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IONIC EQUILIBRIA IN MIXED SOLVENTS. IX.
THE AUTOPROTOLYSIS CONSTANTS OF MIXTURES OF WATER AND AN AMPHIPROTIC SOLVENT

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A thermodynamic consideration is made for the autoprotolysis constant of a mixture of water and an amphiprotic solvent on the basis of equilibria of hydronium-lyonium and hydroxyl-lyate ions. The autoprotolysis constants of various water-methanol solutions are calculated and compared with those in literature. The calculated values of autoprotolysis constants of water-ethanol and water-n-propanol solutions are presented.

The autoprotolysis constant of water has been determined by many authors under various conditions. However, a very limited number of data have been reported for the autoprotolysis constant of aqueous mixed solvent and few theoretical treatments have been demonstrated for this subject. When we study acid-base reactions in mixed solvents with varying solvent compositions, it is essential to know how the autoprotolysis constant of a solvent is affected by the change of the solvent composition, because the autoprotolysis constant provides a measure of acid-base properties, especially the scale of pH in the solution. The aim of the present work is to throw more light to the problem of the autoprotolysis constant of binary mixtures of water and an amphiprotic solvent.

In a mixture of water and an amphiprotic solvent (HSol), the following equilibria are established for both solvents:

$$2H_2O = H_3O^+ + OH^- \qquad K_{W(H_2O)} = a_{H_3O}\cdot a_{OH}/a_{H_2O}^{\ 2} \qquad (1)$$

$$2HSol = H_2Sol^+ + Sol^- \qquad K_{W(HSol)} = a_{H_2Sol}\cdot a_{Sol}/a_{HSol}^{\ 2} \qquad (2)$$

The equilibrium constant of the distribution reaction of a proton between two solvent molecules is given as follows:

$$H_3O^+ + HSol \overset{\kappa_a}{\rightleftharpoons} H_2Sol^+ + H_2O \qquad (3)$$

$$\kappa_a = \frac{a_{H_2Sol}\cdot a_{H_2O}}{a_{H_3O}\cdot a_{HSol}} = \frac{x(1-y)}{y(1-x)}\cdot\frac{f_{H_2Sol}\cdot f_{H_2O}}{f_{H_3O}\cdot f_{HSol}} \qquad (4)$$

where x denotes a fraction of a lyonium ion H_2Sol^+ produced from one mole of proton and y the mole fraction of the amphiprotic solvent in a solvent mixture. f stands for the activity coefficient.

Since activity coefficients of ionic species H_3O^+ and H_2Sol^+ in a given solution can reasonably be assumed to be unity because of their low concentrations, x is given as follows:

$$a_{H_2Sol} = [H^+]\cdot x = \frac{a_{HSol}\cdot\kappa_a}{a_{H_2O} + a_{HSol}\cdot\kappa_a}\cdot[H^+] \tag{5}$$

Since both hydronium and lyonium ions are considered to be thermodynamic entities which determine the chemical potential of hydrogen ion, the activity of hydrogen ion $a_{\underline{H}}$ is given as

$$a_{\underline{H}} = a_{H_3O}{}^{1-x}\cdot a_{H_2Sol}{}^{x} = (1 - x)^{1-x}\cdot x^{x}\cdot[H^+] \tag{6}$$

where $[H^+]$ represents the concentration of hydrogen ion in solution. Even if we can assume ideal behavior of ionic species in solution ($f_{H_3O} = f_{H_2Sol} = 1$), the activity coefficient of the hydrogen ion should still be changed by $(1 - x)^{1-x}\cdot x^{x}$ with the solvent composition. The term $(1 - x)^{1-x}\cdot x^{x}$ depends upon the equilibrium constant κ_a as well as the solvent composition (see Fig. 1).

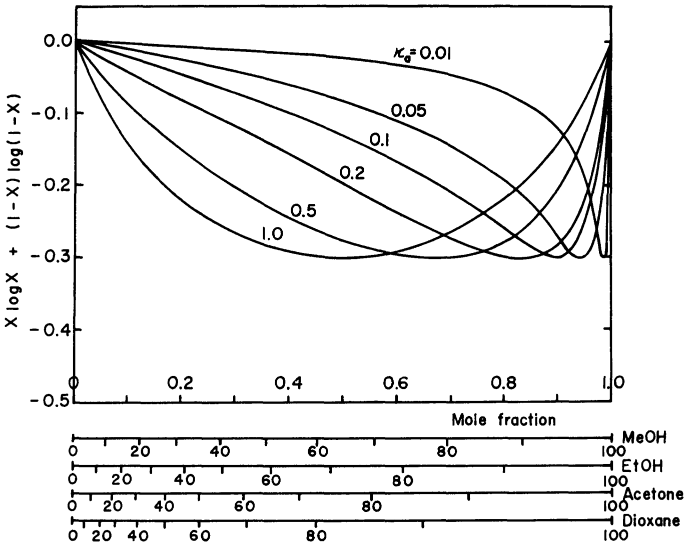

Fig. 1. Variation of $(1 - x)^{1-x}\cdot x^{x}$ with the solvent composition and κ_a. x is given by eq. (5).

