Solvent Deuterium Isotope Effects on Acid-Base Reactions

Part II. Variation of the First and Second Acidity Constants of Carbonic and Sulfurous Acids in Mixtures of Light and Heavy Water

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The first and second acidity constants of carbonic and sulfurous acids have been measured in light and heavy water and in their mixtures. The variation of the activity coefficients of $CO_2(aq)$ and $SO_2(aq)$ within this solvent system has also been studied from the partial pressures of carbon dioxide and sulfur dioxide over their dilute aqueous solutions.

The results are discussed in terms of the equilibrium theory of solvent deuterium isotope effects. It is shown that, if one assumes the ionic activity coefficients to be independent of solvent in the $H_2O - D_2O$ system as postulated by this theory, one should be able to calculate the equilibrium constant, L, for the reaction $2 D_3O^+ + 3 H_2O = 2 H_3O^+ + 3 H_2O$, from the values for the first and second dissociation of the two acids studied. However, the results thus obtained are incompatible with each other and with those measured by other methods. This proves that the activity coefficient quotients involved undergo significant changes when one goes from light to heavy water.

The results suggest an independent method for the determination of L from the data for carbonic and sulfurous acids, or for other acids displaying similar dissociation schemes. The method makes use of the fact that the activity coefficient quotients associated with changes in the isotope composition of the solvent become unity when pure light water is approached. The values obtained in this way, $L = 9.6 \pm 0.3$ (carbonic acid), and $L = 9.6 \pm 0.5$ (sulfurous acid), are in excellent agreement with those derived from other experimental sources.

In the preceding paper [1] it was pointed out that dibasic acids of the "anhydride type" might be particularly suitable for a study of possible medium effects on acid-base equilibria in waters of different hydrogen isotope composition. This, in turn, should permit a more concrete re-evaluation of the assumptions made in the earlier equilibrium theory of solvent deuterium isotope effects on acid-base equilibria and kinetics. The present paper gives the results obtained for the first and second dissociation of carbonic and

sulfurous acids in H_2O-D_2O mixtures. For a more detailed analysis of the data, the variation of the activity coefficients of $CO_2(aq)$ and $SO_2(aq)$ within this solvent system was also studied by solubility measurements.

EXPERIMENTAL

The heavy water used was from Norsk Hydro-Elektrisk Kvaelstofaktieselskab, Norway. The methods of its purification and analysis were those described earlier.[2] The carbon dioxide and sulfur dioxide came from commercial tanks. The other chemicals were of reagent grade throughout.

The equipment employed for the solubility measurements on carbon dioxide was of the Ostwald type.[3,4] Before each measurement, the water was freed from dissolved air by boiling under reflux. The carbon dioxide which was passed into the absorption apparatus was purified by passing it subsequently through solutions of acidic ferric sulfate, iodine, potassium permanganate, and water. The gas was finally dried carefully with magnesium perchlorate. The solubilities measured for carbon dioxide are given in Table 1. The molar solubilities, S_M, given in the last column of the table are those calculated from the equation

$$S_M = 0.03352_2 - 0.00020_5 \, n \tag{1}$$

which was obtained from the data by the method of least squares.

Table 1. Solubility of carbon dioxide in waters of different hydrogen isotope composition at 25°C and at 1 atm pressure. n = deuterium atom fraction of the solvent. S_V = solubility in ml/ml units (Ostwald coefficient), S_M = solubility in moles per liter, N = number of measurements.

n	N	S_V	S_M	S_M (calc.)
0.000	20	0.8196	0.03350	0.03352
0.498₅	20	0.8189	0.03347	0.03342
0.833	23	0.8154	0.03333	0.03335
0.997	18	0.8149	0.03331	0.03332

The solubility of carbon dioxide in the pure waters, H_2O and D_2O, has been earlier studied by Curry and Hazelton.[4] The values of S_V reported, 0.821 ± 0.007 (in H_2O), and 0.819 ± 0.005 (in D_2O), agree within their given precision with the present values.

