves V_1 and V_3 are closed and Mohr’s clip, MC_1, is opened to let the aqueous alkanolamine solution flow down by gravity under a vacuum into the cell. Weighing the flask with tube and needle before and after transfer allows the determination of the exact mass of solvent transferred into the cell.

Once the amine aqueous solution is loaded and the temperature equilibrated, the inert gas pressure P_I corresponding mainly to the solvent vapor pressure plus eventual residual inert gases is measured. Then H_2S is introduced over a very short time (about 2 s) in the upper part of the cell, the resulting pressure being slightly higher than atmospheric pressure. Stirring is started at 100 rpm as soon as valve V_1 is closed. Pressure decay versus time is recorded as a result of the H_2S absorption through the horizontal gas−liquid interface. This procedure corresponds to the study of an initial absorption kinetic. Then,

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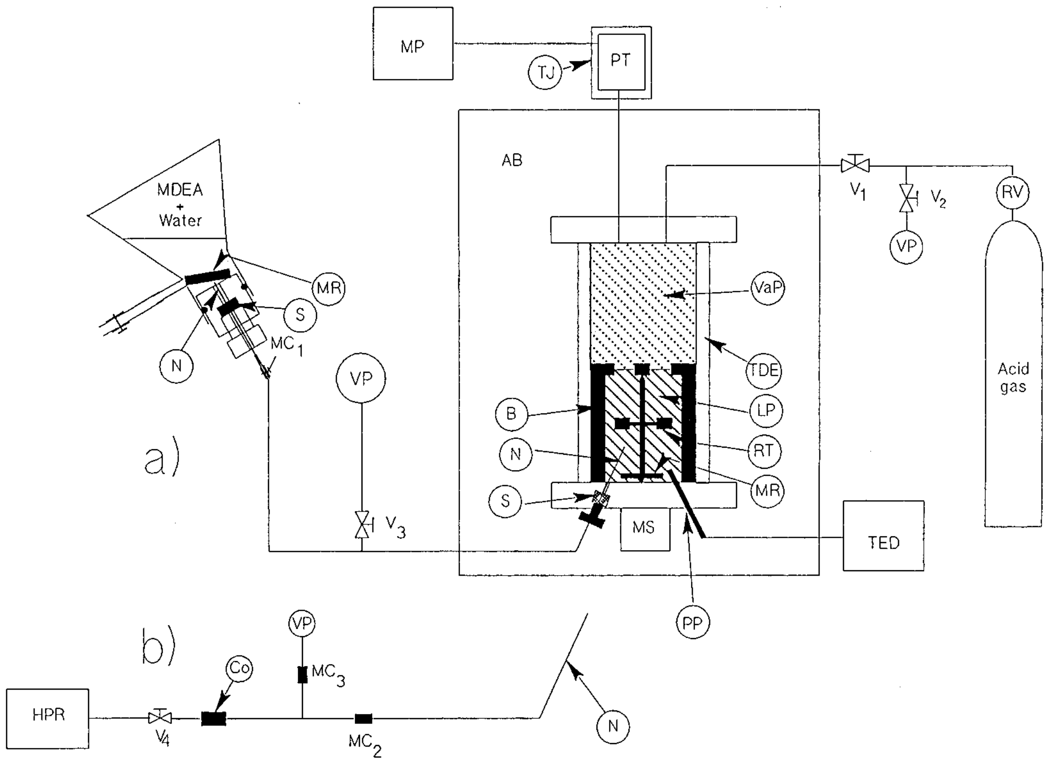

Figure 1. Flow diagram of the absorption equipment. AB, air bath; B, baffles; Co, coupling; HPR, high-pressure reservoir for H_2S; LP, liquid phase; MC_i; Mohr's clip *i*; MP, microcomputer; MR; magnetic rod; MS, magnetic stirrer; N, needle; PP, platinum probe; PT, pressure transducer; RT, Rushton turbine; RV, relief valve; S, septum; TDE, transparent thermostated double envelope; TED, thermal electronic display; TJ, thermostated jacket; V_i, shut-off valve *i*; VaP, vapor phase; VP, vacuum pump.

