2914 *J. Chem. Eng. Data* **2009,** *54,* 2914–2917

pK_a Values of Some Piperazines at (298, 303, 313, and 323) K

Farhad Khalili,[†] **Amr Henni,**[*,§] **and Allan L. L. East**[‡]

Department of Industrial Systems Engineering and Department of Chemistry and Biochemistry, University of Regina, Regina, Sask. S4S 0A2 Canada, and Carbon Management, R & D Centre Saudi Aramco, Dhahran, 31311 Saudi Arabia

The dissociation constants of the conjugate acids of six cyclic diamines [piperazine, 1-methylpiperazine, 2-methylpiperazine, 1-ethylpiperazine, 1-(2-hydroxyethyl)piperazine, and 1,4-dimethylpiperazine] were calculated using the potentiometric titration method at (298, 303, 313, and 323) K. The pK_a values of piperazine were compared with published data to validate the procedure used. The thermodynamic quantities ($\Delta H°$ and $\Delta S°$) for the dissociation processes were determined using the van't Hoff equation. A trend is proposed related to the variation of the pK_a with the addition of different radical groups to the base piperazine molecule.

Introduction

The amount of carbon dioxide in the atmosphere has increased dramatically during the last 50 years due to the combustion of fossil fuels and other hydrocarbons. Today, there is an international inclination to moderate the release of CO_2 into the atmosphere. Carbon dioxide capture and sequestration can play a crucial role in achieving emission cuts required to control greenhouse gas levels.[1]

Analytical scientists and separation engineers require an understanding of pK_a because it impacts the choice of techniques used to identify and isolate the compounds of interest. pK_a is the core property of any electrolyte and defines its biological and chemical behavior. In biological terms, the pK_a value will give an idea about where the molecule will be found with a polar phase or nonpolar phase (partition). From a computational chemistry point of view, pK_a calculations are a benchmark for quantum mechanical and free solvation energy calculations.

Aqueous solutions of alkanolamines such as monoethanolamine (MEA) are the most commercially used chemical solvents in postcombustion CO_2 capture technologies, and their applications in this process have been studied extensively. Recently, other aqueous solutions of diamines such as piperazine became of interest to scientists due to their fast reaction rate with CO_2. Studies show that piperazine has a much faster reaction rate compared to MEA (the most commonly used solvent in CO_2 capture technology).[2] Diamines (for example, piperazine) are also known to have a higher capacity (solubility) for CO_2 absorption than monoamines and can reach very high loading (higher than 3 mol CO_2/mol piperazine) at very high CO_2 partial pressures. However, the absence of a hydroxyl group in piperazine makes it less soluble in water at high concentrations. The solvent is therefore usually proposed, for now, as an additive to other slower reacting alkanolamines such as methyldiethanolamine (MDEA).[3−7]

The basicity of the solvent, quantified by the pK_a of its conjugate acid, is a key factor for the reaction rate and absorption capacity of the solvent in the process. A linear relationship between the pK_a of an acid or base with its catalytic effect on reaction rate was reported by Brønsted et al.[8] In previous work, a Brønsted relationship between the rate constant of the reaction of amines with CO_2 and the basicity of such amines was investigated.[2,9−14]

The pK_a values of many alkanolamines (mostly conventional amines) at different temperatures are available in the literature.[15−18] However, the pK_a values of less common amines, especially piperazines, have not been reported yet. In this work, the pK_a values of a series of six piperazines (diamines) were determined at different temperatures.

Table 1. pH Values of the Calibration Buffers

T/K	pH buffer 1	 buffer 2	 buffer 3
298	4.00 ± 0.00	7.00 ± 0.03	10.00 ± 0.00
303	4.01 ± 0.02	6.99 ± 0.03	9.95 ± 0.05
313	4.03 ± 0.03	6.97 ± 0.00	9.87 ± 0.03
323	4.06 ± 0.02	6.98 ± 0.05	9.81 ± 0.03

