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Theory of Surface Tension of Aqueous Solutions of Dipolar Ions

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A theory of surface tension of solutions of the dipolar ions is proposed. The theory is based on the idea of "image force" at the boundary of air and water. The experimental facts are satisfactorily accounted for by the theory.

1

IT is well known that the surface tension of solutions of inorganic salts is greater than that of the solvent.¹ To explain the phenomena various theories most of which are based on the Debye-Hückel theory of strong electrolyte have been proposed.²⁻⁶ The solutions of inorganic acids behave differently from the solutions of inorganic salts in that the acid solutions give rise to a decrease of surface tension of the solution. This phenomenon was explained quantitatively by the assumption that the hydrogen ions of the acid solutions are adsorbed at the surface of the liquid due to the "hydrogen bond" formation with molecules of water.⁷ The surface tensions of aqueous solutions of practically all organic compounds is less than that of water, though a curious exception is afforded by certain sugars.⁸ Now there is a class of organic molecules, most familiarly represented by the amino acids, which exist in solution preponderantly as dipolar ions, or zwitter ions.⁹ The surface tension of aqueous solutions of dipolar ions may be either greater or smaller than that of water depending largely on the magnitude of the electric moment of the dipolar ions.¹⁰ The aqueous solutions of dipolar ions are different from the solutions of nonpolar organic compounds particularly in the fact that the increment of surface tension per

mole of solute is very small, even smaller than that of the solutions of inorganic salts. No theory has yet been proposed to explain the surface tension behavior of the solutions of the dipolar ions. The present paper gives a theory which explains quantitatively the surface tension of such solutions.

2

The most important characteristic of the dipolar ions is their extremely large electric moment, which accounts for much of their behavior. Thus it is natural to suppose that the surface tension of the solutions of the dipolar ions is also greatly influenced by the electric field due to the large dipole moments of the ions.

Now let us consider the dipolar ion of electric moment μ situated in the liquid at a distance r from the surface of the water. There will be a force acting on the ion due to the image dipole of moment $j\mu$ situated at a distance r above the water surface, where $j = (D-1)/(D+1)$, D being the dielectric constant of the solution. The potential energy of the interaction of these dipoles is given by

$$u = (j\mu^2/8r^3D)(2\cos^2\theta + \sin^2\theta),$$

where θ is the angle the dipole makes with the normal to the surface of the water. The probability of the dipole lying at a distance between r and $r+dr$, and at an angle θ and $\theta+d\theta$ will be proportional to

$$2\pi e^{-u/kT} \sin\theta \, dr d\theta,$$

where θ can vary from 0 to π .

If n_0 is the total number of dipolar ions per cm^3 , then the number of dipolar ions having an orientation between θ and $\theta+d\theta$, and lying at a distance from the surface between r and

¹ Heydweiller, *Ann. d. Physik* **33**, 145 (1910).

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

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

⁴ Oka, *Physico-Math. Soc. Jap.* **14**, 649 (1932).

⁵ Shiba, *Bull. Inst. Phys. Chem. Res. Tokyo*, **13**, 109 (1936).

⁶ Ariyama, *Bull. Chem. Soc. Jap.* **11**, 687 (1936).

⁷ Ariyama, *Bull. Chem. Soc. Jap.* **12**, 109 (1937).

⁸ Traube, *J. Prakt. Chem.* **31**, 177 (1885); Clark and Mann, *J. Biol. Chem.* **52**, 157 (1922).

⁹ For a discussion of dipolar ions, see Cohn, *Am. Rev. Biochem.* **4**, 93 (1935).

¹⁰ J. A. Pappenheimer, Lepie and Wyman, *J. Am. Chem. Soc.* **58**, 1851 (1936).

$r+dr$ is

$$2\pi n_0 e^{-u/kT} \sin \theta \, dr d\theta.$$

Thus the number of ions adsorbed at the surface will be given by

$$\Gamma = 2\pi n_0 \int_a^\infty \int_\pi^0 [e^{-(j\mu^2/8r^3 D kT)(1+\cos^2 \theta)} - 1] d \cos \theta dr,$$

where a is the distance of nearest approach of a dipolar ion to the surface. If $u \ll kT$ then the above integral can be approximated by

$$\begin{aligned} \Gamma &= -2\pi n_0 \int_a^\infty \int_\pi^0 \left[\frac{j\mu^2}{8r^3 D kT} (1 + \cos^2 \theta) \right] d \cos \theta dr \\ &= \frac{-2\pi n_0 j\mu^2}{6a^2 D kT}. \end{aligned}$$

The assumption that $u < kT$ is justified may be seen as follows: Assuming the magnitude of the electric moment $\mu = 20 \times 10^{-18}$ e.s.u. at 300°K, $D = 80$, $j = 1$, the value of u/kT becomes 2, 1, 0.6 and 0.37, respectively, as the value of $2r$ takes on values 4, 5, 6, 7 Å. Since for glycine μ is evaluated¹¹ to be $\mu = 15 \times 10^{-18}$ e.s.u. and the radius of the dipolar ion $a = 2.8$ Å, the condition of $u < kT$ is satisfied even for the distance of nearest approach.

According to the theorem of Gibbs the adsorption Γ_0 which is expressed in moles per cm² is related to the surface tension by the following equation.

$$\Gamma_0 = -\frac{C}{RT} \left(\frac{\partial \sigma}{\partial C} \right),$$

where σ is the surface tension of the solution, C the molar concentration of the solute per liter of the solvent. Comparing the expressions for Γ and Γ_0 we obtain

$$\frac{\partial \sigma}{\partial C} = \frac{2\pi j\mu^2 N}{6a^2 D} \times 10^{-3},$$

where N is Avogadro's number. The factor 10^{-3} is due to the change from the number of dipolar ions per cm³ to the number per liter.

