A Theory of Surface Tension of Aqueous Solutions of Inorganic Acids.

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1. Introduction. Since Heydweiller and his co-workers(1) discovered that the surface tension of the solution of inorganic salts in water increases as the solute is increased, various attempts(2) have been made to explain the phenomenon. The recent theories proposed(3),(4),(5),(6) to account for the phenomenon are all based on the Debye-Hückel(7) theory of strong electrolyte. All these theories treated with varied degrees of success the normal effect, that is, the increase of surface tension with increase in the concentration of the electrolyte. None of these theories, however, treat the anomalous behaviour of inorganic acids which exhibit a decrease of surface tension as the concentration is increased. The lack of any theoretical account for the anomalous effect for inorganic acids is due primarily to the fact that the effect is just opposite to what we might expect from the Debye-Hückel theory of strong electrolyte. This simple fact suggests at once that the structure of water at the surface is the most important factor to be considered in any theoretical discussion of this anomaly. The present paper shows that the anomaly can be explained quantitatively if we accept two hypotheses, that is, a special orientation of water molecules at the surface different from the interior and the semi-empirical structure of water as proposed by Bernard and Fowler.(8)

2. In order to understand the especially high value found for the decrease of surface tension due to ammonia solution of water, we shall discuss briefly the structure of water and similar compounds from a general point of view.(9)

The hydrogen atom occupies a very peculiar position in the structure of atoms, and exhibits in many ways peculiar characteristics different

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(1) Heydweiller, *Ann. Physik*, [4], **33** (1910), 145.

(2) Wagner, *Physik. Z.*, **25** (1924), 474.

(3) Onsager and Samaras, *J. Chem. Phys.*, **2** (1934), 529.

(4) Oka, *Proc. Phys.-Math. Soc. Japan*, [3], **14** (1932), 649.

(5) Shiba, *Bull. Inst. Phys. Chem. Research* (Tokyo), **8** (1934), 110.

(6) Ariyama, this Bulletin, **11** (1936), 887.

(7) See for example Falkenhagen, "Electrolyte."

(8) Bernal and Fowler, *J. Chem. Phys.*, **1** (1933), 515.

(9) The author is indebted to Dr. J. Horiuchi for the following discussion.

from all other elements. Most of these peculiarities owe their origin to the fact that the positive ion of the hydrogen atom is simply a proton, which carries no extra-nuclear electrons. An example of such peculiarity is given in the case of an extraordinarily high absorption of hydrogen by palladium. This is explained if we consider that the hydrogen atom when going into palladium separates into electron and proton, and that these are separately absorbed.(10) The greatest peculiarities appear when hydrogen atoms combine with atoms of oxygen or nitrogen.

The peculiarities are indicated in the structure of the compounds as well as in various chemical and physical properties of the compounds. In the case of water, for example, the distance between the two hydrogen atoms is 0.97Å, while the diameter of hydrogen molecule is 2.76Å. Thus two protons of the water molecule lie within the distance of orbital radius of the outermost electrons of oxygen atoms. Bernal and Fowler(8) in their extensive treatment on water give the following model for the structure of water, basing their argument partially on quantum mechanics and partially on experimental data: If we suppose an oxygen atom at the center of a tetrahedron the two heads of the tetrahedron are occupied by the two protons, and at the other two heads of the tetrahedron are distributed the negative charges. The structure of alcohol is obtained if we replace a hydrogen with an alkyl radical in the tetrahedron. In the case of ammonia, three corners of the tetrahedron are occupied by protons and the remaining corner is occupied by negative charges. If we replace one hydrogen by alkyl radicals we obtain the structure for amines.

If, for example, molecules which have similar structure to water approach a water molecule, it is quite evident from the above discussion that the corners of the tetrahedron of water at which negative charges are distributed will attract the protons of other molecules. Such union of two molecules by means of a proton is called a "hydrogen bond," and this hydrogen bond is considered responsible for the association of water, alcohol, and ammonia molecules.

From these general discussions it may be expected that the hydrogen ions and ammonia molecules behave somewhat differently from all other inorganic ions in water. If the molecules of water are distributed at random both at the surface and in the interior of the liquid, the negative adsorption should result from solutions of inorganic acid. For the ions forming the hydrogen bond between molecules of water will be uniformly distributed everywhere so that the effect due to hydrogen bond can be neglected as far as the distribution of hydrogen ions in water is concerned.

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(10) Frank, *Göttinger Nachrichten*, **1933**, 293.

Thus the hydrogen bond alone does not give rise to the positive adsorption of hydrogen ions at the surface of water.

In order that the positive adsorption of hydrogen ions at the surface of water should result the distribution of the hydrogen bond must be different at the surface than in the interior of the water. If at the surface the number of water molecules having their hydrogen heads facing upward sufficiently exceeds the number having their oxygen atoms facing upward so that as a consequence there is a resultant of hydrogen heads extending into the liquid, we might expect positive adsorption of hydrogen ions at the surface due to the hydrogen bond. Since this seems to be the only way for the positive adsorption of hydrogen ions to occur at the surface, we shall assume that the majority of water molecules are oriented at the surface in such a way that the proton heads of the molecular tetrahedrons lie on the surface causing the negatively charged corners to extend downward into the liquid.