Table 1. Conditions of H_2S Absorption Kinetics by MDEA Solutions

ref no.	T/K	P_0/Pa	P_l/Pa	$P_{H_2S,i}$/Pa	$V_G/10^{-6}$ m^3	α/mol$_{H_2S}$/mol$_{MDEA}$	φ_{H_2S}/mol·m^{-2}·s^{-1}
1	296.05	154 877	2 750	152 127	181.58	0	0.011 55
2	295.85	173 044	2 700	170 344	182.26	0	0.012 53
3	295.95	190 584	2 780	187 804	180.91	0	0.012 84
4[a]	295.95	169 062	2 600	166 462	181.84	0	0.012 01
5	295.95	159 321	2 810	156 511	184.26	0	0.011 68
6[b]	343.05	196 055	36 800	159 255	178.35	0	0.029 30
7[b]	343.05	176 141	38 400	137 741	179.54	0	0.026 06
8	296.05	68 473	2 750	65 723	181.58	0.0116	0.007 20
9[a]	295.95	172 462	2 780	169 682	180.91	0.0118	0.011 72
10	295.85	169 275	2 810	166 465	184.26	0.0829	0.011 42
11	295.95	98 046	2 810	95 236	184.26	0.1217	0.007 93
12	295.75	163 939	2 810	161 129	184.26	0.1736	0.009 72
13	295.85	161 414	2 810	158 604	184.26	0.2365	0.007 51
14	295.85	175 902	2 810	173 092	184.26	0.3246	0.006 99
15	295.85	198 543	2 810	195 733	184.26	0.3796	0.006 10
16	295.75	179 846	2 810	177 036	184.26	0.4421	0.005 50
17[b]	343.05	197 858	38 400	159 458	179.54	0.011	0.018 64
18[b]	343.05	191 696	38 400	153 296	179.54	0.0197	0.017 77
19[b]	343.05	197 581	38 400	159 181	179.54	0.027	0.014 46
20[b]	343.05	197 765	38 400	159 365	179.54	0.0509	0.005 93
21[b]	343.05	171 268	38 400	132 868	179.54	0.0541	0.002 66
22[b]	343.05	172 605	38 400	134 205	179.54	0.0548	0.002 89
23[b]	343.05	197 072	38 400	158 672	179.54	0.0555	0.006 21
24[b]	343.05	179 629	38 400	141 229	179.54	0.0581	0.002 78
25[b]	343.05	198 160	38 400	159 760	179.54	0.0665	0.003 34

[a] MDEA from Merck instead of Aldrich. [b] Volume of cell $V_G + V_L = 343.5$ cm^3 instead of 350.4 cm^3.

after reaching equilibrium the liquid solvent is loaded with H_2S. For these purposes the solvent loading circuit, a, is removed and replaced by the H_2S loading circuit, b. This loading circuit is evacuated prior the transfer by opening MC_2 and MC_3 while valve V_4 is closed and the extremity of the needle is closed by the septum media. Then MC_3 is closed, V_4 is opened, and the extremity of the needle is pushed inside the liquid phase. H_2S is bubbled inside the liquid phase, through the needle, while the Rushton turbine is rotated at full speed, to improve the gas dispersion and consequently the solubilization rate. An estimate of the absorbed H_2S mass is controlled by continuously weighing the high-pressure cell. At the end of the process, the HPR cell is disconnected from the absorption cell and weighted within 10^{-2} g. This mass is compared with that before transfer to get an accurate value of the mass of H_2S transferred. A new absorption experiment for this given loading is done consecutively at the normal Rushton turbine rotation speed.

Theory

It seems generally accepted that reactions which only consist of the exchange of a hydrogen ion between a solute molecule and the solvent or another solute molecule are

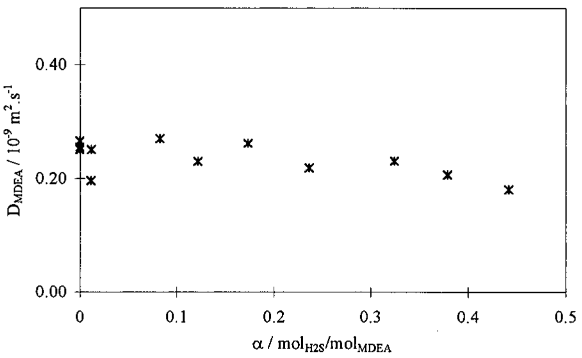

Figure 2. Loading influence on MDEA diffusivity.

