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Dissociation Constant of *N*-Methyldiethanolamine in Aqueous Solution at Temperatures from 278 K to 368 K

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The chemical equilibrium constant for the dissociation of protonated *N*-methyldiethanolamine (MDEA, $CH_3N(C_2H_5OH)_2$) in aqueous solutions is determined from electromotive force measurements at temperatures from 278 K to 368 K. Experimental results are reported and compared to literature values. Experimental results (on molality scale) are correlated by $\ln K = [-819.7/(T/K)] - 79.474 + 10.9756 \ln(T/K)$.

Introduction

Aqueous alkanolamine solutions are widely used for the absorption of sour gases like carbon dioxide or hydrogen sulfide from gaseous effluents, e.g. natural gases, refinery gases, and synthesis gases. Especially *N*-methyl-2,2′-iminodiethanol, commercially often called *N*-methyldiethanolamine (MDEA), is used for the selective removal of hydrogen sulfide from gases containing carbon dioxide. Due to the slower reaction of MDEA with carbon dioxide compared to hydrogen sulfide, in a properly designed absorption column a carbon dioxide rich gas is driven off on the top whereas a hydrogen sulfide rich solution is obtained on the bottom. As the reaction between hydrogen sulfide and MDEA is reversible, the solution rich in hydrogen sulfide is regenerated in a subsequent step, thereby producing hydrogen sulfide as a top product.

Continuing earlier work on the simultaneous solubility of carbon dioxide and hydrogen sulfide in aqueous MDEA solutions (Kuranov et al., 1996), and in order to improve the modeling of vapor−liquid equilibrium of these systems, the chemical equilibrium constant for the dissociation of $MDEAH^+$ (i.e. protonated MDEA) was measured in the temperature range from 278 K to 368 K. Experimental results are reported and compared to literature values.

Procedure

The equilibrium constant for the dissociation of $MDEAH^+$ in aqueous solution:

$$MDEAH^+(aq) \rightleftharpoons MDEA(aq) + H^+(aq)$$

was determined from electromotive force (EMF) measurements. EMF measurements were performed in an electrochemical cell consisting of a separate glass pH electrode and a (Ag, AgCl) electrode in a chloride-containing aqueous electrolyte solution:

$$\text{glass pH electrode}|\text{aqueous electrolyte solution (cont. } Cl^- \text{ ions)}|AgCl(s), Ag(s)$$

The solution must contain chloride, since it is a reaction partner in the half-reaction at the (Ag, AgCl) electrode. Glass pH electrodes have two well-known unpleasant properties (see for example Eisenman (1967) or Pitzer (1991)): (1) Failure to obey the Nernst equation perfectly. This error arises from the fact that the asymmetry potential of a glass pH electrode can vary with the pH of the solution under investigation. Nevertheless, the assumption is normally made that in passing from a standardizing solution to a test solution, the asymmetry potential remains constant. This is probably true in intermediate pH ranges but not for transitions between low- and high-pH solutions. The order of magnitude of this error is about 1 mV. (2) A tendency to drift in potential by millivolts over periods of minutes to days, depending on the electrode and electrolyte solution. Thus, the standard potential of a glass pH electrode might depend on time. This error arises from the fact that the asymmetry potential of a glass pH electrode can vary with time. However, a glass electrode cell can be used to measure the change in activity between two solutions of different composition. Therefore, a two-cell system was used (cf. Figure 1). In such a system, two solutions are being compared. The same electrodes are used in both cells (Serjeant and Warner, 1978). They are transferred back and forth between the two cells while the equilibrium potential is recorded continuously. The time period between two measurements should be as short as possible. With a proper electrometer, adequate shielding and temperature matching of cells, accurate measurements can be achieved. The glass electrode method is experimentally simpler than the hydrogen electrode method, because elaborate precautions for eliminating oxygen are not necessary. It can provide accurate chemical reaction constants and activity coefficient data more rapidly and can also be used under conditions (e.g. in reductive solutions) where the hydrogen electrode fails.

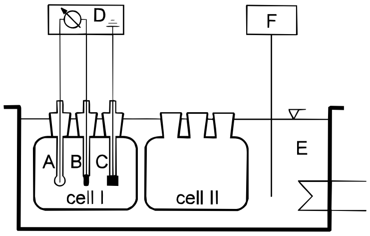

Figure 1. Scheme of the experimental arrangement: (A) glass pH electrode, (B) (Ag, AgCl) electrode, (C) platinum electrode, (D) electrometer, (E) thermostat, (F) measurement of temperature by platinum resistance thermometer.

The glass electrode method has been applied in the present work for determining the equilibrium constant for the dissociation of $MDEAH^+$.

In cell I aqueous hydrogen chloride is used as the electrolyte solution:

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Table 1. Experimental Equilibrium Data

