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Dissociation Constants and Thermodynamic Properties of Amines and Alkanolamines from (293 to 353) K

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The dissociation constants of protonated 2-amino-2-ethyl-1,3-propanediol, 2-amino-2-methyl-1-propanol, diethylmonoethanolamine, diisopropanolamine, dimethylmonoethanolamine, monoethanolamine, 1-amino-2-propanol, methylmonoethanolamine, triethanolamine, and the first and the second dissociation constants of piperazine and hydroxyethylpiperazine have been determined by electromotive force measurements from (293 to 353) K. The dissociation constants of protonated triethylamine have been determined with the same technique from (293 to 333) K. The experimental results and derived values of the standard state thermodynamic properties are reported and compared to available literature values.

Introduction

Aqueous solutions of (alkanol)amines are frequently used for the removal of acid gases, such as CO_2 and H_2S, from a variety of gas streams. The dissociation constant is one of the important factors in the selection of an (alkanol)amine solution for acid gas removal or in the interpretation of the kinetic mechanism of the absorption of the acid gas in the (alkanol)amine solution.[1] Dissociation constants can provide the following information: (1) a measure of the basic strength of the (alkanol)amine at a specific temperature and (2) a conventional acid gas removal plant is operated with an absorption/desorption cooling/heating cycle. In the absorber, the acid gas is (chemically) absorbed by the basic absorbent. At an elevated temperature in the desorber, the basic strength of the absorbent is reduced and the acid gas released. The basic strength is reduced as a result of less dissociation of the unprotonated absorbent at higher temperatures. Temperature-dependent dissociation constants provide the change in the reaction enthalpy which indicates the change of the basic strength of the absorbent within a given temperature range.

The dissociation constants of protonated 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), diethylmonoethanolamine (DEMEA), diisopropanolamine (DIPA), dimethylmonoethanolamine (DMMEA), monoethanolamine (MEA), 1-amino-2-propanol (MIPA), methylmonoethanolamine (MMEA), triethanolamine (TEA), and the first and the second dissociation constants of piperazine (PZ) and hydroxyethylpiperazine (HEPZ) have been determined in this work by electromotive force measurements from (293 to 353) K. The dissociation constants of protonated triethylamine (TREA) have been determined with the same technique from (293 to 333) K. The results from the current work extend the temperature range of available literature values for the compounds investigated. For some of the compounds, no literature values were found, and the current work provides these values.

Theory and Experimental Procedure

The theory and experimental procedure behind the measurements of dissociation constants of an (alkanol)amine have been given in detail elsewhere.[2] Measurements of the first and second dissociation constant of diamines are carried out in a similar manner. A protonated diamine dissociates according to

$$NH_3^+ - R - NH_3^+ + H_2O \rightleftharpoons NH_2 - R - NH_3^+ + H_3O^+ \tag{1}$$

$$NH_2 - R - NH_3^+ + H_2O \rightleftharpoons NH_2 - R - NH_2 + H_3O^+ \tag{2}$$

The equilibrium constants can be determined by electromotive force (EMF) measurements using a combined glass pH electrode.[2−4] By the use of this method, a two-cell system was used

$$\text{Ag(s), AgCl(s)} \mid 3\text{ M KCl(aq)} \parallel \text{HCl(aq, } \bar{m}_{\text{HCl}}) \parallel \text{Glass Electrode} \quad \text{(I)}$$

and

$$\text{Ag(s), AgCl(s)} \mid 3\text{ M KCl(aq)} \parallel \text{HCl(aq, } \bar{m}_{\text{HCl}})\ldots \; NH_2 - R - NH_2(\text{aq, } \bar{m}_{NH_2-R-NH_2}) \parallel \text{Glass Electrode} \quad \text{(II)}$$

The activity of a pure solid was set to unity, and the Nernst equation for cell (I) resulted in

$$E_I = E^\circ(T_I) - \frac{RT_I}{F}\ln(a_{H_3O^+}a_{Cl^-})_I \tag{3}$$

and for cell (II)

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$$E_{\mathrm{II}} = E^{\circ}(T_{\mathrm{II}}) - \frac{RT_{\mathrm{II}}}{F}\ln(a_{\mathrm{H_3O^+}}a_{\mathrm{Cl^-}})_{\mathrm{II}} \tag{4}$$

Both cells were kept at the same temperature, $T_{\mathrm{I}} = T_{\mathrm{II}}$, thus the standard potentials were equal, $E^{\circ}(T_{\mathrm{I}}) = E^{\circ}(T_{\mathrm{II}})$

$$T_{\mathrm{II}}\ln(a_{\mathrm{H_3O^+}}a_{\mathrm{Cl^-}})_{\mathrm{II}} = \frac{F(E_{\mathrm{I}} - E_{\mathrm{II}})}{R} + T_{\mathrm{I}}\ln(a_{\mathrm{H_3O^+}}a_{\mathrm{Cl^-}})_{\mathrm{I}} \tag{5}$$

As HCl was assumed to be completely dissociated, the dissociation of water could be neglected in cell (I). For the determination of the first dissociation constants of a diamine, the mass balances of the diamine, HCl, and water in cell (II) were

$$\bar{n}_{\mathrm{NH_2-R-NH_2}} = n_{\mathrm{NH_2-R-NH_2}} + n_{\mathrm{NH_2-R-NH_3^+}} \tag{6}$$

$$\bar{n}_{\mathrm{HCl}} = n_{\mathrm{Cl^-}} \tag{7}$$

$$\bar{n}_{\mathrm{H_2O}} = n_{\mathrm{H_2O}} + n_{\mathrm{H_3O^+}} + n_{\mathrm{OH^-}} \tag{8}$$

Electroneutrality resulted in

$$n_{\mathrm{NH_2-R-NH_3^+}} + n_{\mathrm{H_3O^+}} = n_{\mathrm{Cl^-}} + n_{\mathrm{OH^-}} \tag{9}$$

The chemical equilibrium conditions for the water dissociation and the first dissociation were

$$K_{\mathrm{w}}(T) = \frac{a_{\mathrm{H_3O^+}}a_{\mathrm{OH^-}}}{a^2_{\mathrm{H_2O}}} \tag{10}$$

$$K_1(T) = \frac{a_{\mathrm{NH_2-R-NH_2}}a_{\mathrm{H_3O^+}}}{a_{\mathrm{NH_2-R-NH_3^+}}a_{\mathrm{H_2O}}} \tag{11}$$

In the case of measurements of the second dissociation constant, eqs 6 to 11 were changed to describe cell (II)

$$\bar{n}_{\mathrm{NH_2-R-NH_2}} = n_{\mathrm{NH_2-R-NH_3^+}} + n_{\mathrm{NH_3^+-R-NH_3^+}} \tag{12}$$

$$\bar{n}_{\mathrm{HCl}} = n_{\mathrm{Cl^-}} \tag{13}$$

$$\bar{n}_{\mathrm{H_2O}} = n_{\mathrm{H_2O}} + n_{\mathrm{H_3O^+}} + n_{\mathrm{OH^-}} \tag{14}$$

$$n_{\mathrm{NH_2-R-NH_3^+}} + 2n_{\mathrm{NH_3^+-R-NH_3^+}} + n_{\mathrm{H_3O^+}} = n_{\mathrm{Cl^-}} + n_{\mathrm{OH^-}} \tag{15}$$

$$K_{\mathrm{w}}(T) = \frac{a_{\mathrm{H_3O^+}}a_{\mathrm{OH^-}}}{a^2_{\mathrm{H_2O}}} \tag{16}$$

The chemical equilibrium condition for the second dissociation was

$$K_2(T) = \frac{a_{\mathrm{NH_2-R-NH_3^+}}a_{\mathrm{H_3O^+}}}{a_{\mathrm{NH_3^+-R-NH_3^+}}a_{\mathrm{H_2O}}} \tag{17}$$

