gases are present, the reaction $Ag_2N_2O_2 = 2Ag + 2NO$, which would introduce large additionala mounts of nitric oxide in the system, containing Ag_2O, probably does not occur.

Conclusion

The primary change in the decomposition of silver hyponitrite appears to be

$$Ag_2N_2O_2 = Ag_2O + N_2O \qquad (I)$$

Apparently this reaction is not accompanied by any other change, such as $Ag_2N_2O_2 = 2Ag + 2NO$. Reaction I is instantly followed by

$$Ag_2N_2O_2 + 2Ag_2O = 2AgNO_2 + 4Ag \qquad (II)$$

The formation of $AgNO_2$ in this way, at 160° and above, is followed by its decomposition (above 128°) producing, ultimately, $AgNO_3$, Ag and oxides of nitrogen. Nitrate is formed from nitrite and not directly; it may be produced, to some extent, by $Ag_2O + NO_2 = AgNO_3 + Ag$. As nitric oxide is formed it reacts with nitrate to regenerate nitrite to some extent, $AgNO_3 + NO \rightleftarrows AgNO_2 + NO_2$.

The decomposition of silver nitrite, which follows reactions I and II, retards the decomposition of silver hyponitrite by reaction I. The formation of nitrite from the hyponitrite also reduces the amount of hyponitrite decomposing by I and explains low percentage of nitrous oxide in the gas; although I is the primary change, the reaction apparently stops as soon as Ag_2O and $AgNO_2$ (optimum) are present and starts again when these approach a limiting concentration. Thus, the decomposition of silver hyponitrite seems to proceed by the propelling action of silver oxide formed, at intervals, during the decomposition.

That I is not accompanied by $Ag_2N_2O_2 = 2Ag + 2NO$ is supported by the following observations: (a) nitric oxide destroys Ag_2O rapidly with the formation of nitrogen dioxide, nitrite and nitrate; (b) silver oxide oxidizes silver hyponitrite even at 150° while the oxides of nitrogen do not do so; and (c) when large quantities of silver nitrite are present in the system containing silver hyponitrite, silver oxide is not found.

The formation of nitrogen is not explained. It is found whenever silver oxide is present or produced in contact with nitric oxide or oxides of nitrogen. As nitric oxide and nitrogen dioxide are both present in the system, it is not likely that the reaction[8] $AgNO_2 + NO = AgNO_3 + {}^1/_2N_2$ occurs to any appreciable extent.

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[CONTRIBUTION FROM THE CHEMICAL INSTITUTE, FACULTY OF SCIENCE, NAGOYA UNIVERSITY]

Measurement of the Amount of Bound Water by Ultrasonic Interferometer

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A general theory which enables us to evaluate the amount of the bound water of non-electrolyte and of high polymer in solution from ultrasonic velocity measurements has been introduced, and applied for glucose, maltose and dextrin solutions. The ultrasonic velocity was measured by an interferometer making use of X-cut crystal of resonance frequency 1 mc. The measurements were made at 20.0°. The amount of bound water was found to be 0.43, 0.23, 0.40 cc./g. of glucose, maltose and dextrin, respectively.

Introduction

It is a well-known fact that, in solutions of electrolytes, the water molecules bound to an electrolyte ion are compressed owing to the strong electric field of the ion to form a very hard structure. Passinski,[1] Wada[2] and Sasaki[3] evaluated the degree of hydration of ions from adiabatic compressibility measurements. They assumed the compressibility of bound water and of the ion itself to be both negligibly small. But the applicability of this method for the evaluation of non-electrolytes or high polymers in aqueous solutions is questionable, the bound water of non-electrolytes or the molecules of high polymers being reasonably supposed to be of appreciable compressibility. We have deduced a more general formula taking account of the compressibilities of bound water and of the solute particle, and have applied it to the solutions of sugars as well as high polymers and estimated the amount of bound water.

Theoretical

If M grams of solute is dissolved in V_0' cc. of solvent, some of the solvent, say v_0' cc., will be attached to the solute and compressed to be v_2' cc., and, consequently, there will result a solution of volume V' cc. Accordingly it follows that

$$V' = V_0' + V_1' + v_2' - v_0' \qquad (1)$$

in which

$V_1' = M/d_1$ = volume of solute in V' cc. soln.
d_1 = true density of solute in soln. (solvation effect being not taken into account)

Differentiating (1) with respect to the pressure, P

$$\frac{dV'}{dP} = \frac{dV_0'}{dP} + \frac{dV_1'}{dP} + \frac{dv_2'}{dP} - \frac{dv_0'}{dP}$$

Let β, β_0, β_1 and β_2 represent the adiabatic compressibility of solution, solvent, solute and bound water, respectively.

