Measurements of the Amounts of Bound Water by Ultrasonic Interferometer. III. Application to Organic Electrolyte

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Recently many studies have been reported in order to estimate the amount of bound water of solute by measuring the ultrasonic velocity in the aqueous solution. In our laboratory, a general theory was suggested which seemed to give proper result in every kind of solution, and has been applied to solutions of saccharides[1], polyvinylalcohol and its derivatives[2]. In the present paper, an attempt is made to test the theory in the cases of the solutions of several organic electrolytes, and the results are discussed in comparison with those obtained by other methods. Authors chose aminoacids and gelatin as examples of low and high molecular electrolytes, respectively.

As introduced in a previous paper,

$$K=(\beta/\beta_0-V_0)/c\cdot\beta_0/\beta_w=\beta_1/\beta_w\cdot 1/d_1 -(\beta_0/\beta_w\cdot v_0/c-\beta_2/\beta_w\cdot v_2/c) \qquad (1)$$

where the notations are as follows:

V_0=apparent specific volume fraction of total solvent, i. e., $V_0=(d-c)/d_0$

v_0=apparent specific vol. fraction of the bound water, the density being assumed normal

v_2=specific vol. fraction of the bound water

d=density of solution

d_1=density of solute in solution, i. e., $(1-V_0)/c=1/d_1$

c=concentration of solute in g./cc. of solution

β=adiabatic compressibility of solution

β_0=adiabatic compressibility of solvent

β_1=adiabatic compressibility of solute molecule

β_2=adiabatic compressibility of bound water

β_w=adiabatic compressibility of water.

In the solutions of electrolytes, it has been supposed that the bound water might be attached so strongly by the electrostatic force of the ionic radicals of the solute molecule that its compressibility becomes negligibly small. Then, Eq. (1) may be rewritten as

$$K=\beta_1/\beta_w\cdot 1/d_1-\beta_0/\beta_w\cdot v_0/c \qquad (2)$$

Here again, the following procedure previously reported is used to estimate the amount of bound water. When any other bad solvent, though miscible with water, is added to the aqueous solution, the amount of bound water decreases. Therefore, using a bad solvent-water mixture containing a high fraction of the bad solvent, v_0/c has to become small and accordingly Eq. (1) reduces to

$$K=\beta_1/\beta_w\cdot 1/d_1 \qquad (3)$$

Thus, K in such solutions depends on β_1 only. In present cases, ethanol was used as the bad solvent.

Experimental

Commercial chemicals of glycine and α-DL-alanine were purified by recrystallization. Gelatin was dissolved in water and purified by electrodialysis until its electroconductivity decreased to the value of water. Its isoelectric point was pH 4.9.

The adiabatic compressibilities of solution and solvent were calculated by Laplace's relation, $\beta=1/d\mu^2$, from the ultrasonic velocity, μ, which was measured by the ultrasonic interferometer. pH of solution was determined by a glass electrode and pH test paper. The measurements were carried out at 30°C for aminoacids and at 35°C for gelatin.

Results and Discussion

In Table I is shown an example of the

TABLE I

EXAMPLES OF THE MEASUREMENTS (GLYCINE)

Ethanol concn. %	c	d	β/β_0	V_0	K
0.0	0.0819	1.0322	0.8958	0.9520	−0.69
21.1	0.0521	0.9893	0.9539	0.9689	−0.25
33.9	0.0105	0.9517	0.9932	0.9937	−0.05
35.3	0.0105	0.9488	0.9941	0.9935	+0.06
44.2	0.0102	0.9307	0.9938	0.9935	+0.07
48.2	0.0102	0.9229	0.9938	0.9941	−0.03

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[1] H. Shiio, T. Ogawa and H. Yoshihashi, *J. Am. Chem. Soc.*, **77**, 4980 (1955).

[2] H. Shiio and H. Yoshihashi, *J. Phys. Chem.*, **60**, 1049 (1956).