Similar relationships to those derived for hydronium and lyonium ions are obtained for hydroxyl and lyate ions by assuming $f_{OH} = f_{Sol} = 1$, thus;

$$a_{\underline{OH}} = a_{OH}{}^{1-x'}\cdot a_{Sol}{}^{x'} = (1 - x')^{1-x'}\cdot x'^{x'}\cdot[OH^-] \tag{7}$$

where x' denotes a fraction of lyate ion Sol^- and is given as

$$x' = \frac{a_{HSol}\cdot\kappa_b}{a_{H_2O} + a_{HSol}\cdot\kappa_b} \tag{8}$$

and κ_b is the equilibrium constant of the reaction

$$OH^- + HSol \xrightleftharpoons{\kappa_b} Sol^- + H_2O;\quad \kappa_b = \frac{a_{Sol}\cdot a_{H_2O}}{a_{OH}\cdot a_{HSol}} = \frac{x'(1-y)}{y(1-x')}\cdot\frac{f_{Sol}\cdot f_{H_2O}}{f_{OH}\cdot f_{HSol}} \qquad (9)$$

Combination of eq. (4) with eq. (9) leads to the following relation;

$$\kappa_a\cdot\kappa_b = K_{W(HSol)}/K_{W(H_2O)} \qquad (10)$$

If we assume that $K_{W(H_2O)}$ and $K_{W(HSol)}$ in any solvent mixture have the same values with those in their pure states, we can estimate the autoprotolysis constant K_W of a mixed solvent by the use of eq. (11), provided that either κ_a or κ_b is known:

$$K_W = \frac{a_{\underline{H}}\cdot a_{\underline{OH}}}{a_{solv}^2} = \frac{a_{\underline{H}}\cdot a_{\underline{OH}}}{\{a_{H_2O}^{1-x}\cdot a_{HSol}^{x}\}^2} = K_{W(H_2O)}^{1-x}\cdot K_{W(HSol)}^{x}\cdot\{x'(1-x')\}^{x'-x} \qquad (11)$$

The autoprotolysis constants of water and methanol are reported as $10^{-14.00}$ and $10^{-16.71}$, respectively. The value of κ_a in water-methanol mixtures was determined by Conway, Bockris and Linton[1] as 0.23. The value determined by Newall and Eastham[2] (κ_a = 0.0084) was much smaller than that of Conway et al. and was close to the value reported by Frank and Ives[3] (κ_a = 0.0073). Inserting the value of κ_a and activities of solvents obtained from vapor pressure data[4] into eq. (11), we can calculate the autoprotolysis constants in various water-methanol solutions. The values of -log K_W thus calculated are tabulated in Table 1 along with values determined by Koskikallio[5].

Table 1. The autoprotolysis constants of water-methanol mixtures calculated by eq. (11).

Methanol %(w/w)	-log K_W (calc)			-log K_W[5]
	κ_a = 0.23[1] (κ_b = 0.0085)	κ_a = 0.0084[2] (κ_b = 0.23)	κ_a = 0.0073[3] (κ_b = 0.27)	
0	14.00	14.00	14.00	14.00
10	14.00	14.04	14.04	14.04
20	14.00	14.06	14.07	14.06
30	14.01	14.08	14.09	14.07
40	14.03	14.10	14.11	14.08
50	14.05	14.12	14.13	14.10
60	14.07	14.13	14.14	14.14
70	14.11	14.16	14.17	14.23
80	14.19	14.20	14.20	14.43
90	14.43	14.29	14.30	14.85
100	16.71	16.71	16.71	16.71

The agreement between calculated and observed values was most satisfactory in the range of the methanol concentration lower than 70 % (w/w) in the case where the κ_a value by Newall and Eastham was used, although almost equally good results were found with the value reported by Frank and Ives. Rather poor agreement was resulted in all cases in 80 and 90 % (w/w) methanol. The disagreement may be due to a simple assumption of the smallest solvation numbers of ionic species.