From definition these β's are given by

$$\beta = -\frac{1}{V}\frac{dV}{dP}$$

therefore we obtain the relation

$$V'\beta = V_0'\beta_0 + V_1'\beta_1 + v_2'\beta_2 - v_0'\beta_0$$

For 1 cc. solution, this can be written in the form

$$\beta = V_0\beta_0 + V_1\beta_1 + v_2\beta_2 - v_0\beta_0. \qquad (2)$$

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(1) A. Passinski, *Acta Physicochimi, U.R.S.S.*, **8**, 385 (1938).

(2) Y. Wada, *Applied Phys.* (*Japan*), **17**, 257 (1948).

(3) T. Yasunaga and T. Sasaki, *J. Chem. Soc. Japan, Pure Chem. Soc.*, **72**, 366 (1951).

where

$$V_1 = V_1'/V', \; V_0 = V_0'/V', \; v_2 = v_2'/V', \; v_0 = v_0'/V'$$

and there exists a relation for V_0

$$V_0 = (d - c)/d_0 \qquad (3)$$

in which

d = density of solution
c = concn. of solute in g./cc. soln.
d_0 = normal solvent density

From (2), we obtain the formula

$$\Delta \equiv \beta/\beta_0 - V_0 = V_1\beta_1/\beta_0 - (v_0 - v_2\beta_2/\beta_0) \qquad (4)$$

And per 1 g. solute

$$\Delta/C \equiv (\beta/\beta_0 - V_0)/c = \beta_1/\beta_0 \times 1/d_1 - (v_0 - v_2\beta_2/\beta_0)/c \qquad (5)$$

β, β_0 can easily be calculated from the results of measurements of the sonic velocities in solutions and solvents, and V_0 from (3) through measurements of the concentration c together with densities d and d_0; therefore, Δ/c may be determined experimentally. The first term of the right side of (5) is due to the compressibility of solute β_1, and the second represents the term due to hydration.

Now, as ethanol, which acts as a precipitating agent for the solutes described above, is added to the solution, the second term, which is due to hydration, decreases gradually.[4,5] The compressibility of the solvent β_0, which is, in the present case, a binary mixture of ethanol and water in various proportions, varies with ethanol %. In order to correct this effect, both sides of (5) are multiplied by β_0/β_w; then, it follows that

$$K = \Delta/c \times \beta_0/\beta_w = \beta_1/\beta_w \times 1/d_1 - (v_0\beta_0/\beta_w - v_2\beta_2/\beta_w)/c \qquad (6)$$

where β_w is the compressibility of pure water.

If we assume that the hydration has been brought to naught on the point of precipitation, K_p, which represents the K at the precipitation point, is given only by the first term of (6), and consequently the compressibility of solute particle β_1 can be found directly from this value. And if β_1 is assumed to remain constant irrespective of variation of ethanol concentration, we obtain the magnitude of the hydration term from the difference of K_w and K_p, which are the value of K for aqueous solution and at the precipitation point in the alcohol-containing aqueous solution, respectively.

Experimental

The ultrasonic velocity was measured by an interferometer making use of X-cut crystal of resonance frequency 1 mc. The methods of measurement were described in previous papers.[6,7] The materials used were purified by reprecipitation from G.P. or E.P. grade chemicals.

Results and Discussion

Measurements were carried out with solutions of glucose, maltose and dextrin at 20.0°. Table I shows the results obtained for glucose solutions as an illustrative example, in which V_0, β_0 and d_0 are values of water–ethanol mixed solvents.

TABLE I

EXAMPLE OF THE MEASUREMENTS (GLUCOSE SOLUTIONS)

Alcohol, %	c(g./cc.)	d_0	d	V_0	β/β_0	K ($\Delta/c \times \beta_0/\beta_w$)
0.0	0.0588	0.9982	1.0206	0.9635	0.9486	−0.253
10.2	.0552	.9814	1.0035	.9663	.9582	− .128
12.0	.0568	.9791	1.0005	.9639	.9567	− .117
19.3	.0560	.9694	0.9922	.9657	.9660	.005
27.0	.0584	.9602	.9837	.9636	.9649	.019
34.2	.0576	.9432	.9670	.9641	.9752	.017
42.3	.0574	.9324	.9564	.9642	.9654	.020
47.2	.0551	.9222	.9456	.9656	.9656	.000
56.1	.0496	.8987	.9200	.9685	.9682	.006

The plots of K against ethanol % are shown in Figs. 1, 2, 3.