	cell I		cell II				
t/°C	$\tilde{m}_{\mathrm{HCl,I}}$/(mol/kg)	E_{I}/mV	$\tilde{m}_{\mathrm{HCl,II}}$/(mol/kg)	$\tilde{m}_{\mathrm{MDEA}}$/(mol/kg)	E_{II}/mV	$E_{\mathrm{II}} - E_{\mathrm{I}}$/mV	10^9K_{exp}
5.15	0.010 149	−148.4	0.010 155	0.025 25	246.8	395.2	1.069
5.15	0.010 150	−148.9	0.010 162	0.050 12	269.6	418.5	1.070
5.1	0.010 173	−148.4	0.010 188	0.074 96	281.3	429.7	1.083
5.25	0.010 156	−148.9	0.010 074	0.099 48	287.0	435.9	1.185*
5.3	0.009 851	−145.7	0.009 819	0.099 82	289.0	434.7	1.248*
5.25	0.009 870	−146.5	0.009 874	0.100 64	289.4	435.9	1.185*
5.2	0.010 163	−147.5	0.010 241	0.125 79	296.1	443.6	1.074
5.15	0.010 157	−147.7	0.010 154	0.150 38	300.1	447.8	1.106
5.15	0.010 151	−146.9	0.010 151	0.175 05	304.2	451.1	1.132
5.3	0.010 155	−144.4	0.010 157	0.200 16	307.5	451.9	1.278*
5.15	0.010 165	−148.2	0.010 159	0.250 31	311.7	459.9	1.142
5.3	0.010 156	−146.6	0.010 152	0.300 20	316.4	463.0	1.224*
5.2	0.010 181	−148.0	0.010 153	0.350 32	319.8	467.8	1.171
5.0	0.009 869	−145.5	0.009 877	0.400 33	325.2	470.7	1.165
5.15	0.010 157	−148.4	0.010 162	0.450 07	325.6	474.0	1.156
5.0	0.010 158	−147.5	0.010 155	0.500 29	327.5	475.0	1.227
5.1	0.010 158	−148.4	0.010 166	0.600 00	331.8	480.2	1.193
5.15	0.010 164	−146.5	0.010 152	0.699 99	336.4	482.9	1.251
5.15	0.010 151	−147.5	0.010 156	0.800 07	339.0	486.5	1.226
5.1	0.010 150	−146.8	0.010 156	0.900 26	342.3	489.1	1.232
5.1	0.010 170	−147.4	0.010 072	0.991 64	344.2	491.6	1.250
15.1	0.010 149	−152.4	0.010 155	0.025 25	244.4	396.8	1.770
15.15	0.010 150	−152.8	0.010 162	0.050 12	267.9	420.7	1.793
15.1	0.010 173	−152.4	0.010 188	0.074 96	280.4	432.8	1.779
15.2	0.010 156	−152.6	0.010 074	0.099 48	286.6	439.2	1.942*
15.2	0.009 851	−147.5	0.009 819	0.099 82	291.0	438.5	1.990*
15.25	0.009 870	−151.3	0.009 874	0.100 64	289.0	440.3	1.858*
15.15	0.010 163	−151.5	0.010 241	0.125 79	295.1	446.6	1.798
15.05	0.010 157	−152.1	0.010 154	0.150 38	298.9	451.0	1.848
15.1	0.010 151	−151.0	0.010 151	0.175 05	303.6	454.6	1.884
15.25	0.010 155	−148.9	0.010 157	0.200 16	307.1	456.0	2.067*
15.05	0.010 165	−152.1	0.010 159	0.250 31	311.7	463.8	1.884
15.25	0.010 156	−150.8	0.010 152	0.300 20	316.4	467.2	2.007*
15.1	0.010 181	−152.1	0.010 153	0.350 32	319.9	472.0	1.926
14.95	0.009 869	−149.3	0.009 877	0.400 33	325.0	474.3	1.984
15.15	0.010 157	−152.0	0.010 162	0.450 07	325.4	477.4	1.994
15.1	0.010 158	−150.8	0.010 155	0.500 29	327.4	478.2	2.147
15.1	0.010 158	−152.7	0.010 166	0.600 00	332.4	485.1	1.949
15.15	0.010 164	−150.1	0.010 152	0.699 99	336.4	486.5	2.165
15.1	0.010 151	−151.1	0.010 156	0.800 07	339.4	490.5	2.093
15.05	0.010 150	−150.6	0.010 156	0.900 26	342.2	492.8	2.138
15.1	0.010 170	−150.9	0.010 072	0.991 64	344.6	495.5	2.158
25.05	0.010 149	−156.8	0.010 155	0.025 25	241.6	398.4	2.840
25.15	0.010 150	−157.4	0.010 162	0.050 12	266.0	423.4	2.834
25.1	0.010 173	−157.3	0.010 188	0.074 96	278.6	435.9	2.819
26.15	0.010 156	−157.4	0.010 074	0.099 48	285.7	443.1	3.189*
25.2	0.009 851	−152.9	0.009 819	0.099 82	289.1	442.0	3.136*
26.15	0.009 870	−155.1	0.009 874	0.100 64	288.4	443.5	3.134*
25.05	0.010 163	−156.5	0.010 241	0.125 79	293.7	450.2	2.838
25.1	0.010 157	−156.3	0.010 154	0.150 38	298.9	455.2	2.887
25.05	0.010 151	−156.3	0.010 151	0.175 05	302.6	458.9	2.933
26.25	0.010 155	−154.1	0.010 157	0.200 16	306.9	461.0	3.334*
25.05	0.010 165	−157.2	0.010 159	0.250 31	311.1	468.3	2.959
26.2	0.010 156	−155.7	0.010 152	0.300 20	316.4	472.1	3.305*
25.15	0.010 181	−157.3	0.010 153	0.350 32	319.1	476.4	3.066
25.05	0.010 157	−157.3	0.010 162	0.450 07	325.1	482.4	3.100
25.1	0.010 158	−156.8	0.010 155	0.500 29	327.5	484.4	3.221
25.1	0.010 158	−157.0	0.010 166	0.600 00	332.1	489.1	3.193
25.1	0.010 164	−155.4	0.010 152	0.699 99	336.2	491.6	3.402
25.05	0.010 151	−156.5	0.010 156	0.800 07	338.7	495.2	3.342
25.05	0.010 150	−155.6	0.010 156	0.900 26	341.9	497.5	3.437
25.05	0.010 170	−155.6	0.010 072	0.991 64	344.0	499.6	3.559
35.0	0.010 149	−161.2	0.010 155	0.025 25	238.3	399.5	4.487
35.05	0.010 150	−162.0	0.010 162	0.050 12	263.1	425.1	4.521
35.0	0.010 173	−161.6	0.010 188	0.074 96	276.4	438.0	4.496
36.15	0.010 156	−161.3	0.010 074	0.099 48	284.5	445.8	5.005*
35.15	0.009 851	−156.3	0.009 819	0.099 82	288.5	444.8	4.908*
35.15	0.009 870	−160.4	0.009 874	0.100 64	285.6	446.0	4.697*
35.0	0.010 163	−161.0	0.010 241	0.125 79	291.9	452.9	4.505
35.0	0.010 157	−161.6	0.010 154	0.150 38	296.3	457.9	4.598
35.05	0.010 151	−160.9	0.010 151	0.175 05	300.9	461.8	4.670
35.15	0.010 155	−158.6	0.010 157	0.200 16	305.2	463.8	5.018*
34.95	0.010 165	−161.6	0.010 159	0.250 31	309.6	471.2	4.741
35.2	0.010 156	−160.2	0.010 152	0.300 20	314.9	475.1	5.004*
35.0	0.010 181	−162.1	0.010 153	0.350 32	317.8	479.9	4.853
35.0	0.009 869	−158.7	0.009 877	0.400 33	323.2	481.9	5.122