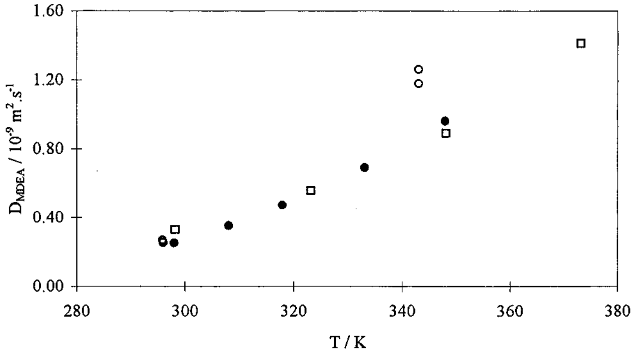

Figure 3. Comparison of D_{MDEA} in 50 mass % MDEA aqueous solution with previous works: ○, this work; ●, Rowley et al. (1997); □, Snijder et al. (1993).

sufficiently fast to be considered as instantaneous with respect to mass transfer (Maddox et al., 1987). The reaction between H_2S and aqueous alkanolamine involves only one proton transfer:

$$MDEA + H_2S \Leftrightarrow MDEAH^+ + HS^- \qquad (I)$$

This reversible reaction can be considered to be infinitely fast, and hence the absorption rate is entirely mass transfer controlled under practical conditions. Equilibrium is then reached everywhere in the solution:

$$K_{eq} = \frac{C_{MDEAH^+}C_{HS^-}}{C_{MDEA}C_{H2S}} \qquad (1)$$

K_{eq} is used as the equilibrium constant corresponding to reaction I but defined in terms of concentrations instead of activities. C_j are the concentrations of species j. Using the stagnant boundary layer model for hydrodynamics at the gas–liquid interface and Fick's law for mass transfer of the species involved in reaction I leads to

$$D_{MDEA}\frac{d^2C_{MDEA}}{d^2z} = D_{H_2S}\frac{d^2C_{H_2S}}{d^2z} = -D_{MDEAH^+}\frac{d^2C_{MDEAH^+}}{d^2z} = -D_{HS^-}\frac{d^2C_{HS^-}}{d^2z} \qquad (2)$$

where D_j are the diffusivities of species j and z is the distance from the gas–liquid interface in the boundary layer. As the gas phase inside the cell is almost a pure H_2S atmosphere, the resistance in the gas phase can be neglected. Assuming that the mean diffusivities of ionic species are equal to MDEA diffusivity, solving eq 2 with the equilibrium eq 1 assumed all through the layer leads to

Table 2. Diffusion Coefficient of MDEA in 50 mass % MDEA Solutions at 296 K

ref no.	T/K	$k_L/10^{-5}$ $m^2{\cdot}s^{-1}$	$\alpha/mol_{H_2S}/mol_{MDEA}$	$D_{MDEA}/10^{-9}$ $m^2{\cdot}s^{-1}$
1	296.05	0.373	0	0.25
2	295.85	0.371	0	0.27
3	295.95	0.372	0	0.27
4	295.95	0.372	0	0.26
5	295.95	0.372	0	0.25
6	343.05	1.112	0	1.26
7	343.05	1.112	0	1.18
8	296.05	0.373	0.0116	0.20
9	295.95	0.372	0.0118	0.25
10	295.85	0.371	0.0829	0.27
11	295.95	0.372	0.1217	0.23
12	295.75	0.370	0.1736	0.26
13	295.85	0.371	0.2365	0.22
14	295.85	0.371	0.3246	0.23
15	295.85	0.371	0.3796	0.21
16	295.75	0.370	0.4421	0.18

$$\varphi_{H_2S} = k_L\,(C_{H_2S,i} - C_{H_2S,b})\left[1 + \frac{D_{MDEA}}{D_{H_2S}}\frac{\Omega}{C_{H_2S,i}}\right] \qquad (3)$$

where $C_{j,i}$ and $C_{j,b}$ are the interfacial and bulk concentrations of species j, k_L is the liquid side mass transfer coefficient for our apparatus, and

$$\Omega = {}^1/_2[(C_{H_2S,i}K_{eq})^2 + 4C_{H_2S,i}K_{eq}C_{MDEA,b}]^{1/2} - {}^1/_2K_{eq}C_{H_2S,i} \qquad (4)$$