Table 2. Comparison for First pK_a of Piperazine with Literature Values

piperazine	T/K 298	 303	 313	 323
Hetzler et al.[22]	5.33	5.24	5.06	4.89
Hamborg and Versteeg[25]	5.41	5.31	5.14	4.96
Pagano et al.[23]	-	5.54	5.37	-
Enea et al.[24]	4.63	5.67	5.47	4.18
this work	5.35	5.27	5.02	4.93

Table 3. Comparison for the Second pK_a of Piperazine with Literature Values

piperazine	T/K 298	 303	 313	 323
Hetzler et al.[22]	9.73	9.61	9.37	9.14
Hamborg and Versteeg[25]	9.71	9.59	9.35	9.12
Pagano et al.[23]	-	9.68	9.48	-
Enea et al.[24]	9.76	9.69	9.48	-
this work	9.73	9.66	9.37	9.14

Chemicals and Apparatus

Piperazine, 2-methylpiperazine, 1-methylpiperazine, 1-ethylpiperazine, 1-(2-hydroxyethyl)piperazine, and 1,4-dimeth-

---

[*] To whom correspondence should be addressed. Tel.: 966 3 872 5304. E-mail: amr.henni@aramco.com.

[†] Department of Industrial Systems Engineering.

[‡] Department of Chemistry and Biochemistry.

[§] R & D Centre Saudi Aramco.

10.1021/je900005c CCC: $40.75

Table 4. First pK_a Values of Amines at Different Temperatures

	T/K			
amine	298	303	313	323
piperazine	9.73 ± 0.02	9.66 ± 0.03	9.39 ± 0.05	9.17 ± 0.03
2-methylpiperazine	9.57 ± 0.03	9.46 ± 0.03	9.16 ± 0.04	8.97 ± 0.02
1-methylpiperazine	9.14 ± 0.03	8.99 ± 0.02	8.79 ± 0.03	8.65 ± 0.05
1-ethylpiperazine	9.20 ± 0.02	9.08 ± 0.02	8.93 ± 0.04	8.72 ± 0.06
1-(2-hydroxylethyl)piperazine	9.09 ± 0.03	8.95 ± 0.04	8.75 ± 0.05	8.63 ± 0.02
1,4-dimethylpiperazine	8.38 ± 0.01	8.27 ± 0.03	8.06 ± 0.04	7.84 ± 0.05

Table 5. Second pK_a Values of Amines at Different Temperatures

	T/K			
amine	298	303	313	323
piperazine	5.35 ± 0.04	5.27 ± 0.05	5.02 ± 0.01	4.93 ± 0.02
2-methylpiperazine	5.24 ± 0.03	5.19 ± 0.03	4.92 ± 0.04	4.84 ± 0.02
1-methylpiperazine	4.63 ± 0.03	4.40 ± 0.02	4.31 ± 0.03	4.18 ± 0.03
1-ethylpiperazine	4.76 ± 0.04	4.58 ± 0.05	4.48 ± 0.02	4.31 ± 0.05
1-(2-hydroxylethyl)piperazine	3.92 ± 0.06	3.89 ± 0.04	3.74 ± 0.02	3.60 ± 0.05
1,4-dimethylpiperazine	3.81 ± 0.03	3.70 ± 0.04	3.64 ± 0.03	3.45 ± 0.04

Table 6. Thermodynamic Quantities for the Dissociation of Amines in Aqueous Solution

	first dissociation, ($K_{a(1)}$)		second dissociation, ($K_{a(2)}$)	
amine	$\Delta H°$/kJ·mol^{-1}	$\Delta S°$/kJ·(mol·K)$^{-1}$	$\Delta H°$/kJ·mol^{-1}	$\Delta S°$/kJ·(mol·K)$^{-1}$
piperazine (literature)	42.9,[22]38.9,[23] 35.6,[24] 42.8[25]	−0.042,[22] −0.042[25]	31.1,[22]26.0,[23] 31.8,[24] 32.3[25]	0.002,[22]0.005[25]
piperazine	44.2[a]	−0.040	31.9[b]	0.004
2-methylpiperazine	45.6[c]	−0.030	32.0[d]	0.007
1-methylpiperazine	34.0[d]	−0.060	29.9[e]	0.013
1-ethylpiperazine	34.7[a]	−0.059	30.6[f]	0.012
1-(2-hydroxylethyl) piperazine	33.8[g]	−0.060	24.4[c]	0.006
1,4-dimethylpiperazine	39.7[a]	−0.027	24.5[d]	0.009