Table 1 (continued)

	cell I		cell II				
t/°C	$\tilde{m}_{\mathrm{HCl,I}}$/(mol/kg)	E_{I}/mV	$\tilde{m}_{\mathrm{HCl,II}}$/(mol/kg)	$\tilde{m}_{\mathrm{MDEA}}$/(mol/kg)	E_{II}/mV	$E_{\mathrm{II}} - E_{\mathrm{I}}$/mV	10^9K_{exp}
35.0	0.010 157	−162.4	0.010 162	0.450 07	324.1	486.5	4.840
35.0	0.010 158	−161.3	0.010 155	0.500 29	326.1	487.4	5.224
34.95	0.010 158	−161.5	0.010 166	0.600 00	330.7	492.2	5.202
35.0	0.010 164	−160.9	0.010 152	0.699 99	335.4	496.3	5.230
34.95	0.010 151	−160.6	0.010 156	0.800 07	338.0	498.6	5.438
35.0	0.010 150	−160.4	0.010 156	0.900 26	340.6	501.0	5.595
34.95	0.010 170	−161.0	0.010 072	0.991 64	342.9	503.9	5.604
44.9	0.010 149	−166.8	0.010 155	0.025 25	233.8	400.6	6.884
44.9	0.010 150	−167.6	0.010 162	0.050 12	259.7	427.3	6.849
44.95	0.010 173	−167.2	0.010 188	0.074 96	273.2	440.4	6.898
45.25	0.010 156	−167.4	0.010 074	0.099 48	280.8	448.2	7.384*
45.15	0.009 851	−162.6	0.009 819	0.099 82	285.3	447.9	7.418*
46.2	0.009 870	−166.0	0.009 874	0.100 64	282.2	448.2	7.743*
44.95	0.010 163	−166.8	0.010 241	0.125 79	289.0	455.8	6.911
44.95	0.010 157	−167.4	0.010 154	0.150 38	293.8	461.2	6.977
44.95	0.010 151	−166.8	0.010 151	0.175 05	298.2	465.0	7.134
46.2	0.010 155	−164.8	0.010 157	0.200 16	302.7	467.5	8.005*
44.95	0.010 165	−167.4	0.010 159	0.250 31	307.1	474.5	7.318
46.2	0.010 156	−166.1	0.010 152	0.300 20	312.3	478.4	8.202*
44.95	0.010 181	−167.5	0.010 153	0.350 32	316.1	483.6	7.433
44.95	0.010 157	−167.4	0.010 162	0.450 07	322.2	489.6	7.641
45.0	0.010 158	−167.3	0.010 155	0.500 29	324.2	491.5	7.951
44.9	0.010 158	−167.4	0.010 166	0.600 00	328.9	496.3	7.942
44.9	0.010 164	−166.5	0.010 152	0.699 99	333.0	499.5	8.267
44.9	0.010 151	−166.4	0.010 156	0.800 07	336.1	502.5	8.421
44.85	0.010 150	−166.0	0.010 156	0.900 26	338.6	504.6	8.752
45.0	0.010 170	−165.1	0.010 072	0.991 64	341.5	506.6	9.207
54.95	0.010 149	−171.7	0.010 155	0.025 25	229.1	400.8	10.691
55.05	0.010 150	−172.3	0.010 162	0.050 12	256.7	429.0	10.439
54.95	0.010 173	−172.2	0.010 188	0.074 96	269.8	442.0	10.630
56.15	0.010 156	−174.3	0.010 074	0.099 48	275.7	450.0	11.906*
55.15	0.009 851	−168.0	0.009 819	0.099 82	282.5	450.5	11.096*
55.1	0.009 870	−173.0	0.009 874	0.100 64	278.3	451.3	10.773
54.9	0.010 163	−171.6	0.010 241	0.125 79	286.1	457.7	10.692
55.0	0.010 157	−172.2	0.010 154	0.150 38	291.2	463.4	10.798
55.0	0.010 151	−171.8	0.010 151	0.175 05	295.7	467.5	10.957
54.95	0.010 165	−172.3	0.010 159	0.250 31	305.0	477.3	11.211
55.15	0.010 156	−171.9	0.010 152	0.300 20	308.4	480.3	12.274*
54.9	0.010 181	−172.4	0.010 153	0.350 32	313.9	486.3	11.489
55.0	0.010 157	−172.5	0.010 162	0.450 07	319.9	492.4	11.916
54.95	0.010 158	−172.1	0.010 155	0.500 29	322.0	494.1	12.467
55.0	0.010 158	−171.8	0.010 166	0.600 00	326.7	498.5	12.780
54.95	0.010 164	−171.4	0.010 152	0.699 99	331.2	502.6	12.882
55.05	0.010 151	−171.0	0.010 156	0.800 07	334.1	505.1	13.496
55.0	0.010 150	−171.0	0.010 156	0.900 26	336.8	507.8	13.716
54.9	0.010 170	−171.2	0.010 072	0.991 64	339.1	510.3	13.984
64.9	0.010 149	−178.0	0.010 155	0.025 25	223.9	401.9	15.614
64.95	0.010 150	−176.9	0.010 162	0.050 12	252.3	429.2	16.162
64.95	0.010 173	−178.6	0.010 188	0.074 96	265.3	443.9	15.776
65.15	0.010 156	−177.8	0.010 074	0.099 48	273.4	451.2	17.382*
66.2	0.009 870	−179.6	0.009 874	0.100 64	272.7	452.3	17.524*
64.9	0.010 163	−178.1	0.010 241	0.125 79	281.8	459.9	15.977
64.95	0.010 157	−178.2	0.010 154	0.150 38	286.9	465.1	16.478
64.95	0.010 151	−178.1	0.010 151	0.175 05	291.7	469.8	16.428
66.25	0.010 155	−175.7	0.010 157	0.200 16	294.8	470.5	19.637*
65.0	0.010 165	−179.2	0.010 159	0.250 31	301.2	480.4	16.589
66.3	0.010 156	−177.0	0.010 152	0.300 20	303.3	480.3	21.414*
64.95	0.010 181	−178.6	0.010 153	0.350 32	310.1	488.7	17.611
64.95	0.010 157	−178.7	0.010 162	0.450 07	316.6	495.3	17.930
64.85	0.010 158	−179.1	0.010 155	0.500 29	318.6	497.7	18.293
65.0	0.010 164	−178.0	0.010 152	0.699 99	328.0	506.0	19.351
64.95	0.010 151	−177.5	0.010 156	0.800 07	330.8	508.3	20.259
65.0	0.010 150	−177.1	0.010 156	0.900 26	333.4	510.5	21.138
75.05	0.010 149	−181.7	0.010 155	0.025 25	219.1	400.8	24.183
75.1	0.010 150	−183.1	0.010 162	0.050 12	248.9	432.0	22.586
74.95	0.010 173	−183.9	0.010 188	0.074 96	261.4	445.3	23.335
76.25	0.010 156	−184.6	0.010 074	0.099 48	268.8	453.4	26.415*
75.2	0.009 851	−177.6	0.009 819	0.099 82	276.2	453.8	24.838*
75.0	0.010 163	−183.3	0.010 241	0.125 79	278.1	461.4	24.019
74.95	0.010 157	−183.9	0.010 154	0.150 38	283.8	467.7	23.861
74.95	0.010 151	−183.5	0.010 151	0.175 05	288.1	471.6	24.560
75.1	0.010 155	−183.3	0.010 157	0.200 16	292.0	475.3	25.125
75.0	0.010 165	−184.2	0.010 159	0.250 31	297.8	482.0	25.230
75.2	0.010 156	−185.3	0.010 152	0.300 20	303.0	488.3	24.798*
75.0	0.010 181	−183.8	0.010 153	0.350 32	307.3	491.1	26.338
75.0	0.009 869	−182.6	0.009 877	0.400 33	310.3	492.9	28.131

