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The Variation in the Structure of Water in Ionic Solutions. II

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Earlier experiments with 15 strong electrolytes have been extended to 38 and there continues to be a striking correspondence between the rate of variation of the partial molal ionic volume with concentration and the rate of variation of water structure as crudely indicated by the x-ray diffraction pattern. The concentration in mole fraction of the solutions varied from 0.001 to 0.096 having a mean of 0.028. The influences of concentration on adiabatic compressibility and of solubility on the variation of water structure are mentioned. Qualitative explanation of the effect of the ions in solution may be obtained by assuming a direct effect on the breaking of H bonds and the indirect effect of altering the pure temperature expansion of the water.

THE x-ray diffraction intensity-angular distribution data for water has shown¹ that with increasing temperature the minor diffraction peak is strikingly reduced. Careful measurements have further shown that² the radial density distribution of molecules about any one of them is altered by increasing temperature so that the number of nearest neighbors is increased. This involves breaking hydrogen bonds and producing a more compact water structure, but of course there is also the simultaneous pure temperature expansion. These opposing effects account qualitatively for the existence of a maximum density of water at 4°C. It is well known that in aqueous solutions the variation of the partial molal ionic volume with concentration follows a course that is similar in many strong electrolytes. Again this can be interpreted³ as the formation of new liquid structures occasioned by the breaking of hydrogen bonds and resulting in a greater density of the solvent water. Also it is found³ that with increasing concentration in an ionic solution, the minor x-ray diffraction peak, mentioned above, decreases in a manner similar to the effect with increasing temperature in pure water. The question is, does this similarity of the effect on the diffraction curves in pure water and ionic solutions have any significance? The experimental results gave credence to the view that this similarity is significant. For it was shown³ that with sixteen strong electrolytes at the concentra-

tion of 0.55 mole per liter, the rate of change of the partial molal ionic volume φ , with the concentration c , varied from one electrolyte to another much as did the change in the relative minor peak x-ray intensity. More definitely, an n was found for each electrolyte which would make $(\partial\varphi/\partial c^n)$ constant in the region of 0.55 mole per liter. Then the values of $\partial h/\partial m$, where h is the height of the minor diffraction peak and m is the concentration in mole fraction, were experimentally obtained. When these two variables for the sixteen samples were plotted as coordinates, there was a crudely approximate linear relation. Lines drawn from the origin through each point did not vary from a median straight line by more than 9°. A previous discussion³ indicates that in a dilute solution the relative variation in the experimental intensity distribution curve at the diffraction angles herein considered, may be regarded as approximately a relative variation in the scattering curve for the solvent water. This approximation grows increasingly poorer with concentration. Out of this semi-quantitative, approximate procedure comes the conclusion that the chief cause of $(\partial\varphi/\partial c^n)$ and of $\partial h/\partial m$ is the same, and that ions also break the hydrogen bonds and cause a denser water structure. This is in harmony with the suggestion of Bernal and Fowler.⁴ To this early list of fifteen strong electrolytes are now added twenty-three more. The data for all are now presented in Table I. They are also plotted as before in Fig. 1.

¹ G. W. Stewart, *Phys. Rev.* **37**, 9 (1931).

² J. Morgan and B. E. Warren, *J. Chem. Phys.* **6**, 666 (1938).

³ G. W. Stewart, *J. Chem. Phys.* **7**, 869 (1939).

⁴ J. D. Bernal and R. H. Fowler, *J. Chem. Phys.* **1**, 515 (1933).

TABLE I. Correspondence of the variation of the apparent molal ionic volume with the indicated change in the liquid structure of the solvent, water.