The equilibrium pressure of sulfur dioxide over its solutions in H_2O-D_2O mixtures was studied using an apparatus similar to that described by Hudson.[5] A detailed account of the measurements and of the calculations involved will be published later by one of the authors (A.V.). Because sulfurous acid is relatively strong in its first dissociation, Henry's law is not obeyed even at moderately low concentrations of dissolved sulfur dioxide. However, if one makes a correction for the first dissociation and considers the partial pressure of sulfur dioxide over its solutions as a function of the overall concentration of the undissociated acid, *i.e.*, the concentration of sulfur dioxide plus that of the undissociated sulfurous acid, Henry's law is obeyed in dilute solutions. Those of the results which are of interest in the present context can be summarized by eqn. (2), which was obtained from the data for dilute solutions by the method of least squares:

$$P_{SO_2} \text{ (torr)} = (421 + 125 \, n - 11 \, n^2) \, C_{acid}; \ 25°C \tag{2}$$

Here C_{acid} is the overall concentration of undissociated acid (sulfur dioxide plus sulfurous acid) in moles per liter, and n is the atom fraction of deuterium in the water.

From eqn. (2) one obtains eqn. (3) for the change in the molar activity coefficient of dissolved sulfur dioxide, irrespective of its molecular form in the solution, when going from dilute solution in light water to that in a solvent of deuterium atom fraction n.

$$(f_{SO_2})_n/(f_{SO_2})_{H_2O} = 1 + 0.297\ n - 0.027\ n^2 \tag{3}$$

The technique of the pK measurements in the $H_2O - D_2O$ system was that described earlier.[6-8] Several parallel determinations were made in each case.

RESULTS AND DISCUSSION

Variation of the pK *values with hydrogen isotope composition of the solvent.* The experimental results obtained for carbonic and sulfurous acids are collected in Tables 2 and 3. For a more detailed analysis of the data, in order to minimize the influence of random errors, the method of least squares was applied to the experimental pK values, whereupon the empirical eqns. (4)—(7) were obtained.

$$\Delta pK = 0.414_5\ n + 0.100_0\ n^2 \quad \text{(carbonic acid, 1st diss.)} \tag{4}$$

$$\Delta pK = 0.404_4\ n + 0.212_3\ n^2 \quad (\quad \text{»} \quad\quad \text{»} \quad \text{2nd diss.)} \tag{5}$$

$$\Delta pK = 0.431_4\ n + 0.225_6\ n^2 \quad \text{(sulfurous acid, 1st diss.)} \tag{6}$$

$$\Delta pK = 0.387_0\ n + 0.232_6\ n^2 \quad (\quad \text{»} \quad\quad \text{»} \quad \text{2nd diss.)} \tag{7}$$

The values of ΔpK(calc.) in the tables are those computed from these equations.

The relative acidity constants in the isotopically pure waters, H_2O and D_2O, have been previously measured for carbonic acid. Curry and Hugus [9] reported ΔpK values of 0.43 and 0.64 for the first and second dissociation, respectively; the value obtained by Glasoe and Long [10] for the second dissociation was 0.63. It is seen that the earlier values for the second dissociation

Table 2. Relative pK values for the first and second dissociation of carbonic acid and the changes in molar activity coefficient of dissolved carbon dioxide in $H_2O - D_2O$ mixtures at 25°C. $\Delta pK = pK_n - pK_H$, in which the subscripts refer to a solvent of deuterium atom fraction n and to pure protium oxide, respectively.

| n	$(f_{CO_2})_n/(f_{CO_2})_H$	1st dissociation		2nd dissociation	
		ΔpK	ΔpK(calc.)	ΔpK	ΔpK(calc.)
0.100	1.0006	0.046	0.042	0.041	0.043
0.199	1.0012	0.088	0.086	0.080	0.090
0.299	1.0018	0.138	0.133	0.163	0.140
0.399	1.0024	0.182	0.181	0.197	0.195
0.498	1.0031	0.227	0.231	0.269	0.255
0.598	1.0037	0.280	0.283	0.298	0.318
0.698	1.0043	0.336	0.338	0.385	0.386
0.797	1.0049	0.395	0.394	0.464	0.458
0.897	1.0055	0.452	0.452	0.520	0.534
0.997	1.0061	0.514	0.512	0.627	0.614
1.000	1.0062	—	0.514	—	0.617