For a given temperature and composition, the electromotive forces E_{I} and E_{II} and the temperature in each cell were measured. Activities of HCl and KCl were estimated using the excess energy model of Pitzer from Holmes et al.[5] and Pabalan and Pitzer,[6] respectively. A very brief outline of the excess energy model of Pitzer used in this work is given in Appendix A. Activities of HCl and the diamine in cell (II) were approximated using only the modified Debye−Hückel term in Pitzer's equation, i.e., neglecting binary and ternary parameters. The activity coefficient of the nonprotonated structure of the diamine was set to unity for all molalities and temperatures. The activity of water followed from the Gibbs−Duhem equation. The influence of pressure on the chemical reactions was neglected and set to 1 bar during the described calculations. The changes in the compositions of the electrolyte cells due to the outflow of KCl electrolyte from the electrode were neglected. The water dissociation constant, $K_{\mathrm{W}}(T)$, was taken from Fisher and Barnes.[7] With the given information, eqs 5 to 17 were solved iteratively to yield the "true" number of moles of each species present in cell (II), as well as a preliminary value of the dissociation constant of the diamine. This dissociation constant was called preliminary because it was calculated out of a set of equations in which for cell (II) the activities were not exactly known. The experiments were performed at different overall molalities, and the true equilibrium constant of the dissociation of a diamine was determined by a linear extrapolation procedure

$$\lim_{\substack{\bar{m}_{\mathrm{HCl,II}}\to 0\\ \bar{m}_{\mathrm{NH_2-R-NH_2}}\to 0}} [K_{\eta,\mathrm{exptl}}(T, \bar{m}_{\mathrm{NH_2-R-NH_2}}, \bar{m}_{\mathrm{HCl,II}})] = K_{\eta}(T) \tag{18}$$

where η is equal to 1 for the determination of the first dissociation constant and equal to 2 for the determination of the second dissociation constant.

Thermodynamic Relations

To the experimentally determined dissociation constants, the well-known thermodynamic relations were applied

$$\Delta_{\mathrm{r}}G_{\mathrm{m}} = -RT\ln K \tag{19}$$

$$\Delta_{\mathrm{r}}H_{\mathrm{m}} = -R\frac{d\ln K}{d(1/T)} \tag{20}$$

and the change of standard state properties ($T = T^{\circ} = 298.15$ K) for the dissociation of an (alkanol)amine in water was calculated from eqs 19 and 20 by the use of[8]

$$\ln K_i = \frac{A}{T} + B + C\ln(T) \tag{21}$$

where $i = 0$ for protonated AEPD, AMP, DEMEA, DIPA, DMMEA, MEA, MIPA, MMEA, TEA, and TREA; $i = 1$ for the first dissociation constant of PZ and HEPZ; and $i = 2$ for the second dissociation constant of PZ and HEPZ. The further thermodynamic relations can be calculated by the reader

$$\Delta_r S_m = \frac{(\Delta_r H_m - \Delta_r G_m)}{T} \qquad (22)$$

$$\Delta_r C_{P,m} = \frac{d\Delta_r H_m}{dT} \qquad (23)$$

Experimental

The experimental setup used was similar to the setup described by Hamborg et al.[2] Measurements were performed from (293 to 353) K at 10 K intervals and at 298 K. The overall molality of HCl in cell (I) and cell (II) was held constant ($\bar{m}_{\text{HCl,I}} = \bar{m}_{\text{HCl,II}} \approx 0.01$ mol·kg^{-1}). The molality of the amine was varied between (0.0167 and 0.2941) mol·kg^{-1}. For measurements of the diamines, the molality of HCl and the diamine in cell (II) varied from (0.0105 to 0.1017) mol·kg^{-1} and (0.0065 to 0.2279) mol·kg^{-1}, respectively. Measurements where the temperature in cell (I) and in cell (II) deviated by more than ± 0.1 K were not considered in the described calculations.

Chemicals. AEPD [115-70-8], AMP [124-68-5], DEMEA [100-37-8], DIPA [110-97-4], DMMEA [108-01-0], MEA [141-43-5], MIPA [78-96-6], MMEA [109-83-1], TEA [102-71-6], TREA [121-44-8], PZ [110-85-0], HEPZ [103-76-4], and HCl [7647-01-0] were used as supplied. HCl was provided as 0.1 M standard solutions and was diluted to the desired molality and checked by means of titration. Water was demineralized and further purified by vacuum distillation.

Table 1. Comparison of Correlated Values of the Dissociation Constant, ln(*K*), of AMP at Different Temperatures, *T*, and Thermodynamic Properties with Literature Values

T/K	this work	Littel et al.[9]
	ln(K)/−	
293.00	−22.65[a]	−22.75
303.00	−21.95	−21.92
318.00	−20.96	−21.17
333.00	−20.04	−20.20
$\Delta_r G^\circ_m/\text{kJ}\cdot\text{mol}^{-1}$	55.24	
$\Delta_r H^\circ_m/\text{kJ}\cdot\text{mol}^{-1}$	52.2	

[a] Extrapolated value.

Table 2. Comparison of Correlated Values of the Dissociation Constant, ln(*K*), of DEMEA at Different Temperatures, *T*, and Thermodynamic Properties with Literature Values

T/K	this work	Littel et al.[9]
	ln(K)/−	
293.00	−22.70[a]	−22.47
303.00	−22.21	−21.80
318.00	−21.48	−21.08
333.00	−20.77	−20.04
$\Delta_r G^\circ_m/\text{kJ}\cdot\text{mol}^{-1}$	55.64	
$\Delta_r H^\circ_m/\text{kJ}\cdot\text{mol}^{-1}$	36.2	

[a] Extrapolated value.

Table 3. Comparison of Correlated Values of the Dissociation Constant, ln(*K*), of DIPA at Different Temperatures, *T*, and Thermodynamic Properties with Literature Values

T/K	this work	Blauwhoff & Bos[10]	Kim et al.[17]	Sharma[18]
		ln(K)/−		
293.00	−20.64[a]	−21.37		
298.15	−20.36		−20.45	−21.87
303.00	−20.11	−20.81		
313.00	−19.59	−20.23		
323.00	−19.10	−19.65		
$\Delta_r G^\circ_m/\text{kJ}\cdot\text{mol}^{-1}$	50.47		50.69	
$\Delta_r H^\circ_m/\text{kJ}\cdot\text{mol}^{-1}$	39.2		42.7	

[a] Extrapolated value.

Table 4. Comparison of Correlated Values of the Dissociation Constant, ln(*K*), of DMMEA at Different Temperatures, *T*, and Thermodynamic Properties with Literature Values

T/K	this work	Littel et al.[9]
	ln(K)/−	
293.00	−21.47[a]	−21.25
303.00	−21.01	−20.70
318.00	−20.33	−20.00
333.00	−19.68	−19.23
$\Delta_r G^\circ_m/\text{kJ}\cdot\text{mol}^{-1}$	52.63	
$\Delta_r H^\circ_m/\text{kJ}\cdot\text{mol}^{-1}$	34.4	

[a] Extrapolated value.

Table 5. Comparison of Correlated Values of the Dissociation Constant, ln(*K*), of MEA at Different Temperatures, *T*, and Thermodynamic Properties with Literature Values

T/K	this work	Bates & Pinching[19]	Kim et al.[17]	Antelo et al.[11]
		ln(K)/−		
273.15	−23.52[a]	−23.73		
278.15	−23.14[a]	−23.33		
283.15	−22.78[a]	−22.95		
288.15	−22.42[a]	−22.57		
293.15	−22.08	−22.21		
298.15	−21.74	−21.87	−21.90	−22.08
303.15	−21.42	−21.53		
308.15	−21.10	−21.20		
313.15	−20.80	−20.88		
318.15	−20.50	−20.59		
323.15	−20.21	−20.29		
$\Delta_r G^\circ_m/\text{kJ}\cdot\text{mol}^{-1}$	53.90	54.20	54.23	
$\Delta_r H^\circ_m/\text{kJ}\cdot\text{mol}^{-1}$	48.6	50.5	50.5	

[a] Extrapolated value.

Table 6. Comparison of Correlated Values of the Dissociation Constant, ln(*K*), of MMEA at Different Temperatures, *T*, and Thermodynamic Properties with Literature Values

T/K	this work	Littel et al.[9]
	ln(K)/−	
293.00	−22.98[a]	−22.91
303.00	−22.38	−22.19
318.00	−21.53	−21.52
333.00	−20.72	−20.57
$\Delta_r G^\circ_m/\text{kJ}\cdot\text{mol}^{-1}$	56.20	
$\Delta_r H^\circ_m/\text{kJ}\cdot\text{mol}^{-1}$	44.4	

[a] Extrapolated value.

