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Thermochimica Acta 308 (1998) 171–176

thermochimica
acta

Thermodynamics of carbonate in mixed solvent II
The system of $Na_2CO_3+NaHCO_3+NaCl+15$ mass% glucose+water[1]

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Received 26 August 1996; accepted 17 June 1997

Abstract

The determination of the second dissociation constant of carbonic acid in 15 mass% glucose–water mixed solvent, K_2, has been made on cell of the type: Pt, H_2 (101.325 kPa) $|Na_2CO_3$ (m_1), $NaHCO_3$ (m_2), NaCl (m_3), 15 mass% glucose+water$|$ AgCl–Ag at 278.15–318.15 K. The dependence of pK_2 on temperature has been obtained, that is, $pK_2=-52.01+9561.2/T+9.955\times10^{-2}T$. The maximum value of K_2 in the mixed solvent is found to occur at 310.0 K and the value of pK_2 is 9.683 at this temperature. However, the maximum value of K_2 in pure water occurs at 349.3 K and pK_2 (W)=10.121. It is evident that HCO_3^- species increases in acidic strength and that the temperature occurred maximum value of K_2 decreases when glucose is added to a solvent that is initially pure water. © 1998 Elsevier Science B.V.

Keywords: Bicarbonate; Carbonate; Dissociation constant; Emf; Glucose; Solute–solvent interaction; Thermodynamics

1. Introduction

The cell (A) without liquid junction

$$\mathrm{Pt, H_2(101.325\,kPa)|Na_2CO_3}(m_1), \mathrm{NaHCO_3}(m_2), \mathrm{NaCl}(m_3)|\mathrm{AgCl-Ag} \qquad (A)$$

has early been employed to determine the dissociation constant of HCO_3^-, K_2, at some temperatures [1]. Roy et al. [2] have demonstrated the applicability of the ion-interaction theory of Pitzer and its extension of mixed strong electrolytes by Pitzer and Kim [3] to cell (A) including mixture of carbonate, bicarbonate, and chloride ions. Explicit consideration of the dissociation and disproportionation equilibria:

$$\mathrm{CO_3^{2-}(aq) + H_2O(l) = HCO_3^-(aq) + OH^-(aq)} \qquad (1)$$

$$\mathrm{2HCO_3^-(aq) = CO_3^{2-}(aq) + CO_2(g) + H_2O(l)} \qquad (2)$$

necessitates the use of mixed-electrolyte theory for even stoichiometrically single-solute systems which contain carbonate or bicarbonate.

The changes of pK_2 value as function of the properties of the solvent which allow for a wide range in the dielectric constant may provide useful information in regard to the identification of the nature of these solute–solvent interaction patterns in binary solvent systems. However, direct measurements of this kind of interaction are difficult to perform. As a part of the continuing studies of thermodynamic properties of

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[1] Presented at the 14th IUPAC Conference on Chemical Thermodynamics, held in Osaka, Japan, 15–30 August, 1996.

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PII S0040-6031(97)00345-6

CO_2–carbonate-bicarbonate in mixed solvents [4,5], we extended these measurements of cell (A) to include the mixed solvent made of 15 mass% glucose and water, that is, measurements of cell (B) have been performed at 278.15–318.15 K:

$$\begin{aligned}&\mathrm{Pt, H_2(101.325\,kPa)|Na_2CO_3}(m_1),\\&\mathrm{NaHCO_3}(m_2), \mathrm{NaCl}(m_3),\\&\mathrm{15\ mass\%\ glucose-water|AgCl-Ag.}\qquad \mathrm{(B)}\end{aligned}$$

At the same time, the dependence of pK_2 on temperature has been obtained, and the entropy, enthalpy and heat capacity of the reverse process of the dissociation for HCO_3^- in the mixed solvent have been calculated. The effect of glucose on the solvent properties and the interaction of aqueous glucose with mixture of carbonate, bicarbonate and chloride, which is of biological and thermodynamic interest, have been discussed.