Table 3. Relative pK values for the first and second dissociation of sulfurous acid and the changes in molar activity coefficient of dissolved sulfur dioxide in $H_2O - D_2O$ mixtures at 25°C. The notation is the same as in Table 2.

n	$(f_{SO_2})_n/(f_{SO_2})_H$	1st dissociation		2nd dissociation	
		ΔpK	ΔpK(calc.)	ΔpK	ΔpK(calc.)
0.099	1.029	0.045	0.045	0.047	0.041
0.197	1.057	0.089	0.094	0.064	0.085
0.295	1.085	0.143	0.147	0.135	0.134
0.394	1.113	0.196	0.205	0.194	0.189
0.492	1.140	0.292	0.267	0.248	0.247
0.591	1.166	0.317	0.334	0.320	0.310
0.689	1.194	0.378	0.404	0.385	0.377
0.788	1.217	0.495	0.480	0.450	0.449
0.886	1.242	0.541	0.559	0.511	0.525
0.985	1.266	0.638	0.644	0.625	0.607
1.000	1.270	—	0.657	—	0.620

agree satisfactorily with the present value, 0.62, whereas that for the first dissociation shows a much poorer agreement.

Application of the simple equilibrium theory. The equilibrium theory of solvent deuterium isotope effects considers the equilibria between isotopically exchangeable components of the solutions as the sole factors responsible for the changes in the acid-base equilibrium constants, thus ignoring the possible effects associated with transfer of the components from one solvent to another within the H_2O-D_2O system.[1,6,7,11] In the following, an application of the theory is made to the acid-base equilibria studied in the present work.

It is well known that the first dissociations of carbonic and sulfurous acids are complicated by the anhydride-acid equilibria: $CO_2+H_2O=H_2CO_3$, and $SO_2+H_2O=H_2SO_3$. The equilibrium ratio (acid)/(anhydride) in light water at 25°C is 0.0037 for carbonic acid,[12,13] and less than 0.03 for sulfurous acid.[14] As the undissociated acids are thus substantially in their anhydride forms, the relevant equilibria, as exemplified by carbonic acid in light water, can be written as

$$CO_2+2\ H_2O = H_3O^+ +HCO_3^-;\ K_H^I \tag{I}$$

$$HCO_3^- +H_2O = H_3O^+ +CO_3^{2-};\ K_H^{II} \tag{II}$$
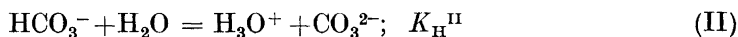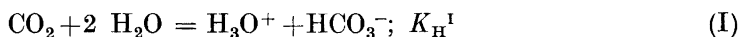
The equilibrium theory of solvent deuterium isotope effects now leads to the following expressions for the variation of these equilibrium constants with the deuterium atom fraction n of the solvent:

$$K_H^I/K_n^I = (1-n+n\varphi)^{-1}(1-n+nl)^{-3};\ K_H^I/K_D^I = \varphi^{-1}\ l^{-3} \tag{8}$$

$$K_H^{II}/K_n^{II} = (1-n+n\varphi)\ (1-n+n\ l)^{-3};\ K_H^{II}/K_D^{II} = \varphi\ l^{-3} \tag{9}$$

Here the isotopic fractionation factors φ and l refer to the bicarbonate (or bisulfite) and hydronium ions, respectively. As the value of l can be considered to be known, 0.69 ± 0.01,[1] the only unknown parameter in eqns. (8) and (9) is the fractionation factor relating to the bicarbonate (or bisulfite) ion. For-

tunately, as seen from the equations, this parameter can be eliminated by multiplication

$$(K_H^I/K_n^I) \times (K_H^{II}/K_n^{II}) = (1-n+nl)^{-6}; \quad (K_H^I/K_D^I) \times (K_H^{II}/K_D^{II}) = l^{-6} \quad (10)$$

Put another way, the above equation should describe the variation of the equilibrium constant of the reaction

$$XO_2 + 3 \ L_2O = 2 \ L_3O^+ + XO_3^{2-} \quad (L = H, \ D; \ X = C, \ S) \quad (III)$$

with the hydrogen isotope composition of the solvent water.