Results and Discussion

Experimental results at averaged temperatures for the dissociation constants of protonated AEPD, AMP, DEMEA, DIPA, DMMEA, MEA, MIPA, MMEA, TEA, TREA, and the first and second dissociation constant of protonated PZ and HEPZ are given in Table 16 in Appendix B with experimental uncertainties. The experimental uncertainties are due to inaccuracies in E_I and E_{II} of ± 0.5 mV. The results are also given with the average and maximum relative

Table 7. Comparison of Correlated Values of the Dissociation Constant, ln(*K*), of TEA at Different Temperatures, *T*, and Thermodynamic Properties with Literature Values

T/K	this work	Bates & Allen[20]	Bates & Schwarzenbach[21]	Kim et al.[17]	Antelo et al.[11]
			ln(K)/−		
273.15	−18.89[a]	−19.09			
278.15	−18.66[a]	−18.82			
283.15	−18.43[a]	−18.58			
288.15	−18.21[a]	−18.34			
293.15	−17.99	−18.10	−18.12		
298.15	−17.78	−17.87	−17.89	−17.96	−18.05
303.15	−17.57	−17.65	−17.68		
308.15	−17.36	−17.43			
313.15	−17.16	−17.22			
318.15	−16.96	−17.01			
323.15	−16.77	−16.81			
$\Delta_r G_m^\circ$/kJ·mol^{-1}	44.07	44.31		44.31	
$\Delta_r H_m^\circ$/kJ·mol^{-1}	31.3	33.5		34.0	

[a] Extrapolated value.

Table 8. Comparison of Correlated Values of the Dissociation Constant, ln(*K*), of TREA at Different Temperatures, *T*, and Thermodynamic Properties with Literature Values

T/K	this work	Cox et al.[22]	Campbell & Lam[12]	Ablard et al.[13]	Fyfe[14]	Bergström & Olofsson[23]
			ln(K)/−			
273.15	−26.21[a]	−26.20				
278.15	−25.89[a]					−25.87
283.15	−25.57[a]	−25.59				
290.15	−25.13[a]	−17.43	−25.25			
293.15	−24.95	−24.98			−24.82	
298.15	−24.64	−24.68		−25.02	−24.57	−24.67
303.15	−24.34	−24.38				
308.15	−24.05				−24.06	
313.15	−23.76	−23.80		−24.08		
318.15	−23.48				−23.50	
323.15	−23.20	−23.24		−23.50		−23.28
348.15	−21.87[a]					−22.00
$\Delta_r G_m^\circ$/kJ·mol^{-1}	61.08	61.21			60.92	
$\Delta_r H_m^\circ$/kJ·mol^{-1}	44.4	44.3			40.6	43.1

[a] Extrapolated value.

Table 9. Comparison of Correlated Values of the First Dissociation Constant, ln(K_1), of PZ at Different Temperatures, *T*, and Thermodynamic Properties with Literature Values

T/K	this work	Hetzer et al.[24]	Pagano et al.[25]	Enea et al.[15]
		ln(K_1)/−		
273.15	−13.63[a]	−13.39		
278.15	−13.38[a]	−13.15		
283.15	−13.14[a]	−12.93	−13.47	
288.15	−12.90[a]	−12.71		
293.15	−12.68	−12.49	−12.96	−13.48
298.15	−12.45	−12.28		−13.26
303.15	−12.24	−12.08	−12.76	−13.05
308.15	−12.03	−11.87		−12.84
313.15	−11.83	−11.66	−12.36	−12.59
318.15	−11.63	−11.47		
323.15	−11.43	−11.27		
$\Delta_r G_m^\circ$/kJ·mol^{-1}	30.87			32.95
$\Delta_r H_m^\circ$/kJ·mol^{-1}	32.3	31.1	26.0[b]	31.8

[a] Extrapolated value. [b] Average value given, (283.15 to 313.15) K.

Table 10. Comparison of Correlated Values of the Second Dissociation Constant, ln(K_2), of PZ at Different Temperatures, *T*, and Thermodynamic Properties with Literature Values

T/K	this work	Hetzer et al.[24]	Pagano et al.[25]	Enea et al.[15]
		ln(K_2)/−		
273.15	−23.92[a]	−23.96		
278.15	−23.59[a]	−23.62		
283.15	−23.27[a]	−23.32	−23.30	
288.15	−22.96[a]	−23.02		
293.15	−22.66	−22.71	−22.77	−22.75
298.15	−22.37	−22.41		−22.49
303.15	−22.08	−22.13	−22.29	−22.31
308.15	−21.80	−21.84		−22.05
313.15	−21.53	−21.57	−21.83	−21.82
318.15	−21.27	−21.30		
323.15	−21.01	−21.05		
$\Delta_r G_m^\circ$/kJ·mol^{-1}	55.45			55.89
$\Delta_r H_m^\circ$/kJ·mol^{-1}	42.8	42.9	38.9[b]	35.6

[a] Extrapolated value. [b] Average value given, (283.15 to 313.15) K.

absolute deviation between the experimental data and the values of the linear fit. These numbers provide insight of the accuracy of the linear extrapolation. The experimental EMF data are tabulated in the available Supporting Information with corresponding "Run no.".

In Table 1 to Table 10, correlated experimental results and the values of the standard state thermodynamic properties are given and compared to available temperature-dependent literature values. Literature dissociation constants based on the molarity scale[9−15] were converted to the molality scale by

$$K = \frac{1}{\rho_W}\left(\frac{c^\circ}{m^\circ}\right)K_c \qquad (24)$$

Table 11. Comparison of Values of the Standard State Thermodynamic Properties ($T = T^\circ = 298.15$ K) of Primary and Secondary (Alkanol)amines

compound	ref	$\Delta_r G^\circ_m$ kJ·mol^{-1}	pK_a	$\Delta_r H^\circ_m$ kJ·mol^{-1}
3-amino-1-propanol (MPA)	30	56.85	9.96	53.6
MMEA	this work	56.20	9.85	44.4
PZ, second group	this work	55.45	9.71	42.8
AMP	this work	55.24	9.68	52.2
MIPA	this work	53.94	9.45	48.8
MEA	this work	53.90	9.44	48.6
2-(2-aminoethoxy)ethanol (DGA)	31	53.74	9.42	50.2
HEPZ, second group	this work	50.94	8.92	35.4
diethanolamine (DEA)	32	50.68	8.88	42.4
DIPA	this work	50.47	8.84	39.2
AEPD	this work	50.32	8.82	47.5
PZ, first group	this work	30.87	5.41	32.3

Table 12. Comparison of Values of the Standard State Thermodynamic Properties ($T = T^\circ = 298.15$ K) of Tertiary (Alkanol)amines

compound	ref	$\Delta_r G^\circ_m$ kJ·mol^{-1}	pK_a	$\Delta_r H^\circ_m$ kJ·mol^{-1}
TREA	this work	61.08	10.70	44.4
DEMEA	this work	55.64	9.75	36.2
DMMEA	this work	52.63	9.22	34.4
methyldiethanolamine (MDEA)	2	48.87	8.56	34.9
TEA	this work	44.07	7.72	31.3
HEPZ, first group	this work	22.68	3.97	21.2