[a] Ref 22. [b] $R^2 = 1.00$. [c] $R^2 = 0.97$. [d] $R^2 = 0.99$. [e] $R^2 = 0.95$. [f] $R^2 = 0.99$. [g] $R^2 = 0.96$. [h] $R^2 = 0.98$.

ylpiperazine with a purity ≥ 98 % were purchased from Sigma-Aldrich. A pH meter, model 270 Denver Instrument, was used to determine the pH values of solutions. The pH meter electrode was calibrated at each required temperature using buffer solutions. The buffer solutions were supplied by VWR International with a precision of (± 0.01) for pH 4.00 and 7.00 and (± 0.02) for pH 10.00. The pH values of the buffer solutions at different temperatures are reported in Table 1. The solutions were prepared using deionized double distilled water. Hydrochloric acid solution (HCl) 0.1000 M (± 0.002) was purchased from VWR International. High purity nitrogen gas (≥ 99.99 %) was provided by Praxair for blanketing the solutions during the titration. A jacket beaker was employed to keep the temperature constant during the titration.

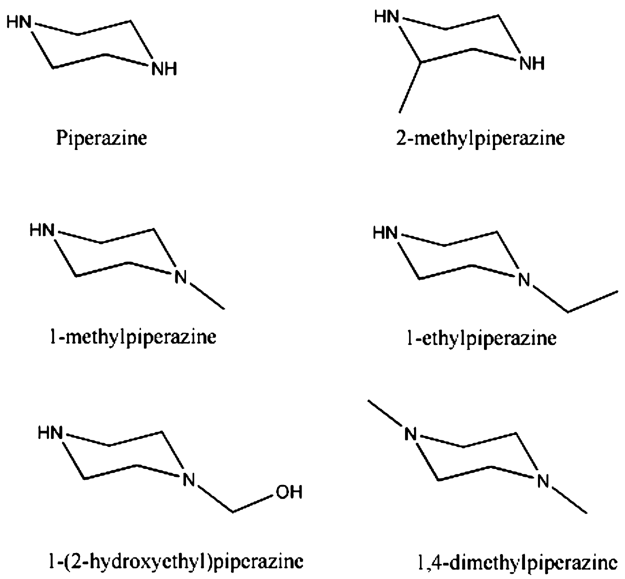

Figure 1. Structures of the studied amines.

Experimental Procedure

Aqueous solutions of amines at 0.010 M (± 0.005) were prepared using deionized double distilled water. The required temperature of titration was set, and then the pH meter was calibrated using buffer solutions. The solution was brought to the required temperature while being blanketed with a slow stream of nitrogen. The amine solutions (50 mL) were titrated with a 0.1000 M aqueous solution of hydrochloric acid. The titrant was added in 20 equal portions, each portion being 0.5 mL. After each addition of the titrant, the pH value was read as soon as equilibrium was reached. The pK_a values were determined using the Albert and Serjeant procedure.[19]

The ionic strength (I) is defined as

$$I = 0.5 \sum C_i z^2 \qquad (1)$$

where C_i is the molecular concentration of an ion and z is its valency.

The following equation converts the concentration of an ionized species (BH^+) to its activity

$$\{BH^+\} = [BH^+] \cdot (\gamma_{BH})^+ \qquad (2)$$

where ($\gamma_{BH}{}^+$) is the activity coefficient of the ionized species and is usually less than one. The activity coefficient of the nonionized species (γ_B) was set equal to one.