2. Experimental

Water deionized was distilled in a quartz-still and its conductivity was $(0.9–1.3)\times10^{-4}\,\Omega^{-1}\,m^{-1}$. Stock solution of hydrochloride acid was prepared from the constant-boiling acid double distilled from the AR grade acid. The acid was standardized by a gravimetric determination of chloride as AgCl. The average difference among five replicate determinations was less than ±0.05%. The glucose (or AR grade) and sodium carbonate (of GR grade) were dried under reduced pressure. The stock solutions were made by introducing one-half an equivalent of a standard hydrochloride acid solution to a standard sodium carbonate solution, whereby the carbonate, bicarbonate and chloride were approximately present in a 1:1:1 ratio. The acid was added very carefully drop by drop in order to a void loss of carbon dioxide by local action. Total ionic strength of each run solution is not larger than 1.0 mol/kg.

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 were aged in 0.1 mol/kg HCl, 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. Ours agree with White's within experimental error.

Table 1
Standard potential of the silver–silver chloride electrode in pure water from 278.15 to 318.15 K

	E^0 (V) at T (K)				
	278.15	288.15	298.15	308.15	318.15
Expt.	0.23435	0.22884	0.22238	0.21575	0.20827
Lit. [6]	0.23410	0.22857	0.22238	0.21566	0.20836

The hydrogen electrodes were lightly coated with platinum black, according to the recommendations of Hills and Ives [9]. Hydrogen electrolytically purified in the usual manner [9] served as the source of hydrogen.

The cells were of all-glass construction with four isothermal presaturetors containing the same solution with measurement. These 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 were measured at 278.15, 288.15, 298.15, 308.15 and 318.15 K by means of a UJ-25-type potentiometer that was calibrated against a standard cell. A mirror-type galvanometer was used as a null detector. The criterion for 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 of temperatures and the height and the degree of latitude. Then, observed values of emf were converted to a hydrogen partial pressure of 101.325 kPa.

The densities (ρ) of the mixed solvent over the range of temperatures involved were measured by usual pycnometric technique. The results are listed in Table 2. The dielectric constant (D) of mixed solvent at different temperatures were measured by

Table 2
Density (ρ) and dielectric constant (D) is 15 mass% glucose–water mixed solvent at 278.15–318.15 K

	Value at T (K)				
	278.15	288.15	298.15	308.15	318.15
ρ (g cm^{-3})	1.0615	1.0601	1.0569	1.0527	1.0488
D	82.5	79.0	75.5	72.3	69.5

means of DK-300 type dekemeter, and the results are also listed in Table 2.

3. Results and discussion

The corrected emfs of cell (B) over the temperature range 278.15–318.15 K at total ionic strengths from 0.07 to about 1.0 mol/kg in 15 mass% glucose–water mixed solvent are listed in Table 3, where each emf value is the average of four cells.

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

The cell (B) emf is given by following Nernst equation:

$$(E - E^0)/k = \mathrm{p}K_2 - \log(m_{\mathrm{HCO_3}}/m_{\mathrm{CO_3}}) - \log(m_{\mathrm{Cl}}/m^0) - \log(\gamma_{\mathrm{HCO_3}}\gamma_{\mathrm{Cl}}/\gamma_{\mathrm{CO_3}}), \quad (4)$$

where m^0=1 mol/kg, m_i and γ_i are molality and activity coefficient of species i, respectively, E^0 means the standard potential of Ag–AgCl electrode in 15 mass% glucose–water mixed solvent and its value was taken from Yang [10], pK_2=−log K_2. k=(RT ln 10)/F, R is the gas constant, T is the thermodynamic temperature and F is Faraday constant. Consequently, on the basis of the extended Debye-Hückel equation, an extrapolation working equation can be obtained from rearrangement of the above Eq. (4):

$$\begin{aligned}\mathrm{p}K' &= (E - E^0)/k + \log[m_{\mathrm{HCO_3}}m_{\mathrm{Cl}}/m_{\mathrm{CO_3}}m^0] \\ &\quad + 2A(I\rho/C^0)^{1/2}/[1 + \mathrm{B}a^0[I\rho/C^0)^{1/2}] \\ &= \mathrm{p}K_2 - b(I/m^0), \end{aligned} \quad (5)$$

where C^0=1 mol/dm^3, I is total ionic strength in the cell solution, b is an empirical constant. A and B are Debye-Hückel parameters, a^0 is ion-size parameter, pK' is the extrapolation function which may be obtained from experimental data.