Table 1 (continued)

	cell I		cell II				
t/°C	$\tilde{m}_{\mathrm{HCl,I}}$/(mol/kg)	E_{I}/mV	$\tilde{m}_{\mathrm{HCl,II}}$/(mol/kg)	$\tilde{m}_{\mathrm{MDEA}}$/(mol/kg)	E_{II}/mV	$E_{\mathrm{II}} - E_{\mathrm{I}}$/mV	$10^9 K_{\mathrm{exp}}$
75.0	0.010 157	−181.8	0.010 162	0.450 07	313.2	495.0	29.587
74.95	0.010 158	−182.3	0.010 155	0.500 29	316.1	498.4	29.287
75.05	0.010 158	−182.6	0.010 166	0.600 00	321.0	503.6	29.589
74.95	0.010 164	−183.4	0.010 152	0.699 99	324.7	508.1	29.541
74.95	0.010 151	−183.4	0.010 156	0.800 07	327.2	510.6	30.868
75.05	0.010 150	−182.4	0.010 156	0.900 26	330.3	512.7	32.491
75.0	0.010 170	−183.0	0.010 072	0.991 64	332.1	515.1	33.517
85.0	0.010 149	−189.9	0.010 155	0.025 25	213.4	403.3	32.319
85.0	0.010 150	−188.9	0.010 162	0.050 12	242.5	431.4	34.302
85.1	0.010 173	−190.2	0.010 188	0.074 96	257.2	447.4	33.130
85.1	0.010 156	−192.8	0.010 074	0.099 48	263.6	456.4	34.751
85.05	0.009 851	−187.9	0.009 819	0.099 82	267.7	455.6	35.461
86.2	0.009 870	−192.0	0.009 874	0.100 64	265.3	457.3	35.229*
85.15	0.010 163	−190.0	0.010 241	0.125 79	272.4	462.4	35.916
85.05	0.010 157	−188.3	0.010 154	0.150 38	279.7	468.0	36.659
85.2	0.010 151	−190.5	0.010 151	0.175 05	282.7	473.2	36.540
86.25	0.010 155	−190.4	0.010 157	0.200 16	286.3	476.7	39.277*
85.05	0.010 165	−191.4	0.010 159	0.250 31	292.6	484.0	37.076
86.35	0.010 156	−190.8	0.010 152	0.300 20	297.3	488.1	41.421*
85.25	0.010 181	−191.2	0.010 153	0.350 32	301.2	492.4	40.308*
85.15	0.010 157	−189.7	0.010 162	0.450 07	309.3	499.0	41.394
85.0	0.010 158	−190.4	0.010 155	0.500 29	311.1	501.5	42.110
85.0	0.010 158	−188.8	0.010 166	0.600 00	316.7	505.5	44.207
85.1	0.010 164	−188.6	0.010 152	0.699 99	319.9	508.5	47.161
85.15	0.010 151	−187.8	0.010 156	0.800 07	321.2	509.0	53.058
85.2	0.010 150	−188.2	0.010 156	0.900 26	323.5	511.7	54.668
85.1	0.010 170	−188.7	0.010 072	0.991 64	325.8	514.5	55.672
95.0	0.010 149	−194.4	0.010 155	0.025 25	207.3	401.7	48.545
95.0	0.010 173	−196.8	0.010 188	0.074 96	250.7	447.5	48.851
94.6	0.009 870	−197.2	0.009 874	0.100 64	259.8	457.0	49.886*
94.9	0.010 163	−196.5	0.010 241	0.125 79	267.3	463.8	51.065
94.9	0.010 157	−192.8	0.010 154	0.150 38	276.4	469.2	52.931
94.95	0.010 151	−196.6	0.010 151	0.175 05	277.9	474.5	52.671
95.1	0.010 155	−196.3	0.010 157	0.200 16	281.3	477.6	55.172
94.95	0.010 165	−196.8	0.010 159	0.250 31	288.1	484.9	54.959
94.5	0.010 156	−196.1	0.010 152	0.300 20	292.4	488.5	57.951*
94.85	0.010 181	−196.6	0.010 153	0.350 32	296.4	493.0	59.922
94.8	0.009 869	−195.5	0.009 877	0.400 33	300.8	496.3	61.081
94.95	0.010 157	−194.7	0.010 162	0.450 07	302.4	497.1	67.767
94.95	0.010 158	−196.0	0.010 155	0.500 29	305.5	501.5	65.448
94.95	0.010 164	−196.7	0.010 152	0.699 99	313.0	509.7	70.659
95.0	0.010 151	−196.4	0.010 156	0.800 07	314.7	511.1	77.093
94.9	0.010 150	−196.2	0.010 156	0.900 26	318.7	514.9	76.301
95.0	0.010 170	−196.3	0.010 072	0.991 64	319.1	515.4	84.671

glass pH electrode|HCl (aq, $\tilde{m}_{\mathrm{HCl,I}}$)|AgCl(s), Ag(s) cell I

As the activity of a pure solid is set to unity, for cell I the Nernst equation results in

$$E_{\mathrm{I}} = E°(T) - \frac{RT}{F}\ln(a_{\mathrm{H^+}}a_{\mathrm{Cl^-}})_{\mathrm{I}} \qquad (1)$$

E_{I} is the electromotive force of cell I, and $E°$ is its standard potential. Since HCl is completely dissociated in diluted aqueous solution, the dissociation of water can be neglected. For a given temperature and overall molality of HCl ($\tilde{m}_{\mathrm{HCl,I}}$) activities $(a_{\mathrm{H^+}})_{\mathrm{I}}$ and $(a_{\mathrm{Cl}}-)_{\mathrm{I}}$ were calculated using the excess Gibbs energy model of Pitzer (cf. appendices 1 and 2).