With the very weak ionic strength of the solution studied here, the ionic activity coefficients were calculated by the Debye–Hückel equation

$$-\log(\gamma_i) = \frac{Az_i^2 I^{1/2}}{1 + Bk_i I^{1/2}} \quad (3)$$

where the terms A and B are the Debye–Hückel equation constants, which depended on the dielectric constant and temperature of the solvent; z_i is the ion valence; the term k_i is the ionic size parameter, i.e., the mean distance of approach of the ions; and I represents the ionic strength and depends on the concentration of the solution. The values of A and B at different temperatures were obtained from Manov et al.,[20] and the ionic size parameter (k_i) values were taken from Kielland et al.[21]

Results and Discussion

The first and second dissociation constants of piperazine in water were measured by Hetzer et al.,[22] Pagano et al.,[23] and Enea et al.[24] Hamborg and Versteeg[25] also published new $\mathrm{p}K_a$ data for piperazine and other amines while this manuscript was under review. Comparisons with literature values for piperazine are shown in Tables 2 and 3.

Values of $\mathrm{p}K_{a(1)}$ measured in this study, when compared to the values reported by Hetzer et al.,[22] Pagano et al.,[23] Enea et al.,[24] and Hamborg and Versteeg,[25] deviated by 0.13 %, 0.95 %, 0.59 %, and 0.34 %, respectively. Values of $\mathrm{p}K_{a(2)}$ measured in this study, when compared to the values reported by Hetzer et al.,[22] Pagano et al.,[23] Enea et al.,[24] and Hamborg and Versteeg,[25] deviated by 0.63 %, 6.04 %, 11.31 %, and 1.21 %, respectively. As reported by Hamborg and Versteeg, the $\mathrm{p}K_a$ values had larger deviations with published values for the second dissociation than the first.

Tables 4 and 5 show the values of the first and second $\mathrm{p}K_a$ of the amines, respectively. The values of the ionic strength, I, were quite low and less than 0.009 for the first dissociation and less than 0.02 for the second.

Among the amines studied in this work, piperazine and 2-methylpiperazine have the highest $\mathrm{p}K_a$ values, and 1,4-dimethylpiperazine has the lowest value. Generally, secondary amines are stronger bases than their corresponding tertiary amines. Thus, 1,4-dimethylpiperazine, with two tertiary amine groups, is the weakest base, and piperazine and 2-methylpiperazine, with two secondary amine groups, are the most basic amines. Due to a steric effect, 2-methylpiperazine is a weaker base than piperazine. The methyl group on the α carbon in this amine (Figure 1) causes steric hindrance to the solvation on the cation formation which lowers the basicity. Intramolecular hydrogen bonding also lowers the basicity. Consequently, 1-(2-hydroxyethyl)piperazine, an alkanolamine with an intramolecular hydrogen bonding tendency, has as a lower $\mathrm{p}K_a$ value than 1-ethylpiperazine.[26]

Table 7. Thermodynamic Quantities for the Dissociation of Various Amines in Aqueous Solution

amine	$\Delta H°$ kJ·mol^{-1}	$\mathrm{p}K_a$
monoethanolamine (MEA)[25]	48.6	9.44
diethanolamine (DEA)[27]	42.8	8.88
triethanolamine (TEA)[25]	31.1	7.72
methyldiethanolamine (MDEA)[28]	34.9	8.56
hydroxyethylpiperazine (HEPZ)[25]	35.4	8.92
	21.2	3.97
3-amino-1-propanol (MPA)[29]	53.6	9.96
2-amino-2-methyl-1-propanol (AMP)[25]	52.2	9.68
2-(2-aminoethoxy)ethanol (DGA)[30]	50.2	9.42
diisopropanolamine (DIPA)[25]	39.2	8.84
1-amino-2-propanol (MIPA)[25]	48.8	9.45

To summarize and provide a clear picture of the change of $\mathrm{p}K_a$ with the addition of the different radicals to piperazine, we propose the following rules. Starting with the piperazine molecule with two secondary amines, the addition of a methyl group on any carbon of the ring introduces a hindrance effect and lowers the $\mathrm{p}K_a$. The addition of an ethyl group to piperazine further lowers the $\mathrm{p}K_a$. The addition of a methyl group lowers the $\mathrm{p}K_a$ more than in the case of an ethyl group. The addition of a hydroxyl group to 1-ethylpiperazine or a hydroxyethyl group to piperazine reduces the $\mathrm{p}K_a$ further than any previous addition (hydrogen bonding). Finally, the addition of a methyl radical to each secondary amine of piperazine to form two tertiary amines (1,4-dimethylpiperazine) leads to the lowest $\mathrm{p}K_a$. These conclusions are valid for the first and second $\mathrm{p}K_a$ of the amines considered in this study.