In the above derivation it was assumed that the presence of the acid forms of the undissociated acids, i.e., L_2CO_3 and L_2SO_3, has no effect on the variation of the measured equilibrium constants. Though the postulates of the simple equilibrium theory were accepted, a question might arise, whether the isotope exchange equilibria between these acidic species and the solvent affected the results. This difficulty is, however, circumvented by considering the equilibria at constant activities of the dissolved anhydrides, that is, at constant equilibrium pressures of CO_2 and SO_2. Such a treatment, which makes the degree of hydration of the anhydrides immaterial, involves measurement of the changes in the activity coefficients of the dissolved anhydrides in the H_2O-D_2O system, and taking these changes into account in the above equations, eqn. (10) now takes the form

$$(K_H^I/K_n^I) \times (K_H^{II}/K_n^{II}) = (1-n+n \ l)^{-6} \times (f_H/f_n);$$
$$(K_H^I/K_D^I) \times (K_H^{II}/K_D^{II}) = l^{-6} \times (f_H/f_D) \quad (10')$$

where the activity coefficients f (in molar units) refer to the dissolved anhydrides.

The interesting feature of eqn. (10′) is that it should permit an independent calculation of the value of l, the fractionation factor relating to the hydronium ion. When one uses the data given in Tables 2 and 3 for the isotopically pure solvents, H_2O and D_2O, one obtains the following values for l: 0.647 (carbonic acid data), and 0.589 (sulfurous acid data). These correspond, respectively, to values of 13.6 and 23.9 for the equilibrium constant L of the reaction

$$2 \ D_3O^+ + 3 \ H_2O = 2 \ H_3O^+ + 3 \ D_2O; \quad L \quad (IV)$$
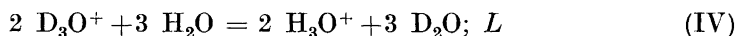
For comparison, some other recent values for L may be listed: 9.7 ± 1.5 [15] (NMR); 11.4 ± 0.7 [16] (NMR); 8.2 ± 1.0 [17] (isotopic distribution of hydrogen between acid solutions and their vapors); 9.0 ± 0.3 [18] (electrochemical measurements). It is seen that, whereas the results from the other measurements agree reasonably well, the values derived from the present data, 13.6 and 23.9, are definitely too high and, moreover, incompatible. This fact, in turn, proves the inadequacy of the equilibrium theory for the present type of ionic equilibria.

An idea about the magnitude of the medium factors incorporated in the relative acidity constants may be gained in the following way. As discussed in the preceding paper,[1] the refined expressions corresponding to eqns. (10) and (10′) can be written as

$$(K_H{}^I/K_n{}^I) \times (K_H{}^{II}/K_n{}^{II}) = (1-n+n\,l)^{-6}\ F(n);$$
$$(K_H{}^I/K_D{}^I) \times (K_H{}^{II}/K_D{}^{II}) = l^{-6}\ F(1) \tag{11}$$

$$F(n) = \left\{ \frac{f_{CO_2}\, f_{H_2O}{}^3}{f_{CO_3{}^{2-}} f_{H_3O^+}} \right\}_{H_2O} \times \left\{ \frac{f_{CO_3{}^{2-}}\, f_{H_3O^+}{}^2}{f_{CO_2}\, f_{H_3O^+}{}^3} \right\}_n \tag{12}$$

As the value of l is known, and the variation of the activity coefficients of the dissolved anhydrides has been studied separately, the combined effect of changes in the other activity coefficients in eqn. (12) can be computed from the experimental pK values. The latter effect, in turn, must be essentially due to the divalent anions alone, because the activity coefficients of H_2O and H_3O^+ can be considered to be substantially solvent-independent within the $H_2O - D_2O$ system. This conclusion is supported by the fact that the solvent system under discussion is ideal,[1] and by the observation that the hydronium ion can be directly incorporated into the "water clusters" without disturbing the internal structure of the liquid water.[19] Eqn. (12) thus takes the form

$$F(n) = (f_{CO_2}/f_{CO_3{}^{2-}})_{H_2O} \times (f_{CO_3{}^{2-}}/f_{CO_2})_n \tag{12'}$$