Cell II is filled with an aqueous solution of MDEA and HCl:

glass pH electrode|MDEA(aq, $\tilde{m}_{\mathrm{MDEA}}$),
HCl(aq, $\tilde{m}_{\mathrm{HCl,II}}$)|AgCl(s), Ag(s) cell II

The Nernst equation results in

$$E_{\mathrm{II}} = E°(T) - \frac{RT}{F}\ln(a_{\mathrm{H^+}}a_{\mathrm{Cl^-}})_{\mathrm{II}} \qquad (2)$$

The mass balance equations for water, MDEA, and HCl give

$$\tilde{n}_{\mathrm{W}} = n_{\mathrm{W}} + n_{\mathrm{OH^-}} \qquad (3)$$

$$\tilde{n}_{\mathrm{MDEA}} = n_{\mathrm{MDEA}} + n_{\mathrm{MDEAH^+}} \qquad (4)$$

$$\tilde{n}_{\mathrm{HCl}} = n_{\mathrm{Cl^-}} \qquad (5)$$

The condition of electroneutrality results in

$$0 = n_{\mathrm{H^+}} - n_{\mathrm{OH^-}} + n_{\mathrm{MDEAH^+}} - n_{\mathrm{Cl^-}} \qquad (6)$$

In cell II the dissociation of water is taken into account:

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{OH^-(aq)}$$

The conditions for chemical equilibrium for both reactions present are

$$K_{\mathrm{W}}(T) = \exp\left\{-\frac{\mu^{\infty}_{\mathrm{H^+},m} + \mu^{\infty}_{\mathrm{OH^-},m} - \mu^{\mathrm{pure}}_{\mathrm{W,liq}}}{RT}\right\} = \frac{a_{\mathrm{H^+}}a_{\mathrm{OH^-}}}{a_{\mathrm{W}}} \qquad (7)$$

$$K(T) = \exp\left\{-\frac{\mu^{\infty}_{\mathrm{MDEA},m} + \mu^{\infty}_{\mathrm{H^+},m} - \mu^{\infty}_{\mathrm{MDEAH^+},m}}{RT}\right\} = \frac{a_{\mathrm{MDEA}}a_{\mathrm{H^+}}}{a_{\mathrm{MDEAH^+}}} \qquad (8)$$

The influence of pressure on the chemical reactions is neglected. The chemical equilibrium constant K_W for the dissociation of water was taken from the literature (Fisher et al., 1972). Activities were approximated using only the modified Debye-Hückel term in Pitzer's equation, i.e. neglecting binary and ternary parameters.

As both cells are at the same temperature, they have the same standard potential $E°$. Thus, subtracting eq 1 from eq 2 results in

$$\ln(a_{\mathrm{H^+}}a_{\mathrm{Cl^-}})_{\mathrm{II}} = \frac{F}{RT}(E_{\mathrm{I}} - E_{\mathrm{II}}) + \ln(a_{\mathrm{H^+}}a_{\mathrm{Cl^-}})_{\mathrm{I}} \qquad (9)$$

For given temperatures and compositions in both cells (cell I, $\tilde{m}_{\mathrm{HCl,I}}$; cell II, $\tilde{m}_{\mathrm{MDEA}}$, $\tilde{m}_{\mathrm{HCl,II}}$), the electromotive forces E_{I} $(=E_{\mathrm{I}}(T,\tilde{m}_{\mathrm{HCl,I}}))$ and E_{II} $(=E_{\mathrm{II}}(T,\tilde{m}_{\mathrm{MDEA}},\tilde{m}_{\mathrm{HCl,II}})$ were measured. With this information, the set of equations (eqs 3−9) can be solved in an iterative procedure to yield the "true" number of moles of each species present in cell II, as well as a preliminary number for the dissociation constant of MDEAH$^+$: $K_{\mathrm{exp}}(T,\tilde{m}_{\mathrm{MDEA}},\tilde{m}_{\mathrm{HCl,II}})$. This dissociation constant is called preliminary because it is calculated out of a set of equations in which for cell II activities are not exactly known but only approximated using the modified Debye−Hückel term in Pitzer's equation. For constant temperature T and constant overall molality of HCl ($\tilde{m}_{\mathrm{HCl,II}}$) measurements were performed at different overall molalities of MDEA ($\tilde{m}_{\mathrm{MDEA}}$). The true equilibrium constant for the dissociation of MDEAH$^+$ is determined in a two-step extrapolation procedure:

$$\lim_{\substack{\tilde{m}_{\mathrm{HCl,II}}=\mathrm{const}\\ \tilde{m}_{\mathrm{MDEA}}\to 0}} \{K_{\mathrm{exp}}(T,\tilde{m}_{\mathrm{MDEA}},\tilde{m}_{\mathrm{HCl,II}})\} = K_{\mathrm{exp}}(T,\tilde{m}_{\mathrm{HCl,II}}) \qquad (10)$$

$$\lim_{\tilde{m}_{\mathrm{HCl,II}}\to 0} K_{\mathrm{exp}}(T,\tilde{m}_{\mathrm{HCl,II}}) = K(T) \qquad (11)$$

However, if $\tilde{m}_{\mathrm{HCl,II}}$ is small enough (e.g. $\tilde{m}_{\mathrm{HCl,II}} \lesssim 0.01$ mol/kg), the second extrapolation is not necessary.

Experimental Section

For the EMF measurements a high-resolution electrometer (Metrohm, pH Voltmeter, type 713, resolution 0.1 mV) with a very large input resistance ($>10^{13}$ Ω) was used. A glass pH electrode (Metrohm, separate pH glass electrode with inner (Ag, AgCl) reference electrode, type 6.0133.100) was combined with a (Ag, AgCl) electrode of the thermal type (Sensortechnik Meinsberg, type SG, specially manufactured). The electrolyte solutions were saturated with AgCl to avoid the dissolution of AgCl from the (Ag, AgCl) electrode. A platinum electrode (Sensortechnik Meinsberg, hydrogen electrode, type MC30), which was also immersed in the electrolyte solution, was used for electrostatic and electromagnetic shielding of the cell. When not in use, the electrodes were stored in distilled water, which was also saturated with AgCl. Electrodes have to be washed before they are transferred from one cell to the other. Washing was accomplished by carefully rinsing an electrode first with distilled water and then transferring it through five glass bottles, each containing the same solution as the cell into which the electrode was supposed to be immersed for the EMF measurement. The cells were completely filled with the electrolyte solution, hermetically sealed, and mounted in a thermostatically controlled bath. The temperature was measured by resistance thermometry (estimated uncertainty: ±0.05 K). A constant electrometer reading was attained about 15−30 min after the electrodes had been transferred into a cell.

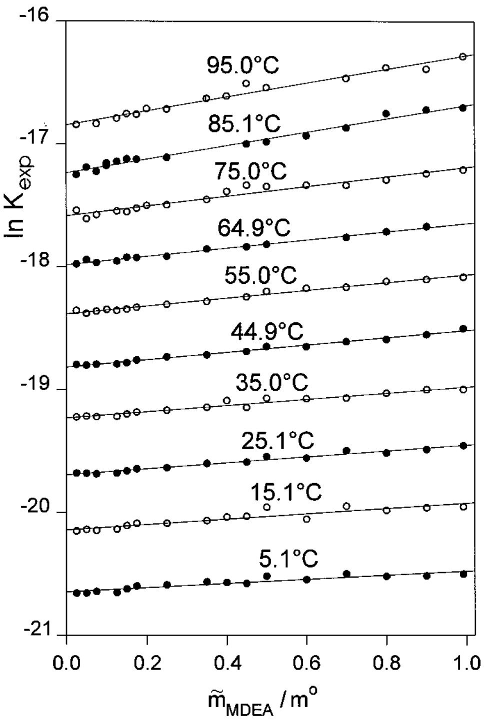

Figure 2. Influence of the overall molality of MDEA on the experimental results for ln K_{exp}.