A mass transfer correlation between dimensionless numbers has been established for our apparatus from the Pani et al. (1997) data of N_2O absorption in MDEA aqueous solutions

$$Sh = 0.25Re^{0.63}Sc^{0.42} \qquad (5)$$

where $Sh = k_LD_T/D_{CO_2}$ is the Sherwood number, $Re = dND_{Ag}{}^2/\mu$ is the stirrer Reynolds number, and $Sc = \mu/dD_{CO_2}$ is the Schmidt number, N is the rotation speed of the Rushton turbine, 1.67 Hz; D_T is the cell internal diameter $(6.00 \pm 0.02) \times 10^{-2}$ m; d is the density; μ is the viscosity. The correlation, presented in Pani et al. (1997), included absorption data of N_2O by MDEA aqueous solutions and of CO_2 by water. As CO_2 absorption may be enhanced by its reaction with hydroxide ions, only the N_2O absorption in MDEA solutions experiments have been considered here, leading to eq 5. For Pani et al. (1997) results, taking one or the other of the two mass transfer correlations is of no influence on their conclusions because CO_2 absorption in MDEA aqueous solutions takes place according to a fast regime of reaction, insensitive to the liquid side mass transfer resistance.

Viscosity and density were determined using the correlations proposed by Al-Ghawas et al. (1989). The diffusivity of H_2S into aqueous MDEA solutions was calculated with the Haimour and Sandall (1984) correlation for the diffusivity of H_2S into water in the temperature range (288–303 K)

$$\frac{(D_{H_2S}/m^2{\cdot}s^{-1})(\mu/Pa{\cdot}s)^{0.74}}{(T/K)} = 3.4756 \times 10^{-14} \qquad (6)$$

The interfacial H_2S concentration is at equilibrium with

Table A1. H_2S Absorption Kinetics[a]