Electrolyte	Temperature	Concentration (mole fraction)	$(\partial\varphi/\partial c^n)$ (Exp.)	(n)	$0.01 \partial h/\partial m$ at 25°C
NH ₄ C ₂ H ₃ O ₂	17°	0.0908	0.58	(1)	1.00
LiNO ₃	17°	.0557	0.78	(0.8)	1.6
KCN	15°	.0647	1.03	(1)	0.73
KCNO	15°	.0527	1.15	(1)	1.12
NH ₄ F	15°	.07359	1.27	(1)	0.49
NH ₄ Cl	25°	.0325 .0619 .0960	1.33	(0.5)	1.18
LiCl	25°	.0357 .0853	1.67	(0.5)	1.38
NaCl	25°	.0231 .0331 .0799	2.06	(0.5)	1.48
LiOH	15°	.0543	2.2	(0.8)	1.7
KClO ₃	15°	.0086	2.46	(0.5)	5.0
KCl	25°	.0152 .0378	2.73	(0.5)	2.25
NaClO ₄	15°	.033	3.6	(0.4)	1.86
NaOH	15°	.0375	2.59	(1.0)	2.0
H ₂ SO ₄	15°	.018	3.63	(0.5)	3.0
MgCl ₂	25°	.0182 .0431 .018	3.8	(1)	3.8
	15°		3.8	(1)	3.6
Mg(NO ₃) ₂	15°	.00848	4.0	(1)	4.6
Ca(NO ₃) ₂	15°	.02605	4.8	(1)	2.2
(NH ₄) ₂ SO ₄	15°	.01016	6.0	(1)	5.3
H ₃ PO ₄	15°	.025	6.3	(<0.2)	3.3
Al(NO ₃) ₃	15°	.00935	8.54	(0.5)	6.2
MnSO ₄	15°	.014	6.85	(0.5)	5.5
K ₂ CO ₃	15°	.01424	8.6	(1)	4.6
CdCl ₂	15°	.019	7.6	(0.5)	2.5
KHCO ₃	15°	.02203	8.8	(0.1)	4.3
KNaC ₄ H ₄ O ₆	15°	.0149	9.57	(0.5)	5.55
MgSO ₄	15°	.00945	9.6	(0.5)	7.5
K ₂ SO ₄	15°	.00613	10.7	(1)	9.5
ZnSO ₄	15°	.0104	10.8	(1)	4.5
CuSO ₄	15°	.00878	12.4	(0.5)	9.4
AlCl ₃	15°	.0090	14.0	(0.3)	7.9
CoCl ₂	15°	.0065	16.0	(0.5)	8.1
K ₂ Cr ₂ O ₇	17°	.00491	16.0	(1)	16.0
NiCl ₂	17°	.0048	17.3	(0.5)	14.0
Na ₂ AsO ₄	15°	.00378	22.2	(0.8)	23.5
CoSO ₄	15°	.00806	22.8	(0.25)	7.3
Ce ₂ (SO ₄) ₃	15°	.003	79.0	(0.2)	23.7
Co(NO ₃) ₂	15°	.00175	38.8	(0.5)	36.0
Co(C ₂ H ₃ O ₂) ₂	15°	.0010	100	(1)	60.0

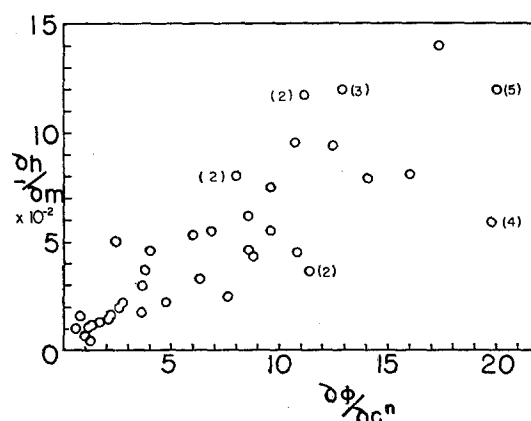


FIG. 1. The values of rate of change of minor peak height (major peak 100) with mole fraction, divided by 100, compared with values of $(\partial\varphi/\partial c^n)$. Coordinates should be multiplied by the number in parenthesis.