When we start the same discussion from another assumption of solvation numbers of proton, somewhat different and better conclusion is derived. If we assume that a proton is hydrated with four water molecules in water and is solvated with one amphiprotic solvent molecule in the solvent and that no mixed solvated proton exists in a mixed solvent, the equations derived in the previous treatment may be changed as follows:

$$5H_2O = H(H_2O)_4^+ + OH^- \qquad K_{W(H_2O)} = a_{H(H_2O)_4}\cdot a_{OH}/a_{H_2O}^5 \tag{1'}$$

$$2HSol = H_2Sol^+ + Sol^- \qquad K_{W(HSol)} = a_{H_2Sol}\cdot a_{Sol}/a_{HSol}^2 \tag{2}$$

$$H(H_2O)_4^+ + HSol \overset{\kappa_a}{\rightleftharpoons} H_2Sol^+ + 4H_2O \tag{3'}$$

$$\kappa_a = \frac{a_{H_2Sol}\cdot a_{H_2O}^4}{a_{H(H_2O)_4}\cdot a_{HSol}} \tag{4'}$$

and

$$a_{H_2Sol} = [H^+]\cdot x = \frac{a_{HSol}\cdot\kappa_a}{a_{H_2O}^4 + a_{HSol}\cdot\kappa_a}\cdot[H^+] \tag{5'}$$

Under an assumption that hydroxyl and lyate ions exist as OH^- and Sol^- as in eq. (9), the autoprotolysis constant K_W of a mixed solvent is given as eq. (11') which is essentially similar to eq. (11):

$$K_W = \frac{a_{\underline{H}}\cdot a_{\underline{OH}}}{\{a_{H_2O}^{5(1-x)}\cdot a_{HSol}^{2x}\}} = K_{W(H_2O)}^{1-x}\cdot K_{W(HSol)}^{x}\cdot\{x'(1-x')\}^{x'-x} \tag{11'}$$

Insertion of values of $K_{W(H_2O)}$, $K_{W(HSol)}$ and κ_a leads to the results summarized in Table 2.

The autoprotolysis constants of water-methanol mixtures reported by Koskikallio were best reproduced by the use of eq. (11') and the value of κ_a reported by Conway et al. in the sense of the minimum error square sum. The values of K_W calculated with κ_a proposed by Newall and Eastham were in fairly good agreement with those of Koskikallio in aqueous mixed solutions containing methanol less than 80 % (w/w).

Since the usefulness of eq. (11') was thus confirmed, the above treatment was applied to water-ethanol and water-n-propanol solutions in order to calculate the autoprotolysis constants of the solutions, knowing $\kappa_a = 0.059$[1] and 0.037[1], respectively. The autoprotolysis constants thus calculated are listed in Table 3.

Table 2. The autoprotolysis constants of water-methanol mixtures calculated by eq. (11').

Methanol %(w/w)	$-\log K_W$ (calc)		
	$\kappa_a = 0.23$ (Δ)*	$\kappa_a = 0.0084$ (Δ)*	$\kappa_a = 0.0073$ (Δ)*
0	14.00	14.00	14.00
10	14.00 (-0.04)	14.04 (±0.00)	14.04 (±0.00)
20	14.00 (-0.06)	14.06 (±0.00)	14.07 (+0.01)
30	14.02 (-0.05)	14.09 (+0.02)	14.09 (+0.02)
40	14.04 (-0.03)	14.11 (+0.03)	14.11 (+0.03)
50	14.07 (-0.01)	14.12 (+0.02)	14.13 (+0.03)
60	14.12 (-0.02)	14.15 (+0.01)	14.15 (+0.01)
70	14.23 (±0.00)	14.18 (-0.05)	14.19 (-0.04)
80	14.52 (+0.04)	14.31 (-0.17)	14.30 (-0.18)
90	15.03 (+0.18)	15.12 (+0.27)	15.07 (+0.22)
100	16.71	16.71	16.71
	$\Sigma\Delta^2 = 0.0431$	$\Sigma\Delta^2 = 0.1061$	$\Sigma\Delta^2 = 0.0848$

* $\Delta = \log K_W$ (obs) $- \log K_W$ (calc).

Table 3. The autoprotolysis constants of water-ethanol and water-n-propanol solutions calculated by eq. (11')6).

%(w/w)	Water-Ethanol Solution	Water-n-Propanol Solution
0	14.00	14.00
10	14.00	14.02
20	14.02	14.03
30	14.03	14.03
40	14.04	14.04
50	14.06	14.04
60	14.09	14.05
70	14.13	14.05
80	14.22	14.06
90	14.79	14.09
100	18.88 7)	19.43 7)

It seems probable that $K_{W(H_2O)}$, $K_{W(HSol)}$ and κ_a vary with the solvent composition because of the changes of the dielectric constant of the solution and of other physicochemical properties such as structure making and breaking effects of solvents themselves and mixed solvation of ions, etc. The present treatment contains a simple assumption that these quantites are remained unchanged over the whole range of the solvent composition varied. Nevertheless, the variation of the autoprotolysis constant of mixed solvents is satisfactorily interpreted in terms of equilibria of hydronium-lyonium and hydroxyl-lyate ions. The results may be improved by introduction of variable $K_{W(H_2O)}$, $K_{W(HSol)}$ and κ_a, although some extrathermodynamic considerations may be necessary to estimate the variation of these quantities.

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