t/s	*P*/Pa	*t*/s	*P*/Pa	*t*/s	*P*/Pa	*t*/s	*P*/Pa	*t*/s	*P*/Pa	*t*/s	*P*/Pa	*t*/s	*P*/Pa	*t*/s	*P*/Pa
0.00	154 877	47.02	147 091	94.15	139 629	141.16	132 502	187.58	125 524	233.99	118 666	280.45	112 060	326.87	105 517
0.66	154 719	47.63	147 006	94.75	139 540	141.77	132 353	188.18	125 420	234.59	118 588	281.06	111 921	327.47	105 445
1.27	154 532	48.28	146 921	95.36	139 484	142.37	132 364	188.78	125 325	235.25	118 517	281.66	111 861	328.07	105 365
1.87	154 477	48.89	146 785	96.01	139 433	143.03	132 253	189.44	125 229	235.85	118 416	282.32	111 788	328.68	105 261
2.53	154 288	49.49	146 746	96.62	139 278	143.63	132 115	190.05	125 152	236.46	118 302	282.93	111 619	329.34	105 179
3.14	154 253	50.15	146 616	97.22	139 176	144.24	132 047	190.65	124 997	237.06	118 240	283.53	111 565	329.94	105 059
3.74	154 162	50.76	146 582	97.88	139 128	144.90	131 892	191.31	124 847	237.72	118 140	284.13	111 528	330.55	105 046
4.34	153 958	51.36	146 448	98.49	139 050	145.50	131 865	191.91	124 880	238.33	118 101	284.79	111 368	331.21	104 909
5.00	153 817	51.96	146 361	99.09	138 813	146.11	131 784	192.52	124 753	238.93	117 979	285.40	111 362	331.81	104 920
5.61	153 731	52.62	146 252	99.69	138 803	146.71	131 613	193.12	124 739	239.59	117 847	286.00	111 226	332.41	104 798
6.21	153 681	53.23	146 089	100.35	138 717	147.37	131 604	193.73	124 591	240.19	117 704	286.66	111 091	333.07	104 706
6.82	153 539	53.83	146 057	100.96	138 664	147.97	131 479	194.39	124 538	240.80	117 625	287.27	111 087	333.68	104 609
7.47	153 499	54.44	145 882	101.56	138 514	148.58	131 356	194.99	124 426	241.46	117 628	287.87	110 923	334.28	104 562
8.08	153 368	55.10	145 744	102.17	138 477	149.18	131 264	195.59	124 299	242.06	117 510	288.53	110 811	334.89	104 432
8.68	153 337	55.70	145 782	102.77	138 354	149.84	131 151	196.20	124 220	242.67	117 424	289.13	110 767	335.54	104 330
9.29	153 180	56.30	145 672	103.43	138 314	150.45	131 074	196.86	124 106	243.27	117 302	289.74	110 740	336.15	104 177
9.95	153 052	56.96	145 482	104.03	138 180	151.05	130 944	197.46	124 069	243.87	117 237	290.34	110 721	336.75	104 223
10.55	152 903	57.57	145 436	104.64	138 132	151.71	130 914	198.07	123 835	244.53	117 139	290.95	110 532	337.41	104 055
11.15	152 784	58.17	145 391	105.30	137 931	152.31	130 749	198.67	123 873	245.14	117 133	291.60	110 420	338.02	104 050
11.76	152 869	58.78	145 270	105.90	137 876	152.92	130 734	199.27	123 733	245.74	116 933	292.21	110 310	338.62	103 934
12.36	152 676	59.43	145 159	106.51	137 766	153.58	130 621	199.93	123 679	246.40	116 915	292.87	110 325	339.28	103 782
13.02	152 644	60.04	145 038	107.11	137 636	154.18	130 559	200.54	123 594	247.00	116 819	293.47	110 202	339.88	103 719
13.63	152 589	60.64	145 032	107.77	137 598	154.78	130 357	201.14	123 526	247.61	116 680	294.08	110 087	340.49	103 708
14.23	152 404	61.25	144 854	108.37	137 459	155.39	130 255	201.80	123 347	248.27	116 696	294.68	110 004	341.09	103 582
14.83	152 299	61.91	144 717	108.98	137 461	156.05	130 154	202.41	123 267	248.87	116 627	295.28	109 903	341.70	103 449
15.49	152 180	62.51	144 595	109.64	137 362	156.65	130 091	203.01	123 179	249.48	116 440	295.94	109 876	342.36	103 403
16.10	152 091	63.11	144 592	110.24	137 210	157.26	130 087	203.67	123 166	250.08	116 411	296.55	109 776	342.96	103 348
16.70	152 035	63.72	144 522	110.84	137 136	157.92	129 955	204.27	123 003	250.68	116 366	297.15	109 625	343.56	103 264
17.31	151 913	64.38	144 394	111.45	137 059	158.52	129 861	204.88	122 918	251.34	116 141	297.76	109 626	344.22	103 171
17.97	151 754	64.98	144 244	112.11	136 811	159.12	129 751	205.54	122 845	251.95	116 117	298.41	109 553	344.83	103 057
18.57	151 698	65.64	144 113	112.71	136 789	159.73	129 699	206.14	122 772	252.55	116 042	299.02	109 404	345.43	102 980
19.17	151 542	66.24	144 104	113.32	136 719	160.33	129 479	206.74	122 636	253.16	115 907	299.62	109 347	346.09	102 927
19.78	151 501	66.85	143 944	113.92	136 603	160.99	129 537	207.40	122 564	253.76	115 773	300.23	109 224	346.69	102 795
20.44	151 381	67.45	143 878	114.58	136 564	161.60	129 298	208.01	122 453	254.42	115 671	300.89	109 148	347.30	102 678
21.04	151 185	68.06	143 856	115.18	136 467	162.20	129 271	208.61	122 399	255.02	115 597	301.49	109 054	347.90	102 627
21.65	151 208	68.72	143 727	115.79	136 351	162.86	129 219	209.22	122 346	255.63	115 505	302.09	108 984	348.51	102 568
22.30	151 140	69.32	143 578	116.45	136 277	163.46	129 112	209.88	122 110	256.23	115 444	302.75	108 856	349.17	102 509