The standard state enthalpy change ($\Delta H°$) and standard state entropy change ($\Delta S°$) of both dissociation processes of each amine were calculated using the van't Hoff equation

$$\ln K = \frac{-\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \quad (4)$$

The results are presented in Table 6. Values for $\Delta H°$ and $\mathrm{p}K_a$ for other primary, secondary, and tertiary amines of importance in gas sweetening are presented in Table 7.

In the present study, $\Delta S°$ values were almost negligible compared to the contribution of the ($\Delta H°/T$) term. The higher the value of $\Delta H°$, the larger is the shift in basicity from low temperature (high basicity leading to better absorption of CO_2) to the higher temperature (lower basicity leading to better regeneration of CO_2). Accordingly, 2-methylpiperazine and piperazine should be the most attractive amines for gas sweetening in terms of cyclic capacity.

Literature Cited

(1) Wilson, E. J.; Gerard, D. *Carbon Capture and Sequestration: Integrating Technology, Monitoring and Regulation*; Blackwell Pub., 2007.

(2) Cullinane, J. T.; Rochelle, G. T. Kinetics of Carbon Dioxide Absorption into Aqueous Potassium Carbonate and Piperazine. *Ind. Eng. Chem. Res.* **2006**, *45*, 2531–2545.

(3) Appl, M.; Wagner, U.; Henrici, H. J.; Kuessner, K.; Volkamer, F.; Ernst Neust, N. Removal of CO_2 and/or H_2S and/or COS from Gases Containing These Constituents, U.S. Patent 4336233.

(4) Bishnoi, S.; Rochelle, G. T. Thermodynamics of Piperazine/ Methyldiethanolamine/Water/Carbon Dioxide. *Ind. Eng. Chem. Res.* **2002**, *41*, 604–612.

(5) Bishnoi, S.; Rochelle, G. T. Absorption of Carbon Dioxide in Aqueous Piperazine/ Methyldiethanolamine. *AIChE J.* **2002**, *48*, 2788–2799.

(6) Dang, H. CO_2 Absorption Rate and Solubility in Monoethanolamine/ Piperazine/Water, M.Sc. Thesis in Chemical Engineering, University of Texas, Austin, 2001.

(7) Cullinane, J. T.; Rochelle, G. T. Carbon Dioxide Absorption with Aqueous Potassium Carbonate Promoted by Piperazine. *Chem. Eng. Sci.* **2004**, *59*, 3619–3630.

(8) Brønsted, J. N.; Guggenheim, E. A. Contribution to the Theory of Acid and Basic Catalysis: The Mutarotation of Glucose. *J. Am. Chem. Soc.* **1927**, *49*, 2554–2584.

(9) Sharma, M. M. Kinetics of Reactions of Carbonyl Sulphide and Carbon Dioxide with Amines and Catalysis by Brønsted Bases of the Hydrolysis of COS. *Trans. Faraday Soc.* **1965**, *61*, 681–687.

(10) Versteeg, G. F.; van Dijck, L. A. J.; van Swaaij, W. P. M. On the Kinetics Between CO_2 and Alkanolamines both in Aqueous and Non-Aqueous Solution: An Overview. *Chem. Eng. Commun.* **1996**, *144*, 113–158.

(11) Penny, D. E.; Ritter, T. J. Kinetic Study of the Reaction between Carbon Dioxide and Primary Amines. *J. Chem. Soc., Faraday Trans I* **1983**, *79*, 2103–2109.

(12) Blauwhoff, P. M. M.; Versteeg, G. F.; van Swaaij, W. P. M. A Study on the Reaction between CO_2 and Alkanolamines in Aqueous Solutions. *Chem. Eng. Sci.* **1984**, *39*, 207–225.

(13) Littel, R. J.; Versteeg, G. F.; van Swaaij, W. P. M. Kinetics of Carbon Dioxide with Primary and Secondary Amines in Aqueous Solutions. I. Zwitterion Deprotonation Kinetics for DEA and DIPA in Aqueous Blends of Alkanolamines. *Chem. Eng. Sci.* **1992**, *47*, 2027–2035.

