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The second dissociation constant of carbonic acid in ethanol–water mixture from 5°C to 45°C[1]

Jia-Zhen Yang[a,*], Dian-Zhen Lu[a], Chao-Jun Hou[a], Jie Wang[b]

[a]*Department of Chemistry, Liaoning University, Shenyang 110036, China*
[b]*Department of Chemistry, Liaoning Education College, Shenyang 110031, China*

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Abstract

The determination of the second dissociation constant of carbonic acid in 5, 15 and 25 mass% ethanol–water mixed solvents has been made with a cell of the type: Pt, H_2 (101.325 kPa) |$NaHCO_3$ (m_1), Na_2CO_3 (m_2), NaCl (m_3), X mass% ethanol+Water| AgCl–Ag at 278.15–318.15 K. The dependence of pK_2 on temperature is given by pK_2=A_1+A_2/T+A_3T.

According to thermodynamic relationship and above equation, the thermodynamic quantities for the dissociation process were determined. The dependence of pK_2 on the dielectric constant of mixed solvent is discussed in terms of Beveradge model. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thermodynamics; Dissociation constant; Mixed solvent ethanol; Carbonate; Bicarbonate; Activity coefficient

1. Introduction

The effect of ethanol–water mixture on the second dissociation constant of carbonic acid is of interest not only for biologists but also for analytical chemists and chemical engineers, because it may provide useful information with regard to the identification of the nature of the solute–solvent interaction patterns in binary solvent system [1,2].

As a part of the continuing studies of thermodynamic properties of the CO_2-carbonate–bicarbonate system in mixed solvents [3–5], this paper reports that the second dissociation constants of carbonic acid, K_2, were determined at five temperatures from 278.15 to 318.15 K in 5, 15 and 25 mass% ethanol–water mixed solvents from precise emf measurements with cell (A) of a type without liquid junction: Pt, H_2 (101.325 kPa) |$NaHCO_3$ (m_1), Na_2CO_3 (m_2), NaCl (m_3), X mass% ethanol–water| AgCl–Ag.

The dependence of pK_2 on temperature has been obtained and the entropy and enthalpy of the dissociation process of HCO_3^- in the mixed solvents was calculated. The effect of ethanol on the solvent properties and the interaction of ethanol with a mixture of carbonate, bicarbonate and chloride is discussed.

2. Experimental

Deionized water was distilled in a quartz-still. Its conductivity was 0.9–1.4×10^{-4} Sm^{-1}. Hydrochloric acid was prepared from constant-boiling acid, double distilled from the AR grade acid, the first and last

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*Corresponding author. Fax: +86-024-86852421.

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fractions being rejected. The acid was standardized by a gravimetric determination of chloride as AgCl. The average difference among five determinations was less than ±0.05%. Sodium carbonate (GR grade) was dried under reduced pressure. Absolute ethanol, which was AR grade, was distilled from Grinard reagent over a 100 cm long column after drying on molecular sieves 3 Å. The middle fraction was collected. The stock solution was made by introducing one-half equivalent of a standardized hydrochloric acid solution to a standardized sodium carbonate solution whereby the carbonate, bicarbonate and chloride were approximately present in a 1:1:1 molar ratio. The acid was added very carefully drop by drop in order to avoid the loss of carbon dioxide by local action.

All solutions to be measured were freshly prepared by weighing with calibration of air buoyancy. The molalities of all run solutions were known to be within ±0.03%.

The silver–silver chloride electrodes were of the thermal electrolytic type [6] and aged in 0.1 mol kg^{-1} HCl solution, which was deoxygenated by bubbling hydrogen. Three days after preparation, the finished electrodes were intercompared and had bias potentials usually less than ±0.04 mV. Standard electrode potentials of silver–silver chloride in pure water were measured by Bates's method [7] and are listed in Table 1. White's data [8] are also listed in Table 1, and agreed with our data within the experimental error. Standard electrode potentials of silver–silver chloride in the mixed solvents were measured by the same method [5] and are listed in Table 1 also. Compared with Patterson's data [9], the values of the potentials in the mixed solvents are reasonable.