Table 2. Extrapolated Experimental Results for the Dissociation Constant of MDEAH$^+$

$\bar{t}$/°C	10^9K	$\pm\bar{\Delta}K$/%
5.12	1.080	1.65
15.09	1.787	2.03
25.08	2.798	1.03
35.00	4.454	1.18
44.94	6.740	0.89
54.98	10.40	0.97
64.94	15.52	0.88
75.00	23.13	2.39
85.09	32.82	2.13
94.95	48.41	2.13

Substances. MDEA (Merck Schuchardt, *N*-methyl-2,2′-iminodiethanol for synthesis, purity 98.4 mass % according to analyze certification (GC), water content less than 0.2 mass %, other impurities unknown) and HCl (Merck, HCl Ultrapur) were used without further purification. Water was deionized and further purified by vacuum distillation. HCl stock solutions were gravimetrically analyzed with a relative uncertainty of ±0.05%.

Results

Measurements were performed from 278 K to 368 K at 10 K intervals. The overall molality of HCl in both cells was held constant in all solutions ($\tilde{m}_{\mathrm{HCl,I}} \approx \tilde{m}_{\mathrm{HCl,II}} \approx 0.01$ mol/kg). The overall molality of MDEA was between 0.025 mol/kg and 1 mol/kg. The experimental results for the EMF-measurements $E_{\mathrm{I}}(T,\tilde{m}_{\mathrm{HCl,I}})$ and $E_{\mathrm{II}}(T,\tilde{m}_{\mathrm{MDEA}},\tilde{m}_{\mathrm{HCl,II}})$ are given in Table 1 together with the preliminary (i.e. not extrapolated) numbers for the dissociation constant of MDEAH$^+$ (K_{exp}). In Figure 2, ln K_{exp} is plotted against the overall molality of MDEA. Extrapolations were done by linear regression. In Table 1 superscript * denotes results

Table 3. Comparison of Correlated Values with Literature Data

	10^9K				
T/K	this work	Schwabe et al. (1959)	Kim et al. (1987)	Oscarson et al. (1989)	Littel et al. (1990)
293.0	2.21 ± 0.03				1.74 ± 0.08
298.15	2.81 ± 0.03	3.07	3.02 ± 0.24		
298.2	2.82 ± 0.03			2.76 ± 0.20	
299.9	3.05 ± 0.03			2.99 ± 0.21	
303.0	3.51 ± 0.04				3.25 ± 0.15
308.15	4.42 ± 0.05	4.89			
311.0	5.01 ± 0.06			5.00 ± 0.36	
318.0	6.78 ± 0.06				5.30 ± 0.25
318.15	6.82 ± 0.06	7.57			
333.0	12.62 ± 0.12				10.4 ± 0.5
333.15	12.70 ± 0.12	13.8			
333.2	12.73 ± 0.12			12.9 ± 0.9	
361.0	37.06 ± 0.79			38.0 ± 2.7	
388.0	95.8[a]			97.9 ± 7.0	
422.1	286.4[a]			287.5 ± 20.6	

[a] Extrapolated values.

Table 4. Comparison of Reaction Standard State Properties with Literature Data

	this work	Schwabe et al. (1959)	Kim et al. (1987)	Oscarson et al. (1989)
$\Delta_r G_m^\circ$/(kJ/mol)	48.81 ± 0.03	48.59 ± 0.17	48.63 ± 0.17	48.86 ± 0.18
$\Delta_r H_m^\circ$/(kJ/mol)	34.0	35.7	35.2 ± 0.3	35.2 ± 1.0
$\Delta_r S_m^\circ$/(J/(mol·K))	−49.6	−43.2	−45.1 ± 1.6	−45.8 ± 4.0
$\Delta_r C_{P,m}^\circ$/(J/(mol·K))	91.3			73.3

of experiments where temperature deviated by more than ±0.15 K from the corresponding isotherm. Those results were not considered in the extrapolation and are not shown in Figure 2. Average temperatures ($\bar{t}$) and chemical equilibrium constants as resulting from the linear extrapolation (K) are given in Table 2. Additionally, the relative deviation ($\pm\bar{\Delta}K$) is given in Table 2. It represents the average deviation between the direct experimental data and the linear fit and thus provides insight into the quality of the extrapolation. $\bar{\Delta}K$ is predominantly below 2% and at maximum smaller than 2.4%. The final results for the chemical equilibrium constant (on molality scale) are correlated by

$$\ln K = \frac{-819.7}{(T/\mathrm{K})} - 79.474 + 10.9756 \ln(T/\mathrm{K}) \quad (12)$$

with an average deviation of 0.9% (0.004) and a maximum deviation of 2% (0.009) in K (pK). Those deviations have to be compared with the experimental uncertainty. The scattering of the results for K_{exp} is due to uncertainties in $E_{\mathrm{I}} - E_{\mathrm{II}}$ of about ±0.5 mV. A systematic error can result from impurities in MDEA. In the evaluation of the extrapolated data no impurities were taken into account. However, when MDEA samples are treated as a mixture of 98.4 mass % of MDEA and 1.6 mass % of water, the numerical values for K are reduced by about 2%.

Comparison with Literature Data

Experimental results for the chemical equilibrium constant for the dissociation of $\mathrm{MDEAH^+}$ have been reported by Schwabe et al. (1959) at temperatures between 298.15 K and 333.15 K, Kim et al. (1987) at 298.15 K, Oscarson et al. (1989) at temperatures between 298.2 K and 422.1 K, and Littel et al. (1990) at temperatures between 293 K and 333 K. The results of Schwabe et al., Oscarson et al., and Littel et al. are based on a different reference state (using molarity scale). They were converted to the reference state used in the present work by