Since the anion CO_3^{2-} undergoes hydrolysis at high pH values, it is necessary to correct the reaction in the extrapolation to determine the value of pK_2:

$$CO_3^{2-} + H_2O = HCO_3^- + OH^-. \quad (6)$$

The thermodynamic constant for this reaction, K_h, may be written as

$$\begin{aligned} K_h &= K_w/(K_a \cdot a_w) \\ &= (m_{\mathrm{HCO_3}}m_{\mathrm{OH}}/m_{\mathrm{CO_3}})(\gamma_{\mathrm{HCO_3}}\gamma_{\mathrm{OH}}/\gamma_{\mathrm{CO_3}}/a_w), \end{aligned} \quad (7)$$

$$K_w = a_H \cdot a_{OH}. \quad (8)$$

Table 3
Emf values in volts for cell (B) corrected to 101.325 kPa at 278.15–318.15 K

10^2 m_1	10^2 m$_2$	10^2 m$_3$	T (K)				
(mol kg)	(mol/kg)	(mol/kg)	278.15	288.15	298.15	308.15	318.15
0.7500	0.7600	0.7600	–	0.87685	0.89075	0.91043	–
0.9800	0.9800	0.9800	0.87447	0.87872	0.88637	0.89901	0.91933
1.960	1.970	1.970	0.86844	0.87619	0.88562	0.89406	0.91271
2.790	2.810	2.810	0.86205	0.87189	0.88225	0.89466	0.90841
3.700	3.720	3.720	0.85265	0.86317	0.87361	0.88375	0.89361
5.620	5.650	5.650	0.84351	0.85425	0.86478	0.87439	0.88461
6.640	6.680	6.680	0.82867	0.84423	0.85725	0.86875	0.88076
7.800	7.850	7.850	0.83764	0.84823	0.85844	0.86881	0.87942
8.930	8.980	8.980	0.83299	0.84354	0.85415	0.86568	0.87724
9.440	9.500	9.500	0.83084	0.84393	0.85531	0.86683	0.87842
19.10	19.21	19.21	0.81746	0.82761	0.83875	0.85068	0.86187
	pK_2		10.054	9.813	9.750	9.685	9.697
	10^2 s_K		2.4	2.6	2.4	2.4	2.5

For these equations we can obtain

$$(K_w/K_2)(\gamma_{CO_3}/\gamma_{OH}/\gamma_{HCO_3}) = m_{OH}(m_2 + m_{OH})/(m_1 - m_{OH}), \quad (9)$$

where m_{OH} the molality of the hydroxide ion in the cell. The activity coefficient function was assumed to be given by

$$\log(\gamma_{CO_3}/\gamma_{OH}/\gamma_{HCO_3}) = -2AI^{1/2}/(1 + Ba^0I^{1/2}). \quad (10)$$

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 have been altered by hydrolysis. This, in turn, required a recalculation of the right-hand member of Eq. (10). The change caused by this computation is quite small as compared with that in the extrapolation function caused by hydrolysis correction of the ratio of the molalities.

Then the least-squares estimate of the intercept for the linear regression of pK' vs. I from Eq. (5) was termed as pK_2 and its standard deviations s_K using the proper values a^0. These values are listed in Table 3. In order to obtain the best linear fit of the data, several values of a^0 (from 0.1 to 0.9 nm) were inserted into the extrapolation equation. The true values of pK_2 were those which gave the smallest standard deviation of regression. It is evident from Table 3 that the pK_2 of carbonic acid at 298.15 K is 9.750 in 15 mass% glucose–water, as compared with 10.329 in pure water at the same temperature. Thus, the acidic strength of the dissociation of HCO_3^- increases when pure water is substituted by 15 mass% glucose–water as the solvent. This observation conforms to the same trend as that of glycine whose pK_2 is 9.702 in 0.1 mol fraction of 1,2-propanediol–water [11] at 298.15 K as compared with 9.780 in pure water at the same temperature [12].

3.2. The dependence of pK$_2$ on temperature

The value pK_2 obtained at different temperature have been fitted by the method of least-squares to an empirical equation [11,13]:

$$pK_2 = A_1 + A_2/T + A_3T. \quad (11)$$

The values of the parameters A_i have been obtained: $A_1=-52.02$, $A_2=9561.2$, $A_3=9.955\times10^{-2}$, with a fitting standard deviation $s_f=2.0\times10^{-3}$. The maximum value of the second dissociation constant of carbonic acid, K_2, in the mixed solvent is found to occur at 310.0 K and the value of pK_2 is 9.683 at this temperature. However, the maximum value of K_2 in pure water occurs at 349.3 K and pK_2 (W)=10.121 [1]. It is evident from the above data that the HCO_3^- species increases in acidic strength as temperature increases and that the temperature occurred maximum values of K_2 decreases when glucose is added to a solvent that is initially pure water.