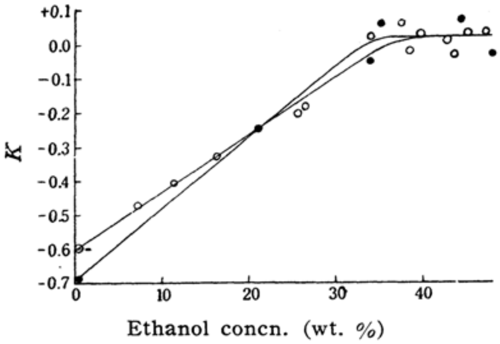

Fig. 1. ●, Glycine; ○, α-DL-alanine

measurements. The results of aminoacids are given in Fig. 1, in which are illustrated the plots of K against ethanol concentration in solvent. The situations are exactly the same as in the cases of glucose and maltose in the previous paper. As the ethanol concentration in solvent increases to some magnitude, K becomes nearly zero. However, in the solutions containing more than about 35 per cent. of ethanol, the solubility of both aminoacids becomes so small that the measurements give inaccurate results. Therefore, the line to which the K curve approaches is not determined exactly, but K may be assumed to be nearly zero in these region. Thus, by extrapolation of this part of the curve to pure aqueous solution, β_1 in aqueous solution is calculated by means of Eq. (3), giving the value approximately zero. Consequently, in such cases of the electrolytic solutions as well as non-electrolytic solutions, the term containing β_1 in Eqs. (1) and (2) can be assumed to be always zero, and so Eq. (1) becomes

$$K=-(\beta_0/\beta_w\cdot v_0/c-\beta_2/\beta_w\cdot v_2/c)$$

which is similar to the equations proposed by others[3]. This agrees with the fact that when the amount of bound water of the solute of low molecular weight has been calculated from the compressibility difference between solvent and solution, the compressibility of the solute molecule has been ignored by many investigators. Thus, the values obtained by the present procedure are clearly about the same magnitude as those of others[4].

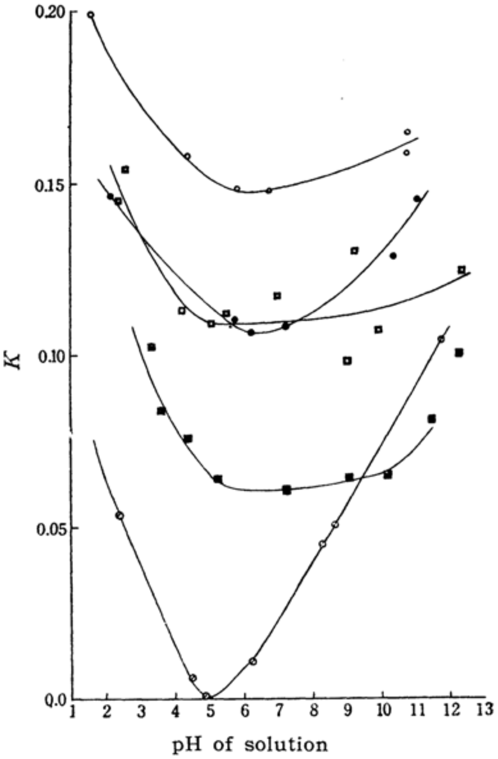

Fig. 2. Ethanol Concn: ⊘, 0%; ●, 12.9%; ○, 25.0%; □, 34.9%; ■, 42.4%.

Results of gelatin solution are collected in Fig. 2. As the solvents for gelatin, various ethanol-water mixtures were made by adding various small amounts of hydrochloric acid or sodium hydroxide to vary their pH. The fluidity of gelatin solution decreases with the increase in ethanol concentration in the solution. When the ethanol concentration exceeds 45 per cent., gelation takes place in a solution containing several per cent. gelatin even at 35°C. It is shown in Fig. 2 that in each ethanol concentration K has the minimum value at a certain pH which is regarded as the isoelectric point of gelatin in each solution. This may be due to the fact that at the isoelectric point, gelatin holds the highest value of the amount of bound water, or, as Miyahara and Shiio have supposed[5], the compressibility of the gelatin molecule acquires a minimum value as a results of the contraction of the molecule by the intramolecular electric field due to its ionic radicals. The plots of K at some definite pH values against ethanol concentration are shown in Fig. 3 by rearranging Fig. 2. The froms of the curves at each pH are similar to each other

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3) T. Yasunaga and T. Sasaki, *J. Chem. Soc. Japan Pure Chem. Sec.*, **72**, 87 (1951); Y. Miyahara, This Bulletin, **25**, 326 (1952).

4) Y. Miyahara, This Bulletin, **26**, 390 (1953).

5) Y. Miyahara and H. Shiio, *J. Chem. Soc. Japan Pure Chem. Sec.*, **73**, 265 (1952).