22.91	150 994	69.92	143 421	117.05	136 236	164.07	128 985	210.48	122 137	256.89	115 398	303.36	108 879	349.77	102 382
23.51	150 945	70.53	143 414	117.66	136 030	164.67	128 880	211.08	122 031	257.50	115 309	303.96	108 763	350.37	102 301
24.12	150 820	71.13	143 283	118.26	135 958	165.28	128 832	211.69	121 945	258.10	115 122	304.62	108 695	350.98	102 252
24.78	150 728	71.79	143 180	118.92	135 803	165.93	128 740	212.35	121 840	258.70	115 094	305.23	108 550	351.64	102 161
25.38	150 622	72.40	143 096	119.52	135 832	166.54	128 649	212.95	121 786	259.36	115 016	305.83	108 481	352.24	102 127
25.98	150 496	73.00	143 017	120.13	135 714	167.14	128 492	213.56	121 635	259.97	115 011	306.43	108 387	352.85	101 954
26.59	150 409	73.60	142 938	120.79	135 669	167.80	128 370	214.16	121 518	260.57	114 807	307.04	108 279	353.51	101 863
27.19	150 326	74.26	142 862	121.39	135 478	168.41	128 378	214.82	121 450	261.23	114 830	307.70	108 234	354.11	101 832
27.85	150 205	74.87	142 722	121.99	135 462	169.01	128 249	215.42	121 367	261.83	114 713	308.30	108 135	354.71	101 779
28.46	150 104	75.47	142 639	122.65	135 254	169.67	128 070	216.03	121 310	262.44	114 590	308.91	107 997	355.37	101 722
29.12	150 060	76.08	142 549	123.26	135 244	170.27	128 106	216.69	121 149	263.10	114 461	309.51	107 961	355.98	101 563
29.72	149 927	76.68	142 499	123.86	135 168	170.88	127 984	217.29	121 119	263.70	114 399	310.17	107 805	356.58	101 418
30.32	149 814	77.34	142 291	124.47	135 052	171.48	127 878	217.89	121 002	264.31	114 356	310.77	107 815	357.19	101 429
30.93	149 712	77.94	142 223	125.07	134 940	172.14	127 719	218.50	120 937	264.97	114 190	311.38	107 645	357.84	101 348
31.53	149 530	78.60	142 098	125.73	134 866	172.75	127 724	219.16	120 758	265.57	114 081	311.98	107 543	358.45	101 253
32.19	149 542	79.21	141 995	126.33	134 715	173.35	127 612	219.76	120 721	266.17	114 050	312.64	107 538	359.05	101 192
32.80	149 372	79.81	141 920	126.94	134 733	173.95	127 580	220.37	120 643	266.83	113 921	313.24	107 431	359.66	101 048
33.40	149 381	80.42	141 882	127.54	134 518	174.56	127 465	220.97	120 588	267.44	113 840	313.85	107 345	360.32	100 961
34.06	149 184	81.07	141 727	128.20	134 405	175.22	127 339	221.63	120 481	268.04	113 762	314.45	107 298	360.92	100 902
34.66	149 059	81.68	141 617	128.81	134 402	175.82	127 224	222.23	120 414	268.65	113 722	315.06	107 215	361.52	100 771
35.27	148 984	82.28	141 546	129.41	134 222	176.43	127 117	222.84	120 230	269.25	113 642	315.72	107 139	362.18	100 752
35.87	148 962	82.89	141 529	130.01	134 183	177.08	127 089	223.50	120 146	269.91	113 565	316.32	106 903	362.79	100 627
36.48	148 729	83.55	141 401	130.67	134 051	177.69	126 974	224.10	120 096	270.51	113 402	316.92	107 001	363.39	100 622
37.13	148 643	84.15	141 258	131.28	134 041	178.29	126 860	224.70	120 030	271.12	113 319	317.58	106 861	364.05	100 498
37.74	148 603	84.75	141 164	131.88	133 929	178.95	126 645	225.31	119 963	271.78	113 269	318.19	106 789	364.66	100 482
38.34	148 466	85.41	141 127	132.49	133 797	179.56	126 736	225.97	119 830	272.38	113 172	318.79	106 643	365.26	100 356
39.00	148 474	86.02	140 896	133.14	133 745	180.16	126 489	226.57	119 743	272.98	112 979	319.40	106 525	365.86	100 222
39.61	148 264	86.62	140 936	133.75	133 625	180.76	126 495	227.18	119 733	273.64	112 874	320.06	106 466	366.52	100 140
40.21	148 169	87.28	140 752	134.35	133 511	181.42	126 426	227.78	119 579	274.25	112 882	320.66	106 412	367.13	100 068
40.87	148 029	87.89	140 707	134.96	133 428	182.03	126 293	228.44	119 485	274.85	112 821	321.26	106 231	367.73	99 942
41.47	147 965	88.49	140 514	135.56	133 324	182.63	126 230	229.04	119 416	275.46	112 670	321.92	106 212	368.34	99 845
42.08	147 918	89.09	140 551	136.22	133 191	183.24	126 119	229.65	119 300	276.12	112 637	322.53	106 138	368.99	99 887
42.68	147 846	89.70	140 383	136.82	133 157	183.90	126 020	230.31	119 268	276.72	112 527	323.13	106 002	369.60	99 704
43.34	147 734	90.41	140 255	137.43	133 096	184.50	125 974	230.91	119 150	277.32	112 397	323.79	105 954	370.20	99 654
43.95	147 644	91.07	140 121	138.03	132 995	185.10	125 893	231.52	119 037	277.98	112 307	324.39	105 772	370.86	99 584
44.55	147 502	91.68	140 107	138.69	132 918	185.71	125 759	232.12	118 991	278.59	112 228	325.00	105 825	371.47	99 477
45.15	147 351	92.28	139 923	139.30	132 773	186.37	125 758	232.72	118 856	279.19	112 241	325.60	105 746	372.07	99 452
45.81	147 303	92.88	139 920	139.90	132 661	186.97	125 569	233.38	118 798	279.85	112 123	326.21	105 626	372.67	99 389
46.42	147 145	93.54	139 886	140.50	132 608										