The hydrogen electrodes were slightly coated with the platinum black according to the recommendation of Hill and Ives [10]. Hydrogen was purified in the usual manner [10].

The cells were made of glass with four isothermal presaturators containing the same solution as which in the measurements. The cells were thermostated at each temperature with an accuracy of ±0.02 K.

All measurements were made with two Ag–AgCl electrodes and two hydrogen electrodes. The equilibrium was reached about 3–4 h after the initiation of hydrogen bubbling. The potentials of the cell (A) were measured at 278.15, 288.15, 298.15, 308.15, 318.15 K by means of a UJ-25-type potentiometer which was calibrated against a standard cell. A mirror-type galvanometer was used as null detector. The criterion for the attainment of equilibrium was a steady reading within ±0.05 mV for a period of about 1 h. The deviation of readings of four cells was less than ±0.1 mV. The emf was measured at 298.15 K at the beginning, in the middle, and at the end of each run. These three readings agreed within ±0.1 mV.

The atmospheric pressure was measured by a barometer and was calibrated for temperatures, the height, and the degree of latitude. The observed values of emf were converted to a hydrogen partial pressure of 101.325 kPa.

3. Results and discussion

3.1. *Extrapolation to determine the second standard dissociation constant of carbonic acid*

The corrected emfs of cell (A) in the temperature range 278.15–318.15 K in ethanol–water solvents

Table 1
Standard potential of the silver–silver chloride electrode in pure water and ethanol–water mixed solvents at different temperatures

	E^0 (V) at T (K)				
	278.15	288.15	298.15	308.15	318.15
0% Ethanol–water					
Expt. lit. [8]	0.23428	0.22871	0.22252	0.21578	0.20845
	0.23410	0.22857	0.22238	0.21566	0.20836
5% Ethanol–water					
	0.22825	0.22303	0.21726	0.21026	0.20300
15% Ethanol–water					
	0.22091	0.21638	0.21119	0.20436	0.19746
25% Ethanol–water					
	0.21413	0.21029	0.20464	0.19752	0.18995

Table 2
Emf values in V for cell (A) corrected to 101. 325 kPa at different temperatures

10^2m_1 (mol kg^{-1})	10^2m_2 (mol kg^{-1})	10^2m_3 (mol kg^{-1})	T (K)				
			278.15	288.15	298.15	308.15	318.15
5% Ethanol–water							
0.7998	0.7758	0.7998	0.91997	0.92827	0.94051	0.95135	0.96188
1.201	1.165	1.201	0.90095	0.92101	0.93265	0.94436	0.95583
1.603	1.555	1.603	0.90139	0.91237	0.92316	0.93508	0.94595
2.005	1.945	2.005	0.89523	0.90634	0.91775	0.92910	0.94049
2.409	2.337	2.409	0.89003	0.90017	0.91105	0.92184	0.93238
2.813	2.729	2.813	0.88542	0.89620	0.90713	0.91845	0.92947
4.031	3.910	4.031	0.87514	0.88550	0.89585	0.91728	0.91728
pK_2			10.626	10.457	10.352	10.269	10.190
10^3S_K			6.0	7.7	5.4	5.1	8.2
15% Ethanol–water							
0.7935	0.7939	0.7935	0.93248	0.94491	0.95715	0.96847	0.97881
1.191	1.192	1.191	0.92190	0.93332	0.94494	0.95720	0.96943
1.590	1.591	1.590	0.91325	0.92446	0.93587	0.94735	0.95994
1.990	1.991	1.990	0.90683	0.91815	0.92983	0.94142	0.95242
2.390	2.391	2.390	0.90113	0.91263	0.92409	0.93563	0.96433
2.791	2.792	2.791	0.89653	0.90792	0.91915	0.93072	0.94098
3.999	4.001	3.999	0.88558	0.89669	0.90768	0.91862	0.92933
pK_2			10.993	10.847	10.726	10.641	10.577
10^3S_K			2.7	2.9	5.4	6.4	7.5
25% Ethanol–water							
0.7935	0.7938	0.7935	0.94488	0.95705	0.96855	0.97951	0.98698
1.198	1.199	1.198	0.93338	0.94551	0.95689	0.96829	0.97896
1.590	1.591	1.590	0.92497	0.93682	0.94822	0.95904	0.97003
1.990	1.990	1.990	0.91834	0.93025	0.94140	0.95232	0.96331
2.390	2.391	2.390	0.91292	0.92424	0.93543	0.94630	0.95706
2.791	2.792	2.791	0.90802	0.91939	0.93051	0.94115	0.95196
3.999	4.001	3.999	0.89660	0.90763	0.91823	0.92886	0.93908
pK_2			11.373	11.220	11.101	11.023	10.932
10^3S_K			1.5	2.4	2.0	5.1	7.0