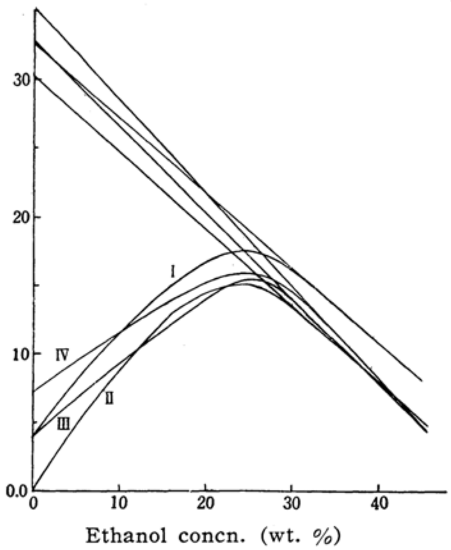

Fig. 3. I, pH 3; II, pH 5; III, pH 8; IV, pH 10

and to those of dextrine and polyvinylalcohol in a previous paper. Accordingly, it may be expected also in the present case that at the left part of curves, their relatively steep slopes are mainly contributed by the decrease in v_0/c and that at the right part of curves their decreases results from the change in β_1 only. On the basis of these assumptions, the values of v_0/c and β_1 in aqueous solution at various pH are evaluated by means of Eqs. (3) and (1), and given in Table II.

TABLE II
THE RESULTS FOR GELATIN IN AQUEOUS SOLUTION

pH	K	$\beta_1/\beta_w \cdot 1/d_1$	$\beta_1 \times 10^{12}$	v_0/c
3	0.04	0.33	21.	0.29
5	0.00	0.30	19.	0.30
8	0.04	0.33	21.	0.29
10	0.07	0.35	22.	0.28

From these values it may be seen that β_1 increases gradually with the deviation of pH from the isoelectric point, while v_0/c changes very little. Consequently, the variation in K in aqueous solution caused by pH change is mainly due to the change of the compressibility of the gelatin particle. The above values of v_0/c agree with the generally assumed values of proteins, and the behavior of v_0/c with pH change agrees with the fact reported by Weber et al.(6).

The hydration of gelatin has been evaluated by Passynski(7). He proposed an approximate equation to calculate the amount of hydration from the compressibility difference between solvent and solution, which was similar to the present ones, and applied it to many solutions. He derived his equation, however, by assuming that when the concentration of solute approached zero, the effect of compressibility of solute could be ignored. But, according to the present procedure, it is shown that K must be also correlated by the compressibility of solute itself, perticularly in high polymer solutions. Consequently, the effect of the compressibility of solute cannot be neglected at the evaluation of the amount of bound water in these procedures. Further more, when the compressibility of solute molecule changes with the variation of composition of solution, the compressibility of solute should be taken into consideration, as the authors have done.

Miyahara has evaluated the compressibility of egg albumin in aqueous solution, giving 13×10^{-12} c.g.s. unit at its isoelectric point by analogical calculation using the date of aminoacids(8). Jacobson has computed also the compressibilities of natural proteins, the magnitude of which is in the order of 10×10^{-12} c.g.s. unit by his own procedure(9). In comparison with these values, the present values of gelatin are appreciably larger. This difference may be due to the difference of properties of molecules, that is to say, natural proteins have the rigid three-dimensionally definite structure, but gelatin is a degradation product of some proteins and has not any definite structure, freely extending, somewhat similar to synthetic polymers such as polyvinylalcohol.

To calculate the values of v_0/c and β_1 of gelatin strictly, however, the facts that there are several interactions between the components of solution must be taken into account. The change of pH of the solution caused by the buffer action of gelatin might also be well considered.

It may be concluded that the present procedure holds not only for the solutions of non-electrolytes but also for those of electrolytes and that the values of the amount of bound water and the compressibility of solute are always separately obtained.

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6) H. H. Weber and D. Nachmannsohn, *Chem. Abst.*, **23**, 1917 (1929).

7) A. Passynski, *Acta Physicochim. U. R. S. S.*, **3**, 779 (1935); **22**, 137 (1947).

8) Y. Miyahara, This Bulletin, **29**, 742 (1956).

9) B. Jacobson, *Arkiv För Kemi*, **2**, 177 (1950).

Summary

1. The previously introduced theory on the amount of bound water and the compressibility of solute has been tested with the solutions of organic electrolytes.

2. The proposed procedure was found to be satisfactory and gave separately the values of the amount of bound water and the compressibility of solute in each case. These results appear to be proper compared with others.

3. The compressibility of the solute could be neglected in aminoacid solutions by the same reason as in the case of glucose where the solute is of low molecular weight.

4. It is shown that the amount of bound water of gelatin varies very little as pH of solution goes apart from the isoelectric point where the compressibility of gelatin molecule has a minimum value, as had been expected.

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