[a] $T = 296.05$ K, solvent = MDEA + H_2O. Initial concentration of MDEA = 4.39 mol/L. Initial H_2S loading: 0 mol H_2S/mol MDEA. Final H_2S loading: 0.0116 mol H_2S/mol MDEA.

the vapor phase

$$C_{H_2S,i} = \frac{P_{H_2S}}{H_{H_2S}} \qquad (7)$$

where H_{H_2S} is the apparent Henry's law constant of H_2S. When no experimental data are available, van Krevelen and Hoftijzer (1948) suggest the use of eq 8 to estimate the effect of salt concentration on the solubility by means of a contribution method. For our solutions

$$\log\left(\frac{H_{H_2S,0}}{H_{H_2S}}\right) = (h_{MDEAH^+} + h_{HS^-} + h_{H_2S})C_{MDEAH^+} \qquad (8)$$

H_{H_2S} is the Henry's constant of the gas in the actual electrolyte solution as compared to that in pure water $H_{H_2S,0}$. The parameters h_{MDEAH^+} and h_{HS^-} are specific to the cation and the anion and are considered as temperature independent. In some cases, estimations hold very well even up to salt concentrations as high as 8 kmol·m^{-3} while, in other cases, significant deviations occur at concentrations lower than 1 kmol·m^{-3}, e.g. because of the concentration dependency of the dissociation degree. Generally, the salting-out effect tends to be overestimated at high electrolyte concentrations, i.e. the predicted values for H tend to be higher than values obtained without taking into account the ionic strength influence. For the absorption of H_2S into the amine solution, an instantaneous reaction planar region is formed near the gas−liquid interface as a result of the reaction between H_2S and MDEA. At the gas−liquid interface, MDEAH$^+$ and HS$^-$ ions are present. The salting-out parameter for MDEAH$^+$ is assumed to be zero as done by Haimour and Sandall (1987) following Danckwerts (1970). The value of the salting-out parameter for HS$^-$ is assumed to have a similar value to that of OH$^-$, i.e. 0.066 m^3·kmol^{-1}. The salting-out parameter for gaseous H_2S is taken as −0.033 m^3·kmol^{-1} (Danckwerts, 1970).