with 5, 15 and 25 mass% are listed in Table 2, where each emf value is also the average of four measurements in different cells.

In ethanol–water mixture, the second dissociation process of carbonic acid is:

$$\mathrm{HCO_3^-} = \mathrm{CO_3^{2-}} + \mathrm{H^+}$$

The second dissociation constant, K_2, is given by

$$K_2 = (m_{\mathrm{CO_3}}/m_{\mathrm{HCO_3}})(m_{\mathrm{H}}/m^0)(\gamma_{\mathrm{CO_3}}\gamma_{\mathrm{H}}/\gamma_{\mathrm{HCO_3}}). \tag{1}$$

The substitution of Eq. (1) into the Nernst equation of cell (A) yields Eq. (2):

$$(E - E^0)/k = \mathrm{p}K_2 - \log(m_{\mathrm{HCO_3}}/m_{\mathrm{CO_3}})(m_{\mathrm{Cl}}/m^0) - \log(\gamma_{\mathrm{HCO_3}}\gamma_{\mathrm{Cl}}/\gamma_{\mathrm{CO_3}}). \tag{2}$$

In Eqs. (1) and (2), m_i and γ_i are molality and activity coefficient of species i, respectively. γ_i can be calculated by the extended Debye-Hückel equation and an extrapolation equation was obtained from rearrangement of the Eq. (2):

$$\begin{aligned}\mathrm{p}K' &= (E - E^0)/k + \log[m_{\mathrm{HCO_3}}m_{\mathrm{Cl}}/m_{\mathrm{CO_3}}m^0] \\ &\quad + 2A(I\rho/C^0)^{1/2}/[1 + Ba^0(I\rho/C^0)^{1/2}] \\ &= \mathrm{p}K_2 - bI/m^0,\end{aligned} \tag{3}$$

where m^0 is the unit molality, C^0 is the unit molarity, I

is the total ionic strength of the cell solution, ρ is the density of the mixed solvent, A and B are the Debye-Hückel parameters, a^0 is the ionic size parameter, b is the empirical parameter and pK' is the extrapolation function which may be calculated from experimental data.

Since the anion CO_3^{2-} undergoes hydrolysis at high pH values:

$$CO_3^{2-} + H_2O = HCO_3^- + OH^-$$

it is necessary to correct the reaction in the extrapolation to determine the value of pK_2. The thermodynamic constant for the hydrolysis reaction, K_h, may be written as

$$K_h = K_w/(K_2 \cdot a_w) = (m_{HCO_3} m_{OH}/m_{CO_3} m^0)(\gamma_{HCO_3}\gamma_{OH}/\gamma_{CO_3}/a_w), \quad (4)$$

$$K_w = a_H \cdot a_{OH} . \quad (5)$$

From these two equations, we obtain

$$(K_w/K_2)(\gamma_{CO_3}/\gamma_{OH}/\gamma_{HCO_3}) = x(m_1/m^0 + x)/(m_2/m^0 - x), \quad (6)$$

where x is molality of OH^-, the ionic activity coefficient, γ_i, may be calculated with the Debye-Hückel equation:

$$\lg(\gamma_{CO_3}/\gamma_{OH}/\gamma_{HCO_3}) = -2A(I\rho/C^0)^{1/2}/(1 + Ba^0(I\rho/C^0)^{1/2}). \quad (7)$$

An examination of this procedure indicates that it is necessary to recalculate the ionic strength at each temperature, since the ratio of molalities used in the first approximation of the ionic strength is changed by hydrolysis. This, in turn, required a recalculation of the right-hand member of Eq. (3). The change caused by this computation is quite small compared with that in the extrapolation function caused by hydrolysis correction of the ratio of the molalities.