Table 13. Parameters for Equation 31

parameter	$\beta^{(0)}_{KCl}$ kg·mol^{-1}	$\beta^{(1)}_{KCl}$ kg·mol^{-1}	C_{KCl} kg^2·mol^{-2}
u_1	$-2.10289 \cdot 10^{-2}$	$2.20813 \cdot 10^{-1}$	0.0
u_2	$6.03967 \cdot 10^{-1}$	-4.61849	$7.64891 \cdot 10^{-4}$
u_3	$3.67768 \cdot 10^{-3}$	$-4.10116 \cdot 10^{-2}$	0.0
u_4	$-7.05537 \cdot 10^{-6}$	$1.10445 \cdot 10^{-4}$	$-1.12131 \cdot 10^{-8}$
u_5	$1.97968 \cdot 10^{-9}$	$-4.73196 \cdot 10^{-8}$	$1.72256 \cdot 10^{-11}$
u_6	$-2.47588 \cdot 10^{-3}$	$-2.74120 \cdot 10^{-2}$	0.0
u_7	$1.44160 \cdot 10^{-1}$	$3.32883 \cdot 10^{-1}$	$-5.71188 \cdot 10^{-3}$
$f_L(T_r, 1\ \text{bar})$	$6.77136 \cdot 10^{-4}$	$9.67854 \cdot 10^{-4}$	$-4.12364 \cdot 10^{-5}$
$f_L(T_r, P_r)$	$6.56838 \cdot 10^{-4}$	$9.67854 \cdot 10^{-4}$	$-4.12364 \cdot 10^{-5}$
$f_G(T_r, 1\ \text{bar})$	$4.8080 \cdot 10^{-2}$	$2.18752 \cdot 10^{-1}$	$-3.94 \cdot 10^{-4}$
$f_G(T_r, P_r)$	$5.0038 \cdot 10^{-2}$	$2.18752 \cdot 10^{-1}$	$-3.94 \cdot 10^{-4}$
K_1	−2931.268116	6353.355434	28.172180
K_2	−33.953143	193.004059	−0.125567

Table 14. Parameters for Equation 33

parameter	B^V_{KCl} kg·mol^{-1}·bar^{-1}
q_1	0.0
q_2	0.0
q_3	$9.45015 \cdot 10^{-8}$
q_4	$-2.90741 \cdot 10^{-10}$
q_5	$3.26205 \cdot 10^{-3}$
q_6	$8.39662 \cdot 10^{-7}$
q_7	0.0
q_8	$-4.41638 \cdot 10^{-9}$
q_9	$6.71235 \cdot 10^{-12}$
q_{10}	$-4.42327 \cdot 10^{-5}$
q_{11}	$-7.97437 \cdot 10^{-10}$
q_{12}	0.0
q_{13}	$4.12771 \cdot 10^{-12}$
q_{14}	$-6.24996 \cdot 10^{-15}$
q_{15}	$4.16221 \cdot 10^{-8}$

Table 15. Parameters for Equations 34 and 35

parameter	$\beta^{(0)}_{HCl}$ kg·mol^{-1}	$\beta^{(1)}_{HCl}$ kg·mol^{-1}	C_{HCl} kg^2·mol^{-2}
q_1	0.17690	0.2973	$0.362 \cdot 10^{-3}$
q_2	−0.09140	16.147	0.0
q_3	0.0	$-17.631 \cdot 10^{-3}$	0.0
q_4	$-4.034 \cdot 10^{-4}$	0.0	$-3.036 \cdot 10^{-5}$
q_5	$0.620 \cdot 10^{-4}$	$7.20 \cdot 10^{-4}$	0.0

where ρ_W is the mass density of pure water taken from Saul and Wagner[16] and K_c is the dissociation constant based on the molarity scale.

No literature values were found for the components AEPD and MIPA.

The dissociation constants of protonated AMP, DEMEA, DMMEA, and MMEA were measured by Littel et al.[9] and compared to the present work in Tables 1, 2, 4, and 6. The values deviate on average by 0.53 %, 2.06 %, 1.60 %, and 0.48 % (in ln(K)) from the correlated values of the present work, respectively.

The dissociation constants of protonated DIPA were measured by Blauwhoff and Bos,[10] Kim et al.,[17] and Sharma[18] and compared to the present work in Table 3. The values by Blauwhoff and Bos,[10] Kim et al.,[17] and Sharma[18] deviate by 3.30 %, 0.43 %, and 7.44 %. Blauwhoff and Bos[10] measured in a solution of 1.00 M KCl and not at infinite dilution as in the present work. This can explain the larger deviation. The larger deviation of Sharma[18] cannot be explained as information about the experimental technique was not provided.

The dissociation constants of MEA have been measured by Bates and Pinching,[19] Kim et al.,[17] and Antelo et al.[11] and compared to the present work in Table 5. The values deviate by 0.60 %, 0.71 %, and 1.56 %, respectively. Antelo et al.[11] did not take activity coefficients of the compounds into consideration when determining the dissociation constants from the experimental data; hence, the activity coefficients were set to unity for all species, and this can explain the larger deviation.

The dissociation constants of TEA have been measured by Bates and Allen,[20] Bates and Schwarzenbach,[21] Kim et al.,[17] and Antelo et al.[11] and compared to the present work in Table 7. The values deviate by 0.55 %, 0.66 %, 1.01 %, and 1.51 %, respectively. As for MEA, Antelo et al.[11] set the activity coefficients to unity, and this can explain the larger deviation.

Dissociation constants of TREA were measured by Cox et al.,[22] Campbell and Lam,[12] Ablard et al.,[13] Fyfe,[14] and Bergström and Olofsson[23] and compared to the present work in Table 8. The values deviate by 0.11 %, 0.47 %, 1.38 %, 0.18 %, and 0.25 %. Ablard et al.[13] determined the dissociation constants by conductance measurements; however, the larger deviation cannot be explained.

The first and second dissociation constants of PZ have been measured by Hetzer et al.,[24] Pagano et al.,[25] and Enea et al.[15] and compared to the present work in Tables 9 and 10. The first dissociation constants deviate on average by 1.48 %, 3.40 %, and 6.54 %, and the second dissociation constants deviate by 0.18 %, 0.73 %, and 0.88 %. The first dissociation constants have a considerably larger deviation from one another than the second dissociation constants. During measurements of the first dissociation constants, the amino groups of PZ have to be partly first-step and second-step protonated. The solution thus contains a mixture of 1:1 and 1:2 salts, and accurate estimates for the activity coefficients are important for an accurate result.[26] The larger deviations have likely followed from this.

For HEPZ, no temperature-dependent dissociation constants were found; however, Castro et al.[27] determined $\ln(K_2)$ to be -21.60 at 298.15 K and ionic strength of 0.2 M. The value of the current work is -20.55. The significant difference between these values cannot be explained as Castro et al.[27] did not provide specific experimental details regarding the measurements.

Table 11shows the values of $\Delta_r G_m^\circ$ and $\Delta_r H_m^\circ$ of primary and secondary (alkanol)amines in comparison to literature values, and Table 12 shows the values of tertiary amines. The compounds are sorted in the order of descending $\Delta_r G_m^\circ$ values. Calculated pK_a values at $T = T^\circ = 298.15$ K are also separately listed for the convenience of the reader. The values given in Tables 11 and 12 can provide the following information: (1) the values of $\Delta_r G_m^\circ$, or pK_a, represent the basic strength of the compounds. From a Brønsted plot,[28,29] a higher basic strength of the (alkanol)amine can indicate a higher reaction rate of the (alkanol)amine with an acid gas (e.g., CO_2), although, for accurate determination of reaction rate constants, kinetic measurements have to be considered; (2) in a commercially operated absorber/desorber acid gas removal plant, the temperature cycle between the absorber and desorber section ranges from about (313 to 393) K depending on the operating conditions.[1] The acid gas reacts with the absorbent in a basic environment in the absorber section and is released in the less basic desorber section. Following from this, during the cooling/heating cycle of the absorbent, it changes its basic strength to absorb or desorb the acid gas. The values of $\Delta_r H_m^\circ$ in Tables 11 and 12 indicates the change of the basic strength of the compounds within a given temperature range. A higher value of $\Delta_r H_m^\circ$ results in a favorable shift of the basic strength of the (alkanol)amine during the cooling/heating cycle of the absorber/desorber sections.

Conclusion

The dissociation constants of protonated 2-amino-2-ethyl-1,3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), diethylmonoethanolamine (DEMEA), diisopropanolamine (DIPA), dimethylmonoethanolamine (DMMEA), monoethanolamine (MEA), 1-amino-2-propanol (MIPA), methylmonoethanolamine (MMEA), triethanolamine (TEA), and the first and the second dissociation constants of piperazine (PZ) and hydroxyethylpiperazine (HEPZ) have been determined in this work by electromotive force measurements from (293 to 353) K. The dissociation constants of protonated triethylamine (TREA) have been determined with the same technique from (293 to 333) K.