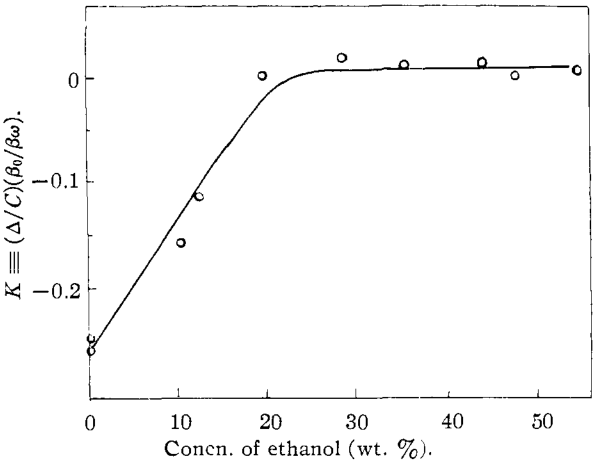

Fig. 1.—Effect of ethanol concentration on K's value of glucose.

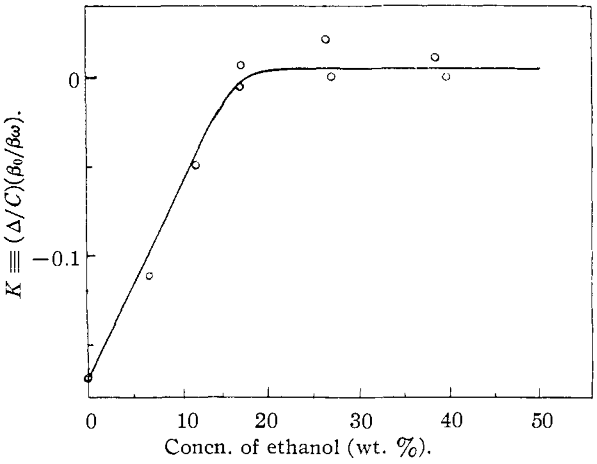

Fig. 2.—Effect of ethanol concentration on K's value of maltose.

The values of K are found to increase with ethanol concentration (Figs. 1, 2); this might be due to the decrease of the hydration term in (6). At ethanol concentrations of about 20% and more, the curve becomes horizontal, this being possibly attributed to the effect that the bound water has been removed from the solute molecules by ethanol, and if this is the case, K values would be given only by the first term of (6) having a bearing on the com-

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[4] H. R. Kruyt and H. G. Bungenberg de Jong, *Kolloidchem. Beihefte*, **28**, 1 (1929).

[5] H. Shiio, *J. Chem. Soc. Japan, Pure Chem. Sec.*, **74**, 203 (1953).

[6] Y. Miyahara, *Bull. Chem. Soc. Japan*, **25**, 326 (1952).

[7] Y. Miyahara, *ibid.*, **26**, 390 (1953).

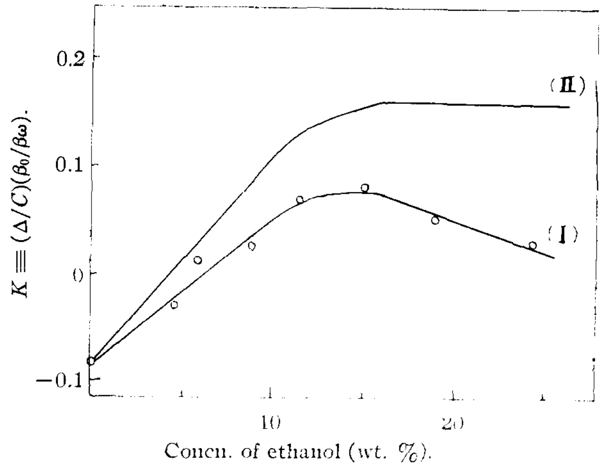

Fig. 3.—Curve 1, effect of ethanol concentration on K's value of dextrin; curve II, effect of ethanol concentration on K_b value (only hydration part of K's value).

pressibility of solute molecule β_1. From this limiting value (K_p), we can calculate β_1 using β_w and d_1 which can also be determined experimentally; however, in the case of glucose and of maltose, the values of K_p thus obtained are found to be so small that they are beyond the limits of experimental accuracy and, therefore, it would be meaningless to discuss the values of β_1 further.