(14) Versteeg, G. F.; Oyevaar, M. H. The Reaction between Carbon Dioxide and Diethanolamine at 298 K. *Chem. Eng. Sci.* **1989**, *44*, 1264–1268.

(15) Perrin, D. D. *Dissociation Constants of Organic Bases in Aqueous Solution*; Butterworths: London, 1965; Supplement, 1972.

(16) Xu, S.; Otto, F. D.; Mather, A. E. Dissociation Constants of Some Alkanolamines. *Can. J. Chem.* **1993**, *71*, 1048–1050.

(17) Littel, R. J.; Bos, M.; Knoop, G. J. Dissociation Constants of Some Alkanolamines at 293, 303, 318, and 333 K. *J. Chem. Eng. Data* **1990**, *35*, 276–277.

(18) Xu, S.; Wang, Y.-W.; Otto, F. D.; Mather, A. E. Physicochemical Properties of 2-Piperidineethanol and Its Aqueous Solutions. *J. Chem. Eng. Data* **1992**, *37*, 407.

(19) Albert, A.; Serjeant, E. P. *The Determination of Ionization Constants; A Laboratory Manual*, 3rd ed.; Chapman and Hall: New York, 1984.

(20) Manov, G. G.; Bates, R. G.; Hamer, W. J.; Acree, S. F. Values of the Constants in the Debye-Hückel Equation for Activity Coefficients. *J. Am. Chem. Soc.* **1943**, *65*, 1765–1767.

(21) Kielland, J. Individual Activity Coefficients of Ions in Aqueous Solutions. *J. Am. Chem. Soc.* **1937**, *59*, 1675–1678.

(22) Hetzer, H. B.; Robinson, R. A.; Bates, R. G. Dissociation Constants of Piperazinium Ion and Related Thermodynamic Quantities from 0 to 50°. *J. Phys. Chem.* **1968**, *72*, 2081–2086.

(23) Pagano, J. M.; Golberg, D. E.; Fernelius, W. C. A Thermodynamic Study of Homopiperazine, Piperazine, and N-(2aminoethyl)-piperazine and their Complexes with Copper (II) Ion. *J. Phys. Chem.* **1961**, *65*, 1062–1064.

(24) Enea, O.; Houngbossa, K.; Berton, G. Chaleurs de protonation de la piperazine et de quelques-uns de ses derivés. *Electrochim. Acta* **1972**, *17*, 1585–1594.

(25) Hamborg, E. S.; Versteeg, G. F. Dissociation Constants and Thermodynamic Properties of Amines and Alkanolamines from (293 to 353) K. *J. Chem. Eng. Data* **2009**, *54*, 1318–1328.

(26) Perrin, D. D.; Dempsey, B.; Serjeant, E. P. *pKa Prediction for Organic Acids and Bases*; Chapman and Hall: New York, 1981.

(27) Bower, V. E.; Robinson, R. A.; Bates, R. G. Acidic Dissociation Constant and related Thermodynamic Quantities for Diethanolamonium Ion in Water from 0° to 50 °C. *J. Res. Natl. Bur. Stand.* **1962**, *66A*, 71–71.

(28) Hamborg, E. S.; Niederer, J. P. M.; Versteeg, G. F. Dissociation Constants and Thermodynamic Properties of Amino Acids Used in CO_2 Absorption from (293 to 353) K. *J. Chem. Eng. Data* **2007**, *52*, 2491–2502.

(29) Shwabe, K.; Graichen, W.; Spiethoff, D. Physicochemical Investigations on Alkanolamines. *Z. Phys. Chem. (Munich)* **1959**, *20*, 68–82.

(30) Oscarson, J. L.; Wu, G.; Faux, P. W.; Izatt, R. M.; Christensen, J. J. Thermodynamics of Protonation of Alkanolamines in Aqueous Solution to 325 °C. *Thermochim. Acta* **1989**, *154*, 119–127.

Received for review January 2, 2009. Accepted June 20, 2009.

JE900005C