The dissociation constants and the thermodynamic properties of the (alkanol)amines presented in this work provide information about the use of these (alkanol)amines as possible absorbents for acid gas removal.

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Nomenclature

$\bar{m}_i$	overall molality of component i/mol·kg^{-1}
$\bar{n}_i$	overall number of moles of component i/mol
a_i	activity of component i
A_ϕ	Debye–Hückel parameter/kg$^{1/2}$·mol$^{-1/2}$
b	constant in the modified Debye–Hückel term/kg$^{1/2}$·mol$^{-1/2}$
B_{ij}	second virial coefficient in Pitzer's equation
c°	reference molarity ($c^\circ = 1$ mol·m^{-3})
C_P	heat capacity/J·(mol·K)$^{-1}$
C_{ijk}	third virial coefficient in Pitzer's equation
E	electromotive force/mV
e	charge of electron/C
E°	standard potential/mV
F	Faradays constant/C·mol^{-1}
f	modified Debye–Hückel term
G	Gibbs energy/kJ·mol^{-1}
H	enthalpy/kJ·mol^{-1}
I_m	ionic strength/mol·kg^{-1}
K	dissociation constant
k	Boltzmann constant/J·K^{-1}
K_w	dissociation constant of water
M	molar mass/g·mol^{-1}
m°	reference molality ($m^\circ = 1$ mol·kg^{-1})
m_i	molality of component i/mol·kg^{-1}
N_A	Avogadro constant/mol^{-1}
n_i	number of moles of component i/mol
P	pressure
R	gas constant/J·(mol K)$^{-1}$
S	entropy/J·(mol·K)$^{-1}$
T	temperature/K
w_S	number of kilograms of solvent, here water/kg
z_i	number of charges of component i

Greek Letters

α	constant in Pitzer's equation/kg$^{1/2}$·mol$^{-1/2}$
$\beta^{(0)}$	binary interaction parameter in Pitzer's equation/kg·mol^{-1}
$\beta^{(1)}$	binary interaction parameter in Pitzer's equation/kg·mol^{-1}
Δ	difference
ϵ_0	permittivity of a vacuum/C^2·N^{-1}·m^{-2}
ϵ_W	relative dielectric constant of water
γ_{ij}	mean activity coefficient of ij
ρ	density/kg·m^{-3}

Superscripts

°	standard state
ex	excess

Subscripts

1	first dissociation constant
2	second dissociation constant
a	acid
c	on molar scale
I, II	cell I, cell II
ij	component i, j
ijk	component i, j, k
m	molar, on molal scale
r	reaction

Abbreviations

aq	in aqueous solution
exptl	experimental
s	solid
W	water

Appendix A. Outline of the Model of Pitzer

A very brief outline of the model of Pitzer introduced by Pitzer[33] is given below. For an electrolyte solution containing

w_S kilograms of solvent, with molalities m_i, m_j, ..., of solute spices i, j, ..., Pitzer[33] introduced the equation for the excess Gibbs energy

$$\frac{G^{\mathrm{ex}}}{RTw_{\mathrm{S}}} = f(I_{\mathrm{m}}) + \sum_i \sum_j m_i m_j B_{ij} + \sum_i \sum_j \sum_k m_i m_j m_k C_{ijk} + ... \quad (25)$$

Pitzer[33] further derived the expression for the activity coefficient. For the dissolved species i:j, the activity coefficients are estimated by

$$\ln(\gamma_{ij,\mathrm{m}}) = -A_\phi\left[\frac{\sqrt{I_{\mathrm{m}}}}{1 + b\sqrt{I_{\mathrm{m}}}} + \frac{2}{b}\ln(1 + b\sqrt{I_{\mathrm{m}}})\right] + mB_{ij} + 3m^2C_{ij} \quad (26)$$

where I_{m} is defined as

$$I_{\mathrm{m}} = \frac{1}{2}\sum_{x=i,j} m_x z_x^2 \quad (27)$$

and $b = 1.2\ \mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$. The Debye–Hückel term is given

$$A_\phi = \frac{1}{3}\sqrt{2\pi N_{\mathrm{A}}\rho_{\mathrm{W}}}\left(\frac{e^2}{4\pi\epsilon_0\epsilon_{\mathrm{W}}kT}\right)^{1.5} \quad (28)$$

where the dielectric constant of water, ϵ_{W}, was taken from Bradley and Pitzer.[34] The second virial coefficient is given

$$B_{ij} = 2\beta_{ij}^{(0)} + \left(\frac{2\beta_{ij}^{(1)}}{\alpha^2 I_{\mathrm{m}}}\right)\left[1 - \left(1 + \alpha I_{\mathrm{m}}^{1/2} - \frac{\alpha^2 I_{\mathrm{m}}}{2}\right) \times \exp(-\alpha I_{\mathrm{m}}^{1/2})\right] \quad (29)$$

where $\beta_{ij}^{(0)}$, $\beta_{ij}^{(1)}$, and C_{ij} are salt specific interaction parameters. For the case considered here, $\alpha = 2.0\ \mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$. In the case where interaction parameters are neglected, the activity of water follows from the Gibbs–Duhem equation in the form of

$$\ln(a_{\mathrm{W}}) = \frac{M_{\mathrm{W}}}{1000}\left\{2A_\phi\frac{I_{\mathrm{m}}^{1.5}}{1 + b\sqrt{I_{\mathrm{m}}}} - \sum_{i\neq\mathrm{W}} m_i\right\} \quad (30)$$

Interaction Parameters for KCl in the Model of Pitzer. The following section reports the temperature dependence of the ion interaction parameters for KCl given by Pabalan and Pitzer.[6] The interaction parameters are calculated from eq 31 and Table 13. T is the temperature in Kelvin; T_{R} is 298.15 K; P is the pressure in bar; and P_{R} is 179 bar. The density of water, ρ_{W}, was taken from Saul and Wagner.[16] The pressure, P, was set to 1 bar. The pressure dependence of the thermodynamic properties are calculated from eq 32 and Table 14. A complete description of the equations below are given in Pabalan and Pitzer.[6]

$$f(T, P_{\mathrm{r}}) = \frac{u_1T^2}{6} + \frac{u_2T}{2} + \frac{u_3T^2\left(\frac{\ln(T)}{2} - \frac{5}{12}\right)}{3} + \frac{u_4T^3}{12} + \frac{u_5T^4}{20} + u_6\left[\frac{T}{2} + \frac{3(227)^2}{2T} + \frac{227(T - 227)\ln(T - 227)}{T}\right] - u_7\left[\frac{2(647 - T)\ln(647 - T)}{T} + \ln(647 - T)\right] - \frac{K_1}{T} - f_{\mathrm{L}}(T_{\mathrm{r}}, P_{\mathrm{r}})\left(\frac{T_{\mathrm{r}}^2}{T}\right) + K_2 + f_{\mathrm{G}}(T_{\mathrm{r}}, P_{\mathrm{R}}) \quad (31)$$

$$\ln\gamma_\pm(P_2) - \ln\gamma_\pm(P_1) = -[A_\phi(P_2) - A_\phi(P_1)]\left(\frac{I_{\mathrm{m}}^{1/2}}{1 + bI_{\mathrm{m}}^{1/2}} + \frac{2}{b}\ln(1 + bI_{\mathrm{m}}^{1/2})\right) + \int_{P_1}^{P_2}\left\{2m\left(\frac{\partial\beta_{ij}^{(0)}}{\partial P}\right)_T + \frac{2m}{\alpha^2 I_{\mathrm{m}}}\left(\frac{\partial\beta_{ij}^{(1)}}{\partial P}\right)_T\left[1 - \left(1 + \alpha I_{\mathrm{m}}^{1/2} - \frac{\alpha^2 I_{\mathrm{m}}}{2}\right)\exp(-\alpha I_{\mathrm{m}}^{1/2})\right] + 3m^2\left(\frac{\partial C_{ij}}{\partial P}\right)_T\right\}\mathrm{d}P \quad (32)$$

where $[(\partial\beta_{ij}^{(0)})/\partial P]_T = B_{ij}^{\mathrm{V}}$ and B_{ij}^{V} is calculated from eq 33 and Table 14. Further, in this case, $[(\partial\beta_{ij}^{(1)})/\partial P]_T = 0$ and $[(\partial C_{ij})/\partial P]_T = 0$.