Application of eqns. (11) and (12') to the data of Tables 1 and 2 gives the following values (in molar units) for the ratios of the activity coefficients of the divalent anions in the isotopically pure solvents:

$$(f_{CO_3{}^{2-}})_{D_2O}/(f_{CO_3{}^{2-}})_{H_2O} = 1.47; \quad (f_{SO_3{}^{2-}})_{D_2O}/(f_{SO_3{}^{2-}})_{H_2O} = 2.59$$

In the calculations, a value of 0.69 was used for l. The above activity coefficient ratios correspond, respectively, to the following values of the free energies of transfer of the divalent anions from their dilute solutions in light water to heavy water to give the same molar concentration:

$$CO_3{}^{2-}(\text{in } H_2O) = CO_3{}^{2-}(\text{in } D_2O); \quad \Delta G^\circ = +230 \text{ cal/mole} \tag{V}$$
$$SO_3{}^{2-}(\text{in } H_2O) = SO_3{}^{2-}(\text{in } D_2O); \quad \Delta G^\circ = +560 \text{ cal/mole} \tag{VI}$$

Although the knowledge of the free energies of transfer from light to heavy water is still very fragmentary, and these energies cannot be measured for individual ions by strict thermodynamic methods without any further assumptions (like that above concerning the transfer free energy of the hydronium ion), the above values can be seen to be of acceptable magnitudes. Thus, for example, the corresponding value of ΔG° for the chloride ion has been estimated to be about $+210$ cal/mole.[18] The fact that the transfer free energy for the sulfite ion is much larger than for the carbonate ion is also compatible with the observation that the transfer free energies of the parent anhydrides, although much smaller, are in the same sequence:

$$CO_2(\text{in } H_2O) = CO_2(\text{in } D_2O); \quad \Delta G^\circ = +4 \text{ cal/mole} \tag{VII}$$
$$SO_2(\text{in } H_2O) = SO_2(\text{in } D_2O); \quad \Delta G^\circ = +140 \text{ cal/mole} \tag{VIII}$$

One might further question, whether the other assumptions inherent in the theory,[1] though satisfactorily supported by experimental results, could weaken the present argumentation that emphasizes the utmost importance of the transfer free energies in the theory of solvent deuterium isotope effects. However, when the *difference* between the standard free energies for the sulfite

and carbonate ions is considered alone, it is easily seen that the calculation of this difference, $+330$ cal/mole, does not necessitate any of the assumptions made. Even the value of l is immaterial. Thus, from the most critical stand-point, one can state that the transfer effects must be significant at least in one of the equilibria (III) studied.

Distribution of hydrogen isotopes between the hydronium ion and water. As discussed above, a direct calculation of l from the present data is not pos-sible. In the following an attempt is made to estimate this quantity from the results by extrapolating the values to isotopically pure light water, whereupon the influence of the medium effects is eliminated. Taking logarithms one obtains from eqn. (11)

$$\Delta pK_n^{I} + \Delta pK_n^{II} = Q(n) = -6 \log(1-n+n\,l) + \log\ F(n) \tag{13}$$

in which the last term includes the combined effect of the variations in the activity coefficients involved. It has been tentatively proposed earlier [20] that the transfer free energies, and thus log $F(n)$, varied proportional to the deuterium atom fraction n of the solvent. As no decisive experimental evidence having bearing on this point exists, and for reasons discussed below, an equa-tion of a more general form (eqn. 14) was chosen for the present purpose.

$$\log\ F(n) = a\ n^x \tag{14}$$

Differentiation gives

$$2.303\ \frac{\partial Q(n)}{\partial n} = \frac{6(1-l)}{1-n+n\,l} + 2.303\ a\,x\,n^{x-1} \tag{15}$$

If one now assumes that the value of x is larger than unity, *i.e.*, that the transfer free energies are changed more abruptly than linear to n, the limiting eqn. (16) is obtained for $n=0$.

$$2.303\ \left(\frac{\partial Q(n)}{\partial\ n}\right)_{n=0} = 6(1-l) \tag{16}$$

The value of l can be calculated from this equation. The value for the deriva-tive at $n=0$ is best estimated from the least-squares eqns. (4)—(7), because this procedure effectively eliminates the influence of random errors. The limiting values and their standard errors (obtained from the least-squares treatment) for this derivative are: 0.819 ± 0.009 (carbonic acid data); 0.818 ± 0.012 (sulfurous acid data). These give, respectively, values of 0.686 ± 0.003 and 0.686 ± 0.005 for l (or, 9.6 ± 0.3 and 9.6 ± 0.5 for L), which agree excellently with each other and with those obtained by earlier methods (see above).