The least-squares estimate of the intercept for the linear regression of pK' vs I from Eq. (3) was termed as pK_2 and its deviation S_K. These values are listed in Table 2. From Table 2, it is found the pK_2 of carbonic acid at 298.15 K is 10.352, 10.726, and 11.101 in ethanol–water solvents with 5, 15, and 25 mass%, respectively, as compared with 10.329 in pure water at the same temperature. It is evident from the above data that the anion, HCO_3^-, decreases in acidic strength when ethanol is added to pure water. In other words, the anion HCO_3^- is more stable in ethanol–water mixed solvents than in pure water.

Table 3
The values of parameters, A_i

	A_1	A_2	$A_3 \times 10^2$	$s \times 10^3$
5 Mass% ethanol–water	−13.118	3961.8	3.414	5.1
15 Mass% ethanol–water	−15.91	4427.7	3.951	4.5
25 Mass% ethanol–water	−9.494	3543.2	2.922	7.8

3.2. The dependence of pK_2 on temperature

The values of pK_2 obtained in ethanol–water solvents with 5, 15, and 25 mass% at different temperature have been fitted by the method of least-squares by an empirical equation [11]:

$$pK_2 = A_1 + A_2/T + A_3 T. \quad (8)$$

The values of the parameters A_i are listed in Table 3.

The standard molar thermodynamic quantities for the dissociation process ΔG^0, ΔH^0, ΔS^0 and ΔC_p^0 are related to the parameters of Eq. (8):

$$\Delta G^0 = R\ln 10(A_1 T + A_2 + A_3 T^2), \quad (9)$$

$$\Delta H^0 = R\ln 10(A_2 - A_3 T^2), \quad (10)$$

$$\Delta S^0 = -R\ln 10(A_1 + 2A_3 T), \quad (11)$$

$$\Delta C_p^0 = -2R\ln 10 A_3 T. \quad (12)$$

The values are listed in Table 4.

Since entropy rather than enthalpy changes are usually a better indicator of structural implications in the solutions, analysis of ΔS^0 values should be more rewarding. The dissociation of anion HCO_3^- results in order-producing ions such as H^+ and CO_3^{2-} which gives negative contributions to ΔS^0. In fact, the values of ΔS^0 for the dissociation process decrease with increasing ethanol content in the mixed solvent. This trend shows that the structure of the mixed solvents lost when ethanol is added into pure water.

3.3. The dependence of pK_2 on dielectric constant

The linear regressions of pK_2 obtained in ethanol–water solvents with 0 [1], 5, 10 [12], 15, and 25 mass%

Table 4
Thermodynamic quantities for the second dissociations of carbonic acid in 5, 15 and 25 mass% ethanol–water at different temperatures

T (K)	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J K^{-1} mol^{-1})	ΔC_p^0 (J K^{-1}mol^{-1})
5% Ethanol–water				
278.15	56.56	25.28	−112	−364
288.15	57.75	21.58	−125	−377
298.15	59.07	17.75	−139	−390
308.15	60.52	13.78	−152	−403
318.15	62.10	9.69	−164	−416
15% Ethanol–water				
278.15	58.58	26.24	−116	−420
288.15	59.82	21.96	−131	−436
298.15	61.21	17.53	−146	−451
308.15	62.75	12.94	−162	−466
318.15	64.44	8.20	−179	−481
25% Ethanol–water				
278.15	60.62	33.91	−96.0	−311
288.15	61.72	26.00	−124	−322
298.15	63.09	17.81	−152	−334
308.15	64.75	9.34	−180	−345
318.15	66.69	5.91	−209	−356

vs $1/D$ (reciprocal dielectric constant of corresponding mixed solvent) at constant temperature, gives a linear empirical equation:

$$\mathrm{p}K_2 = g + h/D, \tag{13}$$

where g and h are empirical parameters. The values of these parameters and their standard deviation of the fitting, s, are listed in Table 5.