The bulk concentrations are calculated from the total MDEA concentration and the initial H_2S loading of each experiment. K_{eq} is estimated using the correlation of Kent and Eisenberg (1976). The equilibrium constants used at 296 and 343 K are respectively 44.6 and 19.3.

Taking into account the uncertainty on several of the above parameters for concentrated and loaded solutions, it was decided to use the absorption rate data obtained with our cell to determine the MDEA diffusion coefficient:

$$D_{MDEA} = D_{H_2S}\frac{C_{H_2S,i}}{\Omega}\left[\frac{\varphi_{H_2S}}{k_L(C_{H_2S,i} - C_{H_2S,b})} - 1\right] \qquad (9)$$

The H_2S absorption rate φ_{H_2S} was determined from pressure−time data by

$$\frac{\varphi_{H_2S}RTA}{V_G} = -\frac{dP_T}{dt} = -\beta \qquad (10)$$

β is the slope of the pressure vs time curve, at the beginning of the absorption process.

Results and Discussion

Reagent grade H_2S was supplied by Alpha Gaz with a purity certified higher than 99.7%. Water had been distilled twice, and MDEA was from two different sources: Aldrich (purity certified higher than 99%) and Merck (purity certified higher than 98%). Liquids were carefully degassed prior to use.

The conditions of the absorption experiments are given in Table 1. All rough results of pressure−time absorption data are compiled; 24 tables are included as Supporting Information, and the first table (Table A1) is given in the Appendix. Table 1 gives in column 1 the reference number of experiment, in column 2 the temperature of experiment, in column 3 the initial pressure, in column 4 the solvent + inert gas pressure, in column 5 the initial H_2S partial pressure, in column 6 the vapor phase volume inside the absorption reactor, in column 7 the H_2S loading, and in column 8 the H_2S absorption rate φ_{H_2S} derived from eq 10.

A good reproducibility for initial absorption is found between two experiments at 296 K with unloaded 50 mass % MDEA solutions using MDEA from Aldrich and two others with MDEA from Merck (see Tables A1−A4). No important deviation is found between MDEA from the two suppliers, despite of their slight differences in purity. Reproducibility has been tested and demonstrated at 343 K with MDEA provided by Aldrich (see Tables A6 and A7).

From the results at 296 and 343 K, we note that the H_2S absorption rate is an increasing function of temperature (see Tables A2 and A7).

Table 2 shows the values of the MDEA diffusion coefficient in a 50 mass % solution, for loadings ranging from 0 to 0.44 mol H_2S per mol MDEA. Figure 2 displays the slight influence of H_2S loading on MDEA diffusivity at 296 K and for 50 mass % MDEA.

The diffusion coefficients of MDEA in water were measured by Rowley et al. (1997) at 20, 35, and 50 mass % MDEA and at 298, 323, and 348 K. The diffusion coefficients of MDEA in water have also been measured by Snijder et al. (1993). Figure 3 shows a comparison between these literature values and ours. This comparison reveals that the three diffusion coefficient sources are in good agreement at 298 K. The correlation used to estimate D_{H_2S} is given for a 15 K temperature range below 303 K. Then our extrapolation up to 343 K is very doubtful, and it would not be surprising if there is a strong disagreement between the direct data from the literature and our indirect evaluations (eq 9). The estimation method of diffusivities in aqueous amine solutions requiring many assumptions appears far from reliable and is certainly the point for which supplementary work is necessary.

Conclusions

Acid gas absorption kinetics have been determined using especially designed equipment where total pressure is recorded as a function of time as in Laddha and Danckwerts (1982). This cell can be also used as a perfectly stirred reactor to quickly increase the acid gas loading of the investigated solution and then determine a series of isothermal absorption kinetics in a short period of time. Reproducibility of measurements is quite good (better than 10%). The cell can be used for either CO_2 or H_2S absorption and whatever the solvent: water with single or mixed amines for a large range of concentrations.

Appendix. Rough Results

Just Table A1 is enclosed for information (Tables A2−A25 are available as Supporting Information).

Supporting Information Available:

Tables A2−A25 for the Appendix are available in electronic form via the Internet. Accessing information is given on any current masthead page.

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