Then it is clear, from this point of view, that the treatments by Passinski,[1] Sasaki[3] and our previous reports,[8] in which the compressibility of solute molecule is put to zero, are only of the first approximation. Now, the difference of K_w and K_p give us the value of $(v_0 - v_2\beta_2/\beta_w)/c$ which is proportional to the hydration of one gram of solute. However, it is more easily understood, if the numerical values of v_0/c are given concretely and, hence, we may evaluate the value v_0/c on the following assumptions: "With non-electrolytes, a strong compression as observed with ions would not result, then $v_0 = v_2$; in that case, hydration may be caused by hydrogen bonds principally, then we can use without much error the compressibility of ice (18×10^{-12} barye^{-1}) for β_2, since their bound water is not so strongly compressed as ion ($\beta_2 = 0$), but not so soft as normal water ($\beta_w = 45 \times 10^{-12}$ barye^{-1})."

"Bound water" should be defined according to the methods of measurement, and it has only a relative significance characteristic to each method. For example, in the determination of the bound water from measurements of viscosity or diffusion constant, bound water is taken as that moving together with the solute particles under ordinary conditions, and in the cases from measurements of negative adsorption of low molecular weight solute (*e.g.*, sugar, $CuSO_4$, etc.), the portion of water adsorbed by the solute particle not accessible to the molecules of low molecular weight is defined the bound water.[9] So we think that bound water due to hydrogen bond principally has the compressibility of ice on average, and that amount of bound water is that of water dehydrated while precipitating agent is added to the precipitation point. Namely our assumption is regarded as a definition of bound water.

From the difference of K_w and K_p in Figs. 1, 2, we can obtain the value of hydration v_0/c. These values are given in Table II.

TABLE II

THE AMOUNT OF BOUND WATER (v_0/c)

Solute	Cc./g.	Mole/mole
Glucose	0.43	4.3
Maltose	.23	5.3
Dextrin	.40	

Now in the case of glucose, we have obtained a reasonable result that the sugar molecule possesses for each of its free OH-radicals nearly one water molecule, but with maltose, the value is fairly small, and this might be considered to be due to the decrease of free OH-radicals owing to intramolecular hydrogen bonding.

In dextrin solution, K initially takes a negative value, but with the addition of alcohol, it gradually increases toward a maximum, and finally drops off (curve I). In the initial increasing part the effect of the hydration term may be predominant as with glucose; in the latter part in which the curve is descending, the effect of decreasing β_1 may be prevailing and the dextrin molecule would be considered to be of a compressed structure as the result of ethanol addition.

Beyond the maximum point, the curve runs downward almost linearly; then we might well assume that the above mentioned effects of β_1 are linear with respect to the ethanol concentration. By subtracting this effect of β_1 from K, we obtain K_b (curve II) which represents the hydration effect alone in K. From this curve we calculated the degree of hydration of dextrin as in the case of glucose. The results are shown in Table II. From curve II in Fig. 3 we obtain 9.2×10^{-12} barye^{-1} as the value of the compressibility β_1 in aqueous solution.

Using the several methods of measurement, various authors[9,10] have estimated the degree of hydration of starch to be 0.3–0.4 cc./g. Our results are completely in accord with their values.

Conclusion

(1) A general theory is introduced which enables us to evaluate the amount of bound water of nonelectrolytes and of high polymers in solutions from ultrasonic velocity measurements.

(2) The compressibility of the solute molecule of lower molecular weight may, in the first approximation, be regarded as being negligibly small.

(3) In high polymers, however, the compressibility of the molecule itself must be taken into consideration.

(4) The amounts of bound water are 0.43, 0.23, 0.40 cc./g. for glucose, maltose and dextrin, respectively.

(5) The compressibility value obtained for the dextrin molecule is 9.2×10^{-12} barye^{-1} in aqueous solution.

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[8] Y. Mihahara and H. Shiio, *J. Chem. Soc. Japan*, *Pure Chem. Sec.*, **72**, 876 (1951).

[9] K. Yoshioka, *ibid.*, **71**, 456 (1950).

[10] A. V. Dumanskii and R. V. Voilsekhovskii, *Kolloid Zhur.*, **10**, 413 (1948); *C. A.*, **43**, 7781 (1949).