The excellent consistency of the values calculated above may be some-what fortuitous in view of the assumption made about the value of x in eqn. (14), which assumption, in effect, means that the value of log $F(n)$ becomes substantially independent of the solvent when light water is approached. However, the fact that the both sets of data give similar results suggests that this assumption must be valid, at least to a good approximation. It was seen above that the free energies of transfer from light to heavy water are positive for all the species involved, the latter thus favoring the light water. One might therefore conceivably argue that the constancy of log $F(n)$ in solvents

of low deuterium content is due to the circumstance that the ionic and other species in question are in these solvents surrounded by the molecules of protium oxide alone. Additionally, some cancellation of the overall medium effect at low deuterium contents of the solvent may also result from the circumstance that in the expression for $F(n)$, eqn. (12), the activity coefficients of CO_2 and CO_3^{2-} (or those of SO_2 and SO_3^{2-}, respectively) influence in the opposite directions.

Variation of ionic activity coefficients in $H_2O - D_2O$ mixtures. It was pointed out above that there are no experimental results indicating the free energies of transfer of ions to be linear functions of deuterium atom fraction in the $H_2O -$ D_2O mixtures. It is unfortunate that practically no studies have been hitherto made to elucidate this point in more detail. The results of some solubility measurements [21] cannot be applied here, as the moderately high electrolyte concentrations used brought about salt effects on the ionic activity coefficients. The only earlier study which is relevant in the present context is that of LaMer and Noonan.[22] They measured the standard free energies for the process:

$$KCl\ (0.1\ M,\ in\ H_2O)\ \rightleftharpoons\ KCl\ (0.1\ M,\ n);\ \Delta G_n^{\circ} \qquad \text{(IX)}$$
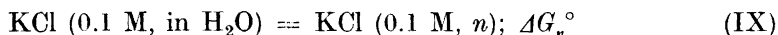
as the function of deuterium atom fraction n and obtained a slightly curved plot for ΔG_n° versus n, *i.e.*, the values of the free energies increased less rapidly with n when the fraction of deuterium in the solvent was low than when this fraction was high. Put another way, if one chooses an equation of the form (14) to describe the variation of ΔG_n° with the deuterium atom fraction, one has to use an exponent x that is higher than unity. Unfortunately, the measurements of LaMer and Noonan did not cover solvents of very low deuterium content. In addition to the pure waters, all the measurements were made on solutions with n equal or higher than about 0.5.
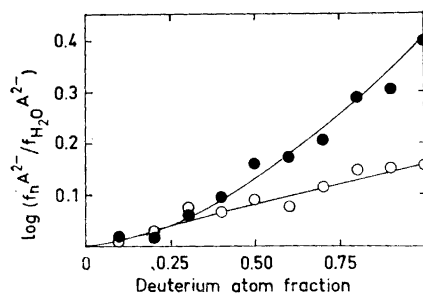

Fig. 1. Plots of log $(f_n^{A2-}/f_{H_2O}^{A2-})$ for carbonate (O) and sulfite (●) ions in $H_2O -$ D_2O mixtures at 25°C. The radius of the circles is 0.01 logarithmic unit.

Another possibility for an inspection of the transfer effects is furnished by the present data when eqns. (11) and (12') are applied to the experimental ΔpK values. The plots shown in Fig. 1 have been made in this way using the directly measured ΔpK values (not those obtained from the least-squares treatment) and the activity coefficients of the dissolved anhydrides. In the calculations, the value 0.69 was used for l. It is seen that, whereas for the carbonate ion the overall change in log f is too small to reveal possible departures from linearity, the case of the sulfite ion is more amenable, the values of log f increasing more rapidly at higher deuterium contents of the solvent.

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