$$f_{\mathrm{V}}(T, P) = q_1 + \frac{q_2}{T} + q_3T + q_4T^2 + \frac{q_5}{647 - T} + P\left[q_6 + \frac{q_7}{T} + q_8T + q_9T^2 + \frac{q_{10}}{(647 - T)}\right] + P^2\left[q_{11} + \frac{q_{12}}{T} + q_{13}T + q_{14}T^2 + \frac{q_{15}}{(647 - T)}\right] \quad (33)$$

Interaction Parameters for HCl in the Model of Pitzer. The following section reports the density, pressure, and temperature dependence on the ion interaction parameters for HCl given by Holmes et al.[5] The ion interaction parameters are given by eq 34 and Table 15. T is the temperature in Kelvin; T^* is 1 K; P^* is 1 MPa; and ρ^* is 1 $\mathrm{kg}\cdot\mathrm{m}^{-3}$. T_{R}, P_{R}, and ρ_{R} are the reference temperature, pressure, and density and are set to 298.15 K, 0.101325 MPa, and 997.062 $\mathrm{kg}\cdot\mathrm{m}^{-3}$, respectively. The pressure and density, P and ρ, are set equal to the reference pressure and reference density.

$$f(\rho, P, T) = q_1 + q_2\ln\left(\frac{\rho}{\rho_{\mathrm{R}}}\right) + q_3\frac{(\rho - \rho_{\mathrm{R}})}{\rho^*} + q_4\frac{(T - T_{\mathrm{R}})}{T^*} + q_5\frac{(P - P_{\mathrm{R}})}{P^*} \quad (34)$$

For HCl, the interaction parameter, C, in eq 26 is defined

$$C = \frac{1}{2}C_{\mathrm{HCl}} \quad (35)$$

Appendix B. Experimental Results

Table 16. Experimental Results of the Dissociation Constants

run no.	T/K	ln(K)	avg. dev./%	max. dev./%	run no.	T/K	ln(K)	avg. dev./%	avg. dev./%
Dissociation Constants of Protonated AEPD					Dissociation Constants of Protonated MMEA				
1	293.12	−20.63 ± 0.04	0.267	0.509	1	293.14	−22.97 ± 0.04	0.109	0.161
2	293.05	−20.63 ± 0.04	0.229	0.469	2	293.07	−22.97 ± 0.04	0.071	0.112
3	293.06	−20.63 ± 0.04	0.237	0.505	3	293.16	−22.98 ± 0.04	0.127	0.225
4	298.26	−20.31 ± 0.04	0.313	0.594	4	298.13	−22.69 ± 0.04	0.067	0.128
5	298.33	−20.29 ± 0.04	0.255	0.543	5	298.15	−22.65 ± 0.04	0.089	0.200
6	298.29	−20.26 ± 0.04	0.264	0.549	6	298.20	−22.67 ± 0.04	0.098	0.199
7	303.16	−19.99 ± 0.04	0.277	0.573	7	303.25	−22.38 ± 0.04	0.083	0.168
8	303.28	−19.97 ± 0.04	0.267	0.607	8	303.14	−22.37 ± 0.04	0.087	0.175
9	303.30	−19.96 ± 0.04	0.229	0.503	9	303.14	−22.39 ± 0.04	0.120	0.217
10	312.89	−19.40 ± 0.04	0.269	0.487	10	313.26	−21.80 ± 0.04	0.101	0.153
11	312.96	−19.39 ± 0.04	0.226	0.499	11	313.21	−21.78 ± 0.04	0.078	0.184
12	312.95	−19.40 ± 0.04	0.196	0.424	12	313.11	−21.80 ± 0.04	0.089	0.146
13	322.96	−18.81 ± 0.04	0.272	0.473	13	323.51	−21.25 ± 0.04	0.077	0.138
14	323.04	−18.81 ± 0.04	0.213	0.462	14	323.24	−21.22 ± 0.04	0.097	0.211
15	322.98	−18.81 ± 0.04	0.173	0.380	15	323.12	−21.23 ± 0.04	0.094	0.153
16	333.09	−18.26 ± 0.04	0.261	0.431	16	333.15	−20.72 ± 0.04	0.102	0.168
17	333.23	−18.26 ± 0.04	0.214	0.435	17	333.14	−20.70 ± 0.04	0.050	0.098
18	333.05	−18.26 ± 0.04	0.224	0.484	18	333.11	−20.71 ± 0.04	0.117	0.252
19	343.11	−17.73 ± 0.04	0.265	0.467	19	343.17	−20.20 ± 0.04	0.076	0.138
20	342.97	−17.74 ± 0.04	0.171	0.370	20	343.21	−20.18 ± 0.04	0.068	0.090
21	342.93	−17.76 ± 0.04	0.197	0.456	21	343.13	−20.21 ± 0.04	0.103	0.207
22	353.11	−17.26 ± 0.04	0.287	0.480	22	353.16	−19.70 ± 0.04	0.070	0.168
23	353.21	−17.26 ± 0.04	0.221	0.459	23	353.20	−19.70 ± 0.03	0.031	0.056
24	353.12	−17.27 ± 0.04	0.189	0.410	24	353.14	−19.71 ± 0.04	0.060	0.121
Dissociation Constants of Protonated AMP					Dissociation Constants of Protonated TEA				
1	293.16	−22.69 ± 0.04	0.179	0.467	1	293.15	−17.94 ± 0.04	0.107	0.186
2	293.12	−22.66 ± 0.04	0.080	0.160	2	293.14	−17.99 ± 0.04	0.124	0.219
3	293.19	−22.61 ± 0.04	0.088	0.164	3	293.09	−18.07 ± 0.04	0.178	0.505
4	298.06	−22.27 ± 0.04	0.199	0.424	4	298.24	−17.77 ± 0.04	0.081	0.195
5	298.14	−22.33 ± 0.04	0.086	0.128	5	298.16	−17.77 ± 0.04	0.122	0.252
6	298.09	−22.23 ± 0.04	0.135	0.279	6	298.11	−17.77 ± 0.04	0.052	0.075
7	303.15	−21.96 ± 0.04	0.164	0.402	7	303.31	−17.57 ± 0.04	0.089	0.227
8	303.08	−21.94 ± 0.04	0.120	0.255	8	303.14	−17.57 ± 0.04	0.078	0.180
9	303.16	−21.89 ± 0.04	0.142	0.299	9	303.17	−17.57 ± 0.04	0.040	0.076
10	313.18	−21.27 ± 0.04	0.126	0.280	10	313.14	−17.19 ± 0.04	0.071	0.168
11	313.06	−21.30 ± 0.04	0.087	0.217	11	313.18	−17.15 ± 0.04	0.096	0.192
12	313.15	−21.25 ± 0.04	0.128	0.273	12	313.37	−17.15 ± 0.04	0.053	0.091
13	323.26	−20.65 ± 0.04	0.162	0.398	13	323.19	−16.77 ± 0.04	0.071	0.142
14	323.43	−20.63 ± 0.04	0.078	0.139	14	323.24	−16.76 ± 0.04	0.047	0.093
15	323.28	−20.62 ± 0.04	0.140	0.257	15	323.21	−16.77 ± 0.04	0.026	0.062
16	333.16	−20.04 ± 0.04	0.190	0.462	16	333.17	−16.39 ± 0.04	0.069	0.144
17	333.15	−20.06 ± 0.04	0.092	0.141	17	333.23	−16.38 ± 0.04	0.043	0.087
18	333.10	−19.99 ± 0.04	0.104	0.202	18	333.21	−16.39 ± 0.04	0.029	0.066
19	343.04	−19.46 ± 0.04	0.187	0.449	19	343.13	−16.02 ± 0.04	0.101	0.145
20	343.01	−19.52 ± 0.04	0.089	0.169	20	343.11	−16.03 ± 0.04	0.067	0.130
21	342.90	−19.43 ± 0.04	0.122	0.251	21	343.02	−16.04 ± 0.04	0.028	0.068
22	353.22	−18.93 ± 0.04	0.190	0.479	22	353.23	−15.66 ± 0.04	0.092	0.175
23	353.14	−18.95 ± 0.04	0.113	0.187	23	353.24	−15.66 ± 0.03	0.054	0.102
24	353.03	−18.87 ± 0.03	0.092	0.187	24	353.21	−15.68 ± 0.03	0.060	0.135
Dissociation Constants of Protonated DEMEA					Dissociation Constants of Protonated TREA				
1	293.17	−22.69 ± 0.04	0.153	0.291	1	293.04	−24.89 ± 0.04	0.153	0.366
2	293.15	−22.73 ± 0.04	0.105	0.239	2	293.10	−24.93 ± 0.04	0.029	0.053
3	293.13	−22.60 ± 0.04	0.080	0.160	3	293.13	−24.89 ± 0.04	0.100	0.209
4	298.16	−22.51 ± 0.04	0.114	0.220	4	298.25	−24.62 ± 0.04	0.162	0.354
5	298.13	−22.47 ± 0.04	0.133	0.305	5	298.17	−24.65 ± 0.04	0.054	0.118
6	298.07	−22.41 ± 0.04	0.060	0.123	6	298.19	−24.59 ± 0.04	0.098	0.203
7	303.35	−22.22 ± 0.04	0.047	0.104	7	303.06	−24.33 ± 0.04	0.158	0.406
8	303.30	−22.22 ± 0.04	0.039	0.098	8	303.03	−24.36 ± 0.04	0.044	0.071
9	303.29	−22.17 ± 0.04	0.029	0.052	9	303.06	−24.35 ± 0.04	0.091	0.182
10	313.36	−21.71 ± 0.04	0.045	0.091	10	313.09	−23.74 ± 0.04	0.164	0.409
11	313.32	−21.73 ± 0.04	0.037	0.069	11	313.12	−23.80 ± 0.04	0.033	0.059
12	313.16	−21.71 ± 0.04	0.027	0.055	12	313.12	−23.76 ± 0.04	0.107	0.201
13	323.10	−21.25 ± 0.04	0.030	0.073	13	323.39	−23.16 ± 0.04	0.173	0.431
14	323.01	−21.23 ± 0.04	0.015	0.046	14	323.54	−23.22 ± 0.04	0.031	0.067
15	322.96	−21.23 ± 0.04	0.003	0.007	15	323.51	−23.17 ± 0.04	0.119	0.257
16	333.05	−20.75 ± 0.04	0.031	0.072	16	332.89	−22.63 ± 0.04	0.207	0.475
17	333.01	−20.77 ± 0.04	0.016	0.041	17	333.14	−22.68 ± 0.04	0.041	0.073
18	332.92	−20.78 ± 0.04	0.020	0.046	18	333.10	−22.68 ± 0.04	0.266	0.730
19	342.93	−20.27 ± 0.04	0.032	0.074					
20	342.86	−20.30 ± 0.04	0.048	0.099					
21	342.75	−20.30 ± 0.04	0.046	0.078					
22	353.11	−19.84 ± 0.04	0.019	0.041					
23	353.03	−19.85 ± 0.03	0.023	0.042					
24	353.11	−19.84 ± 0.03	0.011	0.022					