DISCUSSION OF DATA AND INTERPRETATION

The data for φ were taken from the *International Critical Tables*, volumes 4 and 6, and Landolt and Börnstein, fifth edition. The x-ray diffraction curves for the samples were obtained with the same equipment as previously described.³ There are several unsatisfactory features of the data and their use, though the interpretation here made is not vitiated thereby. The values of φ are, in general, probably not reliable. For example, with KClO₃, φ is recorded in the above sources as decreasing with concentration, whereas Redlich and Bigeleisen have recently shown⁵ that it increases.⁶ Most of the φ data were taken at 20°C, and some of them from 15°C to 18°C. No temperature correction was applied. The experimental determination of h was determined usually at 15°C, and in each case the temperature correction found for water was applied to give the value at 25°C. The values of $(\partial\varphi/\partial c^n)$ and values of n were obtained from the plotted data for φ in the neighborhood of 0.55 mole per liter. The values given in the fourth and sixth column of Table I for H₃PO₄, H₂SO₄, and CdCl₂ are questionable. Nevertheless, with all inaccuracies considered, Table I and Fig. 1 do give striking results. In general large values of $(\partial\varphi/\partial c^n)$ correspond to large values of $\partial h/\partial m$. The change in φ , the

⁵ O. Redlich and J. Bigeleisen, J. Am. Chem. Soc. **64**, 758 (1942).

⁶ The data on KClO₃, using these new values, have been placed in the table and on Fig. 1.

partial molal ionic volume, is interpreted as most importantly caused by the change in specific volume of the water. Hence the larger the $(\partial\varphi/\partial c^n)^7$ the greater the rate of change of the specific volume of the water with the concentration. Thus there should be a general correspondence between the two indicators of the rate of change of the water structure with concentration. A quantitative correspondence, in the very nature of the case, cannot possibly be expected. This general correspondence is strikingly shown by Fig. 1. The experimental results thus give impressive evidence of the correctness of the interpretation, namely, that the changes in φ are caused importantly (not exclusively) by the changes in the structure of the solvent water. Thus the conclusion from the earlier paper is extended and verified.

There are several other comparisons that can be made with $\partial h/\partial m$. One is with the change of *adiabatic compressibility* β of these same electrolytes. In an article shortly to be published, Dr. Victor B. Corey has shown that there is also a definite trend for $-\partial h/\partial m$ to increase with $-\partial\beta/\partial m$. The interpretation is that the change in the structure of the solvent, water, is responsible for both, at least to an important degree.

Solubility has been a property of great interest and complexity as well. If the solubility of these strong electrolytes as found in the *International Critical Tables* be plotted with $-\partial h/\partial m$, the points, though widely scattered, show a marked general trend, the solubility decreasing as the values of $-\partial h/\partial m$ increase. Empirical methods of allowing for the temperature below melting

point, do not decrease the scattering materially. Evidently the more soluble the electrolyte the less disturbance per ion is caused in the water structure. This is in harmony with the simple view that solubility is determined by the ease of participation in the water structure.

In approximately 200 strong electrolytes there are five in which the slope $\partial\varphi/\partial c$ is negative and in none of them is there a linear relation between φ and c^n . In two of them, $\text{Ba}(\text{OH})_2$ and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, the values for $-(\partial h/\partial m)/100$ were measured and are 16.0 and 10.0, respectively, indicating nothing unusual in the change of structure. They are thus exceptional cases and do not fit in with the simple interpretation given above. More exact data for the computation of φ in these cases might alter this situation as in the case of the data for KClO_3 already mentioned.

The effect of the ions on the water structure, on adiabatic compressibility, and on the temperature of minimum compressibility and also the possibility of a decreasing φ with increasing c and yet show no uniqueness in x-ray diffraction, can receive qualitative explanation on the following simple and apparently reasonable hypotheses. In water an increase in temperature (1) breaks hydrogen bonds and alters the water structure, decreasing its molal volume and (2) causes a pure temperature expansion increasing the molal volume. Ions in aqueous solution (1) break hydrogen bonds and alter the water structure, decreasing its molal volume, and as a consequence (2) increase the pure temperature expansion of the solvent. The discussion of this suggestion is reserved for further report.

I wish to express my indebtedness to Dr. James Jacobs and Mr. Harold Froslic, the former for much of the x-ray diffraction data.

⁷ The reasoning is better if but one value of n is used, say $n = \frac{1}{2}$, but the correspondence in Fig. 1 is a little better if n is chosen as here indicated.