$$K = \frac{1}{\rho_W}\left(\frac{c^\circ}{m^\circ}\right)K_c \quad (13)$$

where ρ_W is the mass density of pure water which was taken from Saul and Wagner (1987). In Table 3 correlated values from the present work, including experimental uncertainties, are compared with literature data. For the results by Schwabe et al. experimental uncertainties were estimated to $\Delta pK \approx \pm 0.03$. Kim et al. give $\Delta pK = \pm 0.03$. Oscarson et al. give $\Delta pK = \pm 0.03$ at 298.2 K. Littel et al. give $\Delta pK = \pm 0.02$. Figure 3 shows chemical equilibrium constants from the present work in comparison with literature data. Values from the present work agree with the results of Schwabe et al. within about 10%; however, there is a systematic deviation as the results by Schwabe et al. are always larger than those from the present work. The value reported by Kim et al. agrees very well with the value of Schwabe et al. The data reported by Littel et al. are always smaller than those from the present work. The differences scatter from about 7% up to 22%. The results of the present work are in excellent agreement with the results by Oscarson et al. Differences are within the experimental uncertainties given by Oscarson et al., also at temperatures above 368 K, where the results of the present work are extrapolated. Applying the well-known thermodynamic relations:

$$\Delta_r G_m = -RT \ln K \quad (14)$$

$$\Delta_r H_m = -R\,\frac{\mathrm{d} \ln K}{\mathrm{d}(1/T)} \quad (15)$$

$$\Delta_r S_m = (\Delta_r H_m - \Delta_r G_m)/T \quad (16)$$

$$\Delta_r C_{P,m} = \frac{\mathrm{d}\Delta_r H_m}{\mathrm{d}T} \quad (17)$$

the change of standard state properties ($T = T^\circ = 298.15$ K) for the dissociation of $\mathrm{MDEAH^+}$ in water were calculated from eq 12 resulting in $\Delta_r G_m^\circ = 48.81$ kJ/mol, $\Delta_r H_m^\circ = 34.0$ kJ/mol, $\Delta_r S_m^\circ = -49.6$ J/(mol·K), $\Delta_r C_{P,m} = \mathrm{const.} = 91.3$

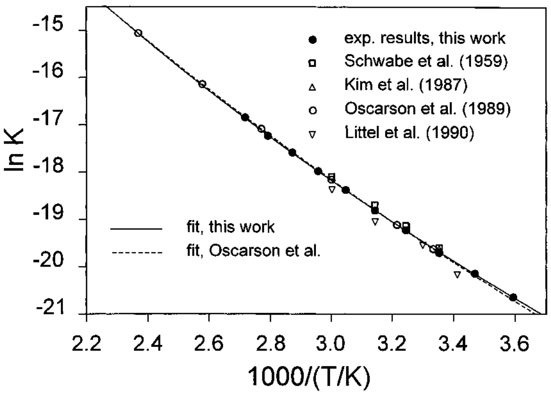

Figure 3. Dissociation constant of MDEAH$^+$.

J/(mol·K). These standard state properties are compared to literature data in Table 4. For that comparison the experimental results for the equilibrium constant of Schwabe et al. and of Oscarson et al. were approximated by

Schwabe et al.

$$\ln K = \frac{-4794.1}{(T/\mathrm{K})} + 6.018 - 1.6744 \ln(T/\mathrm{K}) \quad (18)$$

Oscarson et al.

$$\ln K = \frac{-1609.2}{(T/\mathrm{K})} - 64.506 + 8.8096 \ln(T/\mathrm{K}) \quad (19)$$

As can be seen from Table 4 numbers for $\Delta_r G_m^\circ$ and $\Delta_r H_m^\circ$ from all sources nearly agree within the sum of experimental uncertainties with the results of the present work. The number for $\Delta_r S_m^\circ$ from the present work favorably agrees with the result from Oscarson et al., while, as was to be expected, the largest deviation is observed for $\Delta_r C_{P,m}$. However, considering the experimental uncertainies the agreement with the $\Delta_r C_{P,m}$ results from the work of Oscarson et al. still seems to be reasonable.

Conclusions

The chemical equilibrium constant for the dissociation of MDEAH$^+$ in aqueous solution was determined from EMF measurements at temperatures from 278 K to 368 K. The results extend the temperature region of literature data which ranges from about 293 K to 422 K. New data agree best with the results reported by Oscarson et al. (1989). Differences between both sources are within the experimental uncertainties reported by those authors.

Nomenclature

a_i = activity of component i
A_φ = Debye–Hückel parameter
b = constant in modified Debye–Hückel expression
B_{ij} = second virial coefficient in Pitzer's equation (for interactions between species i and j)
c° = reference molarity ($c^\circ = 1$ mol/L)
C_{ijk} = third virial coefficient in Pitzer's equation (for interactions between species i, j, and k)
C^Φ = see eq 32
C_P = heat capacity
e = charge of proton
E = electromotive force
E° = standard potential
f = modified Debye–Hückel term
F = Faraday constant
G = Gibbs energy
H = enthalpy
I_m = ionic strength (on molality scale)
k = Boltzmann constant
K = equilibrium constant for the dissociation reaction of MDEAH$^+$
K_W = equilibrium constant for the dissociation reaction of water
m_i = true molality of component i
$\tilde{m}_i$ = overall molality of component i
m° = reference molality ($m^\circ = 1$ mol/kg)
M_W = molar mass of water in g/mol
M_W^* = see eq 21
n_i = true number of moles of component i
$\tilde{n}_i$ = overall number of moles of component i
N_A = Avogadro constant
p$K = -\log_{10} K$
$Q_1, ..., Q_5$ = coefficients for the temperature dependence of the H$^+$/Cl$^-$ interaction parameters
R = universal gas constant
S = entropy
t = Celsius temperature
T = absolute temperature
z_i = number of charges of component i

Greek Letters

α = constant in B_{ij} expression
$\beta_{ij}^{(0)}$, $\beta_{ij}^{(1)}$ = binary interaction parameters in Pitzer's equation
Δ = difference
Δ_r = molar reaction change
ϵ_0 = vacuum permittivity
ϵ_W = relative dielectric constant of water
$\gamma_{i,m}^*$ = activity coefficient of component i normalized to infinite dilution (on molality scale)
μ_i = chemical potential of component i
ν^+, ν^- = number of cations and anions in electrolyte MX
ρ_W = saturated liquid mass density of pure water

Subscripts

c = on molarity scale
exp = experimental
i, j, k = component i, j, k
m = on molality scale
r = reaction
I, II = cell I, cell II

Superscripts

E = excess
* = normalized to infinite dilution
∞ = infinite dilution in pure water
° = reference state, standard state

Abbreviations

aq = in aqueous solution
EMF = electromotive force
liq = liquid
MDEA = n-methyldiethanolamine
MX = general electrolyte
M = cation M
X = anion X
s = solid
W = water