Table 16 Continued

run no.	*T*/K	ln(*K*)	avg. dev./%	max. dev./%	run no.	*T*/K	ln(*K*)	avg. dev./%	avg. dev./%
Dissociation Constants of Protonated DIPA					First Dissociation Constants of Protonated PZ				
1	293.05	−20.60 ± 0.04	0.259	0.442	1	293.26	−12.69 ± 0.04	0.302	0.465
2	293.07	−20.66 ± 0.04	0.317	0.495	2	293.17	−12.64 ± 0.04	0.444	1.208
3	293.19	−20.62 ± 0.04	0.281	0.508	3	293.19	−12.66 ± 0.04	0.277	0.410
4	298.11	−20.32 ± 0.04	0.221	0.530	4	298.33	−12.48 ± 0.04	0.395	0.672
5	298.02	−20.37 ± 0.04	0.148	0.332	5	298.28	−12.42 ± 0.04	0.467	1.249
6	298.09	−20.42 ± 0.04	0.215	0.374	6	298.29	−12.48 ± 0.04	0.304	0.497
7	303.26	−20.08 ± 0.04	0.221	0.560	7	303.26	−12.26 ± 0.04	0.377	0.997
8	303.34	−20.08 ± 0.04	0.161	0.268	8	303.41	−12.19 ± 0.04	0.480	1.254
9	303.36	−20.09 ± 0.04	0.126	0.204	9	303.19	−12.23 ± 0.04	0.312	0.478
10	313.24	−19.59 ± 0.04	0.258	0.642	10	313.05	−11.86 ± 0.04	0.428	0.681
11	313.25	−19.59 ± 0.04	0.104	0.158	11	313.11	−11.85 ± 0.04	0.186	0.347
12	313.26	−19.60 ± 0.04	0.144	0.304	12	313.06	−11.82 ± 0.04	0.334	0.512
13	323.14	−19.07 ± 0.04	0.260	0.626	13	323.17	−11.45 ± 0.04	0.477	0.758
14	323.18	−19.07 ± 0.04	0.072	0.162	14	323.21	−11.37 ± 0.04	0.606	1.295
15	323.16	−19.10 ± 0.04	0.141	0.301	15	323.16	−11.44 ± 0.04	0.328	0.495
16	333.12	−18.61 ± 0.04	0.267	0.665	16	333.19	−11.09 ± 0.04	0.466	0.734
17	333.17	−18.61 ± 0.04	0.072	0.184	17	333.27	−11.00 ± 0.04	0.646	1.406
18	333.16	−18.62 ± 0.04	0.152	0.286	18	333.24	−11.08 ± 0.04	0.301	0.539
19	343.10	−18.12 ± 0.04	0.252	0.619	19	343.14	−10.75 ± 0.04	0.452	0.679
20	343.09	−18.14 ± 0.04	0.083	0.179	20	343.23	−10.66 ± 0.04	0.571	1.351
21	343.00	−18.16 ± 0.03	0.121	0.246	21	343.23	−10.72 ± 0.04	0.328	0.457
22	353.11	−17.72 ± 0.03	0.286	0.724	22	353.26	−10.40 ± 0.04	0.492	0.700
23	353.06	−17.69 ± 0.04	0.100	0.232	23	353.41	−10.37 ± 0.04	0.215	0.308
24	352.92	−17.71 ± 0.03	0.171	0.345	24	353.16	−10.35 ± 0.04	0.042	0.084
Dissociation Constants of Protonated DMMEA					Second Dissociation Constants of Protonated PZ				
1	293.27	−21.48 ± 0.04	0.079	0.195	1	293.14	−22.67 ± 0.04	0.071	0.150
2	293.24	−21.46 ± 0.04	0.065	0.131	2	293.15	−22.65 ± 0.04	0.039	0.080
3	293.26	−21.45 ± 0.04	0.080	0.144	3	293.16	−22.67 ± 0.04	0.031	0.071
4	298.18	−21.23 ± 0.04	0.128	0.264	4	298.22	−22.34 ± 0.04	0.024	0.040
5	298.17	−21.22 ± 0.04	0.066	0.132	5	298.13	−22.37 ± 0.04	0.051	0.107
6	298.29	−21.21 ± 0.04	0.095	0.205	6	298.16	−22.40 ± 0.04	0.022	0.045
7	303.31	−21.01 ± 0.04	0.102	0.259	7	303.16	−22.08 ± 0.04	0.035	0.074
8	303.28	−20.98 ± 0.04	0.074	0.178	8	303.05	−22.08 ± 0.04	0.088	0.167
9	303.38	−20.98 ± 0.04	0.103	0.215	9	303.16	−22.08 ± 0.04	0.036	0.060
10	313.29	−20.55 ± 0.04	0.106	0.232	10	313.13	−21.53 ± 0.04	0.057	0.171
11	313.36	−20.56 ± 0.04	0.067	0.124	11	313.10	−21.55 ± 0.04	0.019	0.047
12	313.41	−20.53 ± 0.04	0.075	0.163	12	313.00	−21.54 ± 0.04	0.034	0.078
13	323.36	−20.10 ± 0.04	0.107	0.234	13	323.13	−20.99 ± 0.04	0.018	0.053
14	323.45	−20.10 ± 0.04	0.042	0.084	14	323.13	−21.00 ± 0.04	0.021	0.040
15	323.44	−20.08 ± 0.04	0.080	0.181	15	323.02	−21.02 ± 0.04	0.045	0.087
16	333.46	−19.65 ± 0.04	0.108	0.215	16	333.32	−20.49 ± 0.04	0.053	0.092
17	333.53	−19.65 ± 0.04	0.052	0.104	17	333.26	−20.56 ± 0.04	0.234	0.686
18	333.48	−19.66 ± 0.04	0.099	0.197	18	333.14	−20.53 ± 0.04	0.073	0.185
19	343.20	−19.21 ± 0.04	0.102	0.204	19	343.14	−20.01 ± 0.04	0.060	0.107
20	343.16	−19.24 ± 0.04	0.057	0.088	20	343.21	−20.02 ± 0.04	0.030	0.079
21	343.14	−19.25 ± 0.04	0.097	0.231	21	343.21	−20.07 ± 0.04	0.082	0.176
22	353.14	−18.86 ± 0.03	0.119	0.229	22	353.42	−19.56 ± 0.04	0.042	0.056
23	353.19	−18.84 ± 0.03	0.030	0.052	23	353.41	−19.56 ± 0.04	0.034	0.085
24	353.22	−18.83 ± 0.03	0.109	0.215	24	353.13	−19.62 ± 0.04	0.053	0.075
Dissociation Constants of Protonated MEA					First Dissociation Constants of Protonated HEPZ				
1	293.11	−22.07 ± 0.04	0.087	0.158	1	293.11	−9.33 ± 0.04	0.318	0.796
2	293.11	−22.09 ± 0.04	0.103	0.253	2	293.20	−9.33 ± 0.04	0.279	0.507
3	293.09	−22.08 ± 0.04	0.077	0.144	3	293.15	−9.24 ± 0.04	0.319	0.642
4	298.34	−21.71 ± 0.04	0.080	0.181	4	298.15	−9.19 ± 0.04	0.350	0.876
5	298.24	−21.73 ± 0.04	0.090	0.225	5	298.16	−9.11 ± 0.04	1.654	3.000
6	298.05	−21.76 ± 0.04	0.042	0.088	6	298.15	−9.15 ± 0.04	0.412	0.764
7	303.11	−21.44 ± 0.04	0.070	0.173	7	303.15	−9.03 ± 0.04	0.379	0.926
8	303.04	−21.42 ± 0.04	0.110	0.264	8	303.16	−8.97 ± 0.04	1.667	3.009
9	302.98	−21.44 ± 0.04	0.044	0.074	9	303.14	−8.97 ± 0.04	0.324	0.697
10	313.07	−20.80 ± 0.04	0.058	0.138	10	313.06	−8.77 ± 0.04	0.410	1.011
11	313.17	−20.80 ± 0.04	0.105	0.233	11	313.05	−8.72 ± 0.04	1.697	3.072
12	313.22	−20.80 ± 0.04	0.039	0.072	12	313.05	−8.72 ± 0.04	0.318	0.699
13	323.20	−20.20 ± 0.04	0.053	0.144	13	323.05	−8.54 ± 0.04	0.391	0.955
14	323.34	−20.20 ± 0.04	0.080	0.200	14	323.08	−8.49 ± 0.04	1.770	3.166
15	323.32	−20.20 ± 0.04	0.027	0.043	15	323.05	−8.46 ± 0.04	0.337	0.734
16	333.24	−19.62 ± 0.04	0.051	0.113	16	333.05	−8.30 ± 0.04	0.454	1.094
17	333.28	−19.64 ± 0.04	0.074	0.187	17	332.86	−8.25 ± 0.04	1.809	3.272
18	333.20	−19.66 ± 0.04	0.036	0.057	18	332.62	−8.24 ± 0.04	0.370	0.672
19	343.14	−19.11 ± 0.04	0.052	0.139	19	343.34	−8.01 ± 0.04	3.206	4.139
20	343.17	−19.13 ± 0.04	0.098	0.236	20	342.97	−7.95 ± 0.04	1.898	3.474
21	343.12	−19.13 ± 0.04	0.049	0.100	21	342.69	−7.98 ± 0.04	0.542	1.178
22	353.14	−18.60 ± 0.03	0.058	0.147	22	352.65	−7.82 ± 0.04	0.403	0.935
23	353.26	−18.61 ± 0.03	0.078	0.158	23	352.65	−7.83 ± 0.04	1.218	2.546
24	353.14	−18.64 ± 0.03	0.016	0.031	24	352.06	−7.81 ± 0.04	0.476	0.952