Now, for glycine we have $\mu = 15 \times 10^{-18}$ e.s.u. $a = 2.8$ Å. Assuming $D = 80$, we obtain for

¹¹ Kirkwood, J. Chem. Phys. 2, 351 (1934).

the right-hand side of the above equation the value 2.24. The experimental value¹² for $\Delta\sigma/\Delta C$ is 0.92, which is of the right order of magnitude. The difference of 1.32 between the theory and the experiment may be explained in the following manner. In the above discussion we have entirely neglected the effects other than the repulsive force due to the mirror image of the dipolar ions. As we have stated before almost all organic compounds are positively adsorbed at the surface of water. Thus it is reasonable to suppose that there are attractive forces acting on the dipolar ions in addition to the repulsive force which we have considered previously. The magnitude of the attractive force which the organic molecules experience at the surface of water can be estimated in the following way. We have known from the experimental researches that the logarithms of the activity coefficients of amino acids and peptides are as a first approximation proportional to their dipole moments.¹³ It is also known from experiments and from the theory which we have just given that the effect of increasing the dipole moment without otherwise altering a molecule is to increase the molar increment of the surface tension of the solution. This may be seen from Table I for α and β alanine, α and β aminobutyric acid, or better still, α and ϵ aminocaproic acid. Thus we can extrapolate the curve which relates the molar increment of the surface tension and the logarithm of the activity coefficient to unit activity coefficient, this point corresponding to the zero value of the dipole moment of the dipolar ion. The molar increment of the surface tension formed by this method is always negative indicating a decrease of the surface tension of the solution if a dipole moment is absent provided that the molecule has not been changed otherwise. Using the solubility data listed in Table I, we get $\Delta\sigma/\Delta C = -0.35$ for alanine and $\Delta\sigma/\Delta C = -43$ for aminocaproic acid. Since we have no surface tension data for diglycine or triglycine we cannot estimate the molar increment of surface tension for these molecules without dipole. However, it may be expected that the molar increment of

¹² J. A. Pappenheimer, Lepie and Wyman, J. Am. Chem. Soc. 58, 1851, (1936).

¹³ E. J. Cohn, Chem. Rev. 19, 241 (1936).

TABLE I.*

NAME	INCREMENT OF SURFACE TENSION PER MOLE/LITER OF SOLUTE $\Delta\sigma/\Delta C$ σ in dynes/cm	LOG OF SOLUBILITY RATIO IN WATER- ETHANOL SYSTEM LOG N/N_0
α Alanine	+0.58	
β Alanine	+0.77	-2.856
Glycine	+0.92	-3.139
α Aminocaproic acid	-23	-1.414
ϵ Aminocaproic acid	-0.25	-2.972
α Aminobutyric acid	-0.41	
β Aminobutyric acid	+0.05	

* Taken from Pappenheimer, Lepie and Wyman, J. Am. Chem. Soc. 58, 1851 (1936); Cohn, McMeekin, Edsall, and Weare, J. Am. Chem. Soc. 56, 2270 (1934); 57, 626 (1935); 58, 2173 (1936).

surface tension without dipole for glycine will be about the same or little larger than that of alanine. Thus the difference of 1.32 for glycine between the theoretical and experimental values may be due to the positive adsorption tendency of the molecules without the dipole, and this value may be considered quite reasonable. Thus we may consider that the theory of surface tension of the dipolar ions based on the image force idea explains the experimental facts quite satisfactorily.

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Thermodynamic Functions for Molecules Having Restricted Internal Rotations

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The partition function is considered for molecules having restricted internal rotations, and expressions are obtained which are reasonably accurate for most actual molecules. Tables are presented which list the contributions of a single restricted rotational degree of freedom to the entropy, energy, free energy, and heat capacity.

THE presence of a potential barrier of about 3000 cal./mole restricting rotation about the single bond in ethane, which was shown to exist by Kemp and Pitzer² and confirmed by Howard,³ suggests that the internal rotations of a large number of molecules may be appreciably hindered. It is therefore desirable that as general and simple a procedure as possible be developed for calculating the thermodynamic functions of these molecules. Assuming a reasonable shape of restricting potential, the pertinent theory will be briefly discussed and tables presented, which make possible easy and quite accurate calculations of the complete rotational contribution to the entropy, energy, and heat capacity of almost any molecule. The moments of inertia and potential barriers must, of course, be known, unless the calculation is to be reversed, and one or more of these quantities derived from thermodynamic data.

In a second paper the method here developed will be applied to a number of molecules.

Little is known concerning the exact shape of the restricting potentials, except that they must be the same qualitatively as that expressed by $\frac{1}{2}v(1 - \cos n\phi)$ where v is the height and n the number of potential maxima. This, moreover, is the only form for which the mathematics has been even partially developed, and must, consequently, be adopted. For low barriers the exact shape should make little difference, while for higher barriers the shape near the minimum is the important element so that, although a somewhat incorrect height may need to be used, the thermodynamic functions should be quite accurate.

It is, of course, necessary to use approximate methods if results of general applicability are desired. In the case of high potential barriers, when the restricted rotation becomes essentially a torsional oscillation, the method commonly used with vibrating molecules is applicable. The entropy (or other thermodynamic quantity) is

¹ Shell Research Fellow, Academic Year 1936-37.

² Kemp and Pitzer, J. Chem. Phys. 4, 749 (1936); J. Am. Chem. Soc. 59, 276 (1937).

³ Howard, Phys. Rev. 51, 53 (1937).