Appendix 1. Brief Outline of Pitzer's Model

Pitzer's equation (1973) for the excess Gibbs energy of an aqueous, salt-containing system is

$$\frac{G^{\mathrm{E}}}{n_{\mathrm{W}}RTM_{\mathrm{W}}^{*}} = f(I_m) + \sum_{i\neq \mathrm{W}}\sum_{j\neq \mathrm{W}}\frac{m_i}{m^\circ}\frac{m_j}{m^\circ}B_{ij}(I_m) + \sum_{i\neq \mathrm{W}}\sum_{j\neq \mathrm{W}}\sum_{k\neq \mathrm{W}}\frac{m_i}{m^\circ}\frac{m_j}{m^\circ}\frac{m_k}{m^\circ}C_{ijk} \quad (20)$$

where M_{W}^{*} is defined as

$$M_{\mathrm{W}}^{*} = \frac{M_{\mathrm{W}}m^\circ}{1000\,\frac{\mathrm{g}}{\mathrm{kg}}} \quad (21)$$

The function $f(I_m)$ is a modified Debye–Hückel term:

$$f(I_m) = -A_\varphi\frac{4I_m}{b}\ln(1 + b\sqrt{I_m}) \quad (22)$$

where I_m is the ionic strength:

$$I_m = \frac{1}{2}\sum_i {z_i}^2\left(\frac{m_i}{m^\circ}\right) \quad (23)$$

and $b = 1.2$. A_φ is the Debye–Hückel parameter for the osmotic coefficient:

$$A_\varphi = \frac{1}{3}\sqrt{2\pi N_{\mathrm{A}}\rho_{\mathrm{W}}m^\circ}\left(\frac{e^2}{4\pi\epsilon_0\epsilon_{\mathrm{W}}kT}\right)^{1.5} \quad (24)$$

ϵ_{W} is the relative dielectric constant of water and was taken from Bradley and Pitzer (1979). $B_{ij}(I_m)$ is the ionic strength dependent second virial coefficient:

$$B_{ij}(I_m) = \beta_{ij}^{(0)} + \frac{2}{\alpha^2 I_m}\beta_{ij}^{(1)}[1 - (1 + \alpha\sqrt{I_m})\exp(-\alpha\sqrt{I_m})] \quad (25)$$

where $\beta_{ij}^{(0)}$ and $\beta_{ij}^{(1)}$ are binary interaction parameters. For the case considered here, $\alpha = 2.0$. C_{ijk} are ternary interaction parameters.

The chemical potential of each dissolved species is normalized to infinite dilution in pure water on the molality scale:

$$\mu_i = \mu_{i,m}^{\infty}(T,p) + RT\ln a_i \quad (26)$$

where

$$a_i = \frac{m_i}{m^\circ}\gamma_{i,m}^{*} \quad (27)$$

The chemical potential of water is normalized to the pure liquid substance:

$$\mu_{\mathrm{W}} = \mu_{\mathrm{W}}^{\mathrm{pure}}(T,p)_{\mathrm{liq}} + RT\ln a_{\mathrm{W}} \quad (28)$$

The activity coefficient of a dissolved species i is:

$$\ln\gamma_{i,m}^{*} = -A_\varphi {z_i}^2\left[\frac{\sqrt{I_m}}{1 + b\sqrt{I_m}} + \frac{2}{b}\ln(1 + b\sqrt{I_m})\right] + 2\sum_{j\neq \mathrm{W}}\frac{m_j}{m^\circ}B_{ij}(I_m) - \frac{{z_i}^2}{\alpha^2 {I_m}^2}\left[1 - \left(1 + \alpha\sqrt{I_m} + \frac{\alpha^2}{2}I_m\right)\times \exp(-\alpha\sqrt{I_m})\right]\sum_{j\neq \mathrm{W}}\sum_{k\neq \mathrm{W}}\frac{m_j}{m^\circ}\frac{m_k}{m^\circ}\beta_{jk}^{(1)} + 3\sum_{j\neq \mathrm{W}}\sum_{k\neq \mathrm{W}}\frac{m_j}{m^\circ}\frac{m_k}{m^\circ}C_{ijk} \quad (29)$$

The activity of water follows from the Gibbs–Duhem equation:

$$\ln a_{\mathrm{W}} = M_{\mathrm{W}}^{*}\left\{2A_\varphi\frac{{I_m}^{1.5}}{1 + b\sqrt{I_m}} - \sum_{i\neq \mathrm{W}}\sum_{j\neq \mathrm{W}}\frac{m_i}{m^\circ}\frac{m_j}{m^\circ}[\beta_{ij}^{(0)} + \beta_{ij}^{(1)}\times \exp(-\alpha\sqrt{I_m})] - 2\sum_{i\neq \mathrm{W}}\sum_{j\neq \mathrm{W}}\sum_{k\neq \mathrm{W}}\frac{m_i}{m^\circ}\frac{m_j}{m^\circ}\frac{m_k}{m^\circ}C_{ijk} - \sum_{i\neq \mathrm{W}}\frac{m_i}{m^\circ}\right\} \quad (30)$$

Appendix 2. Interaction Parameters for Pitzer's Equation

The following section reports relations for the temperature dependence of ion interaction parameters H^+/Cl^- (Pitzer, 1987). T is the temperature in Kelvin and $T_{\mathrm{R}} = 298.15$ K. p is the pressure in bars and is set to 1. ρ is the mass density of pure water at the particular p and T (in kg/m^3). In the present work, ρ was set equal to the saturated liquid density of pure water (ρ_{W}).

$$f(T) = Q_1 + Q_2\ln(\rho/997) + Q_3(\rho - 997) + Q_4(T - T_{\mathrm{R}}) + Q_5(p - 1) \quad (31)$$

	$\beta^{(0)}_{\mathrm{H^+,Cl^-}}$	$\beta^{(1)}_{\mathrm{H^+,Cl^-}}$	C^{Φ}
Q_1	0.176 90	0.2973	0.724×10^{-3}
Q_2	-9.140×10^{-2}	16.147	0
Q_3	0	-1.7631×10^{-2}	0
Q_4	-4.034×10^{-4}	0	-6.072×10^{-5}
Q_5	6.20×10^{-6}	7.20×10^{-5}	0

For systems containing a single general electrolyte $\mathrm{M}_{\nu^+}\mathrm{X}_{\nu^-}$, the binary and ternary parameters involving two or more species of the same sign of charge are usually neglected. The ternary parameters $C_{\mathrm{M,X,X}}$ and $C_{\mathrm{M,M,X}}$ are usually reported as third virial coefficients C^{Φ} for the osmotic coefficient. Instead of rewriting eqs 29 and 30 in terms of C^{Φ}, we preferred to set $C_{\mathrm{M,X,X}}$ to zero and calculated the ternary parameters $C_{\mathrm{M,M,X}}$ from numbers reported for C^{Φ}:

$$C_{\mathrm{H^+,H^+,Cl^-}} = \frac{1}{3}C^{\Phi} \quad (32)$$

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