Table 16 Continued

run no.	T/K	ln(K)	avg. dev./%	max. dev./%	run no.	T/K	ln(K)	avg. dev./%	avg. dev./%
Dissociation Constants of Protonated MIPA					Second Dissociation Constants of Protonated HEPZ				
1	293.26	−22.10 ± 0.04	0.086	0.193	1	293.26	−20.79 ± 0.04	0.038	0.100
2	293.51	−22.07 ± 0.04	0.056	0.117	2	293.31	−20.83 ± 0.04	0.067	0.135
3	293.26	−22.09 ± 0.04	0.064	0.144	3	293.35	−20.81 ± 0.04	0.034	0.104
4	298.36	−21.75 ± 0.04	0.077	0.128	4	298.29	−20.58 ± 0.04	0.051	0.087
5	298.38	−21.75 ± 0.04	0.085	0.201	5	298.39	−20.53 ± 0.04	0.037	0.071
6	298.47	−21.74 ± 0.04	0.051	0.112	6	298.39	−20.55 ± 0.04	0.046	0.105
7	303.25	−21.42 ± 0.04	0.092	0.177	7	303.15	−20.34 ± 0.04	0.037	0.060
8	303.32	−21.40 ± 0.04	0.089	0.160	8	303.26	−20.31 ± 0.04	0.049	0.075
9	303.15	−21.44 ± 0.04	0.058	0.130	9	303.26	−20.30 ± 0.04	0.048	0.103
10	313.06	−20.82 ± 0.04	0.088	0.191	10	313.06	−19.84 ± 0.04	0.052	0.108
11	313.08	−20.82 ± 0.04	0.046	0.083	11	313.06	−19.81 ± 0.04	0.052	0.103
12	313.11	−20.82 ± 0.04	0.059	0.138	12	313.06	−19.81 ± 0.04	0.053	0.134
13	323.27	−20.20 ± 0.04	0.094	0.202	13	323.11	−19.36 ± 0.04	0.070	0.138
14	323.32	−20.20 ± 0.04	0.055	0.102	14	323.09	−19.34 ± 0.04	0.055	0.078
15	323.24	−20.21 ± 0.04	0.052	0.112	15	323.04	−19.34 ± 0.04	0.051	0.081
16	333.35	−19.63 ± 0.04	0.093	0.186	16	333.06	−18.90 ± 0.04	0.044	0.092
17	333.42	−19.62 ± 0.04	0.070	0.097	17	333.04	−18.94 ± 0.04	0.078	0.134
18	333.41	−19.64 ± 0.04	0.073	0.152	18	333.01	−18.90 ± 0.04	0.048	0.129
19	343.15	−19.09 ± 0.03	0.097	0.168	19	343.17	−18.52 ± 0.04	0.106	0.192
20	343.26	−19.12 ± 0.04	0.041	0.105	20	343.05	−18.54 ± 0.04	0.090	0.166
21	343.15	−19.11 ± 0.04	0.059	0.162	21	343.06	−18.49 ± 0.04	0.032	0.071
22	353.19	−18.56 ± 0.03	0.092	0.182	22	352.11	−18.13 ± 0.04	0.112	0.179
23	353.24	−18.58 ± 0.04	0.061	0.149	23	351.30	−18.20 ± 0.04	0.096	0.188
24	353.12	−18.59 ± 0.03	0.075	0.154	24	351.18	−18.15 ± 0.04	0.126	0.255

Supporting Information Available:

Tabulated experimental EMF data. This material is available free of charge via the Internet at http://pubs.acs.org.

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