If the reverse process is considered:

$$H^+ + CO_3^{2-} = HCO_3^-, \quad (12)$$

then the standard molar thermodynamic quantities ΔG^0, ΔH^0, ΔS^0, ΔC_p^0 for the association process (12) are simply related to the parameters of Eq. (11):

$$\Delta G^0 = -R\ln 10(A_1T + A_2 + A_3T^2) \quad (13)$$

$$\Delta H^0 = -R\ln 10(A_2 - A_3T^2) \quad (14)$$

$$\Delta S^0 = R\ln 10(A_1 - 2A_3T) \quad (15)$$

$$\Delta C_p^0 = 2R\ln 10A_3T \quad (16)$$

These values are listed in Table 4.

From Table 4, the values of ΔG^0 for association process (12) are all large negative. It is very evident

Table 4
Thermodynamic quantities for the association reaction $H^+ + CO_3^{2-} = HCO_3^-$ in 15 mass% glucose–water at 278.15–318.15 K

T/K	ΔG^0/kJ mol^{-1}	ΔH^0/kJ mol^{-1}	ΔS^0/J(K mol)$^{-1}$	$-T\Delta S^0$/kJ mol^{-1}	ΔC_p^0/J(K mol)$^{-1}$
318.15	−59.10	9.86	217	−69.86	1213
308.15	−57.13	−2.07	179	−55.06	1174
298.15	−55.53	−13.63	140	−41.90	1136
288.15	−54.32	−24.80	102	−29.52	1098
278.15	−53.48	−35.59	64.3	−17.89	1060

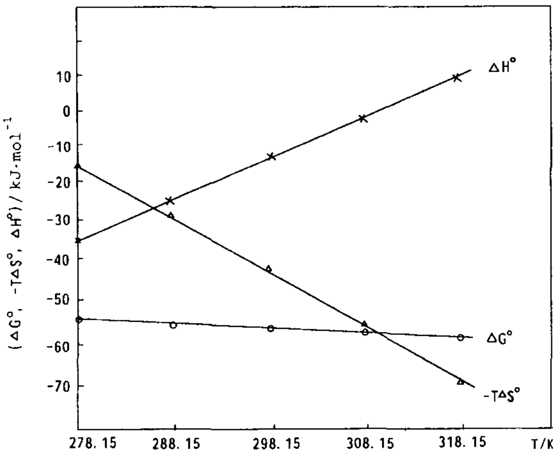

Fig. 1. Driving force of the association process in the mixed solvent. ΔG^0: ○, ΔH^0: ×, $-T\Delta S^0$: △.

that the association process is spontaneous one at constant pressure and temperature. The driving force of the association process (12) is both the association enthalpy, ΔH^0, and association energy, ΔS^0, except at 318.15 K. With temperature increment, ΔH^0 and ΔS^0 increases, and ΔH^0 becomes positive at 318.15 K. These facts mean that the association entropy gradually become a major factor of driving force of the association process with temperature increase. In Fig. 1, it may be demonstrated that the driving force of the association process, $H^+ + CO_3^{2-} = HCO_3^-$, in 15 mass% glucose–water changes with temperature. The same trend has been observed in pure water [1].

The implication of these facts may be discussed in terms of bonding changes (or interaction changes) and changes in the ordering in the system as the association process occurs. If preference solvation of ions in the mixed solvent is suggested, that is, there only are water molecules in the solvation sphere of ions, the overall process is:

$$H^+(H_2O)_x + CO_3^{2-}(H_2O)_y = HCO_3^-(H_2O)_z + (x+y-z)H_2O, \qquad (17)$$

which takes account of hydration of the species in the association process. The process can be viewed as three hypothetically separable steps: (a) a new bond or interaction between H^+ and CO_3^{2-} is formed; (b) the $(x+y-z)$ water molecules are liberated from the hydration spheres of ions; and (c) these liberated waters become bound to bulk mixed solvent. For step (a), ΔH_1^0 and ΔS_1^0 are all expected to be negative. For step (b), ΔH_2^0 and ΔS_2^0 are all expected to be positive as bond and structure are lost, and for step (c), ΔH_3^0 and ΔS_3^0 are expected to be negative. Experimental association entropy ΔS^0 must be sum of above three terms, that is, $\Delta S^0 = \Delta S_1^0 + \Delta S_2^0 + \Delta S_3^0$. By analogy, $\Delta H^0 = \Delta H_1^0 + \Delta H_2^0 + \Delta H_3^0$. From Table 4, $\Delta S^0 > 0$ and the value of ΔS^0 increases while the temperature goes up. The magnitude of the positive changes of ΔS^0 could increase if the number of waters liberated increases with temperature or conversely, if the bulk solvent structure or hydrogen bonding, decreases. The experimental total association enthalpy, ΔH^0, strongly changes with temperature, and becomes positive at 318.15 K, that is, the value of ΔH^0 changes from large negative to little positive when temperature goes up. At these conditions, ΔH^0 opposes association and the predominance of the ΔS^0 increases as temperature increases, resulting from the contribution of an increasingly positive ΔC_p^0 to the two terms. These facts mean that the contribution of the covalent bond (or interaction) to driving force of the association process (12) decreases and the contribution of the ordering in the system gradually becomes essential when temperature goes up.

3.3. The transfer process

The effect of glucose on the solvent of water can be illustrated by transfer thermodynamic function.

With regard to the second dissociation step of carbonic acid, the transfer Gibbs energy of dissociation, ΔG_t^0, pertains to the process

$$H^+(W) + CO_3^{2-}(W) + HCO_4^-(S) = H^+(S) + CO_3^{2-}(S) + HCO_4^-(W), \qquad (18)$$

where W and S indicate water and mixed solvent, respectively. The ΔG_t^0 then can be mathematically expressed by the equation

$$\Delta G_t^0 = (RT \ln 10)[pK_2(S, m) - pK_2(W, m)], \qquad (19)$$

where pK_2 (S, m) is the values obtained in this work, m indicates the values of pK_2 and ΔG_t^0 on the molal scale. The values of pK_2 (W, m) can be obtained from

Table 5
The transfer thermodynamic function of the dissociation process (on mole-fraction scale) for HCO_3^- from water to 15 mass% glucose at 278.15–318.15 K

T/K	ΔG_t^0/kJ mol^{-1}	ΔH_t^0/kJ mol^{-1}	ΔS_t^0/J(K mol)$^{-1}$	ΔC_p^0/J(K mol)$^{-1}$
318.15	−3.75	−19.32	−49.0	−923
308.15	−4.09	−10.24	−20.0	−894
298.15	−4.15	−1.45	9.0	−864
288.15	−3.91	7.05	338.0	−836
278.15	−3.38	15.26	67.0	−807

following empirical equation [1]

$$pK_2(\mathrm{W}, m) = -6.4980 + 2902.39/T + 0.02379T. \quad (20)$$

Since it is easier to make a direct comparison of values for equal numbers of solvent molecules, all the data must be converted to the mole-fraction scale. The following standard equation has been used for this conversion:

$$pK_2(N) = pK_2(m) + 2\log(1000/M), \quad (21)$$

where M is the mean molar mass of the mixed solvent or molar mass of pure water and N denotes a value on the mole-fraction scale. The standard Gibbs energy of transfer, $\Delta G_t^0(N)$, is given by the following equation:

$$\Delta G_t^0(N) = (RT\ln 10)[pK_2(\mathrm{S}, N) - pK_2(\mathrm{W}, N)]. \quad (22)$$

The values of ΔG_t^0 and ΔS_t^0 are different based on different scales, whereas those of ΔH_t^0 and $\Delta C_{p,t}^0$ are the same on each scale. All values of transfer thermodynamic function obtained from Eq. (22) and some thermodynamic relationship are listed in Table 5. Values of ΔG_t^0 for the transfer process of the second dissociation step of carbonic acid at 278.15–318.15 K are negative one which strongly suggested (a) the stabilization of HCO_3^- by water through hydrogen bonding and (b) the interaction of CO_3^{2-} and H^+ with the mixed solvent.

Acknowledgements

This project was supported by the National Natural Science Foundation of China.

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