3. For the quantitative discussion of the surface tension of inorganic acids, we shall take, for sake of simplicity and convenience, one-half molar concentration for all the compounds, and the temperature at which the surface tension is given is corrected to 20°C. unless otherwise stated. The Table 1 shows the experimental data mainly collected from the International Critical Tables.

In the fourth row of the Table the calculated values for the surface tension decrease due to one hydrogen-bond at the surface are given. The methods of the calculations are given in the following: We shall take the case of HCl as an example. The surface tension increase due to half normal solution of NaCl at 20° is 0.83 dynes/cm. Since the charge of Na^+ and Cl^- ions are the same, and their ionic volume approximately the same according to the theories proposed for the negative adsorption of Debye-Hückel electrolyte,(3),(4),(5),(6) the contribution of these two ions to the increase of the surface tension of the solution will be approximately the same. Thus we get the same contribution from Na^+ as from Cl^- namely 0.41 dynes/cm. If the Cl^- behaves in the same way in the half normal solution of HCl as in the half normal solution of NaCl, then the contribution of Cl^- to the increase in surface tension will be the same. Therefore, in order to obtain the decrease of the surface tension of the HCl solution by -0.2 dynes/cm., the contribution due to H^+ should be $-0.2 - 0.41 = -0.61$. dynes/cm. In the similar manner the contribution due to one hydrogen bond for the compounds HNO_3 and HBr is calculated. The values assigned for negative ions for respective compounds are listed

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(11) Rice, *J. Phys. Chem.*, **32** (1928), 583.

Table 1.

$\Delta\gamma$ is the difference between the surface tension of the solution and that of the solvent at the same temperature.

$\Delta\gamma$ is expressed in dynes per centimeter.

Formula	Temperature °C.	$\Delta\gamma$ for 0.5 mol/kg.	$\Delta\gamma$ due to H
HCl	20	-0.16	-0.57 ± 0.1
NH_3	18	-1.4	-0.46 ± 0.3
HNO_3	20	-0.42	-0.61 ± 0.2
HBr	18	-0.38 ± 0.2	-0.56 ± 0.2
H_2SO_4(12)	20	-0.18	-0.55 ± 0.3
Na_2HPO_4	30	-0.81 ± 0.2	-0.23 ± 0.3
KH_2PO_4(12)	20	-0.53 ± 0.05	-0.81 ± 0.3
H_3PO_4(12)	20	0.00 ± 0.3	-0.33 ± 0.3
		The average for the last 3 cases	-0.46 ± 0.3

Table 2.

Uni-valent case

Ions	$\Delta\gamma$
Na^+	0.41
Cl^-	0.41
NO_3^-	0.19
OH^-	0.50
Br^-	0.29
NH_4^+	0.5

Bi-valent case

Ions	$\Delta\gamma$
Na^+	0.23
SO_4^{--}	0.91

Tri-valent case

Na^+	0.11
K^+	0.11
PO_4^{---}	0.99

in the Table 2. These values can be used to check their reasonableness with many other compounds containing these negative ions in the solutions.

When the negative ions happen to be bi-valent or of the higher valency, the calculation is carried out in the following manner: Let us take as an example the half normal solution of Na_2SO_4. According to the theories of the negative adsorption,(3),(4),(5),(6) the contribution of ions

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(12) Morgan and Bole, *J. Am. Chem. Soc.*, **35** (1913), 1750.

to the increase in the surface tension of the solution is proportional to the number of respective ions and to the squares of their ionic charges. Thus the increase of surface tension by 1.36 dynes/cm. for the Na_2SO_4 solution gives 0.91 dynes/cm. to SO_4 ions, that is 4/6 of the total effect. A similar argument applies to the case of H_3PO_4 and the related compounds. The values assigned for the negative ions are given in Table 2. Using these values for the negative ions, we obtain values for one hydrogen-bond for various compounds.

The calculation for ammonia differs from the above procedure. As we have already discussed, the ammonia molecule has a very similar structure to water, and any one of three protons of the ammonia molecule can form a hydrogen bond with a water molecule. Thus the probability of ammonia being adsorbed by water molecules at the surface is approximately three times as large as that of single hydrogen ion, so that it is to be expected that the half normal ammonia solution will show three times as large an effect as is to be expected from HCl solution. Therefore, we simply divide -1.4 dynes/cm. by 3 to obtain the effect due to a single hydrogen bond. We obtain a value for the single hydrogen-bond which agrees within experimental error with those found for other compounds.

The examination of NH_4NO_3, NH_4Cl, and NH_4Br indicates that the NH_4^+ ion behaves as if it were a metallic ion which gives rise to the negative adsorption. Therefore when the ammonia NH_3 is dissolved in water,⁽¹¹⁾ the NH_3 molecule is adsorbed at the surface of water forming a hydrogen bond with a water molecule, and the NH_3^+ ion is not formed by the capture of hydrogen ions in water. This is a very interesting conclusion which we can derive from the above experimental data.

As is clearly indicated in Table 1, the values found for $\Delta\gamma$ due to the hydrogen bond agree very well within the experimental error. This fact strongly supports the assumptions which we have stated at the beginning of the paper. Thus the anomaly of the surface tension exhibited by inorganic acids can be attributed to the hydrogen-bond formation at the surface of water.

In conclusion, the author wishes to express his thanks to Professor H. Erikson for his kind encouragement.