For the second dissociation process of carbonic acid the standard free energy change, ΔG^0, can be expressed in following equation:

$$\Delta G^0 = \Delta G^0_{\mathrm{H}+} + \Delta G^0_{\mathrm{CO}_3^-} - \Delta G^0_{\mathrm{HCO}_3^-} \tag{14}$$

where ΔG^0_i is the standard solvation free energy of ion, i. As we pointed out in previous work [13], ΔG^0_i can be assumed to consist of an electrostatic part, ΔG^0_i (el), resulting from a change in the dielectric constant of the medium, and a non-electrostatic part, ΔG^0_i (non), resulting from specific chemical interactions between the ions and the mixed solvent which depends on the basicity of the solvent. Thus

$$\Delta G^0_\mathrm{i} = \Delta G^0_\mathrm{i}\ (\mathrm{el}) + \Delta G^0_\mathrm{i}\ (\mathrm{non}). \tag{15}$$

Some authors have applied a Born model to calculate ΔG^0_i (el) [14,15], but the Born model has been criticized. One reason for its failure is that it does not consider the dielectric saturation effect near the ionic cophere. However, we propose to apply the concentric continua model proposed by Beveridge [16], who gave a theoretical treatment for the energy of an arbitrary charge distribution embedded in a central spherical cavity surrounded by two concentric dielectric continua. According to this model and our previous work [13], ΔG^0_i (el) may be calculated from:

$$\Delta G^0_\mathrm{i}\ (\mathrm{el}) = (Z_\mathrm{i}^2 e^2 N/J)[-(b_\mathrm{i} + a_\mathrm{i})/(4a_\mathrm{i}b_\mathrm{i}) + 1/(2b_\mathrm{i}D)], \tag{16}$$

where a_i is the radius of ion, i, $b_\mathrm{i}=a_\mathrm{i}+\Delta$, Δ is the thickness of the first solvent shell, N is the Avogadro constant, e is the electron charge, Z_i is the ionic charge, D, D_i, D_loc (according to Abraham [17], D_i=1,

Table 5
The values of parameters, g and h, in Eq. (13) and the standard deviation of the fitting, s

T (K)	h	g	$s\times10^2$
278.15	355.8	6.389	2.8
288.15	323.8	6.439	2.6
298.15	280.5	6.739	5.6
308.15	262.4	6.705	4.7
318.15	235.7	6.851	5.4

D_{loc}=2) are the dielectric constants of bulk solvent, ion and first solvent shell, respectively, J is the conversion factor of energy. Combining above equations, we can obtain the following equation:

$$\begin{aligned}\mathrm{p}K_2 = (RT\ln 10)^{-1}\Big\{\sum \Delta G_{\mathrm{i}}^{0}(\mathrm{non}) - (e^2N/J) \\ \times \sum \big[Z_{\mathrm{i}}^2(a_{\mathrm{i}} + b_{\mathrm{i}})/(4a_{\mathrm{i}}b_{\mathrm{i}})\big] \\ + \big[(e^2N)/(JRT\ln 10)\big]\sum (Z_i^2/2b_i)/D\Big\}.\end{aligned} \tag{17}$$

When Eq. (17) was compared with the empirical Eq. (13), it is found that

$$\begin{aligned}g = (RT\ln 10)^{-1}\Big\{\sum \Delta G_{\mathrm{i}}^{0}\ (\mathrm{non}) - (e^2N/J) \\ \times \sum \big[Z_{\mathrm{i}}^2(b_{\mathrm{i}} + a_{\mathrm{i}})/(4a_{\mathrm{i}}b_{\mathrm{i}})\big]\Big\},\end{aligned} \tag{18}$$

and

$$h = \big[(e^2N)/(JRT\ln 10)\big]\sum (Z_{\mathrm{i}}^2/2b_{\mathrm{i}}). \tag{19}$$

Plots of g or h obtained from our experiments vs $1/T$, produce approximately straight lines. Thus, it may be considered that ions in mixed solvents of ethanol and water can only be solvated by the water molecules.

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