[Contribution from the Kent Chemical Laboratory of the University of Chicago]

THE STRUCTURE OF FILMS OF WATER ON SALT SOLUTIONS
I. SURFACE TENSION AND ADSORPTION FOR AQUEOUS SOLUTIONS OF SODIUM CHLORIDE

By William D. Harkins and H. M. McLaughlin

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Introduction

This investigation was undertaken in 1917 in order to obtain accurate data from which the negative adsorption of sodium chloride from the surface of its aqueous solution might be calculated. The negative adsorption of the salt indicates that the water is positively adsorbed from its solution; that is, the salt solution is covered by a thin film of water. Water is a much less polar substance than salt, and experience has exhibited the fact that the least polar of the constituents of a solution is the one which is positively adsorbed on the surface. The lack of polarity in one end of the adsorbed molecules is often the deciding factor. Thus, with butyric, valeric and other similar acids the carboxyl group at one end of the molecule is markedly polar, but the hydrocarbon radical is so slightly polar that it is highly adsorbed on the surface of the water, so that the adsorbed molecules of the acid are oriented with this radical toward the vapor phase while the carboxyl groups on the whole turn toward the body of the liquid. Now it has been found that the characteristics of a film of butyric acid are best explained if it is assumed that it is a monomolecular and tightly packed array of the molecules of the acid. Thus, if it were not for the molecular vibration due to heat, such a film would be of uniform thickness, and the assumption that it is practically of uniform thickness is in entire accord with its known characteristics, even although it is apparent from kinetic theory that this is true only for a highly idealized representation of the film, but not of the film itself.

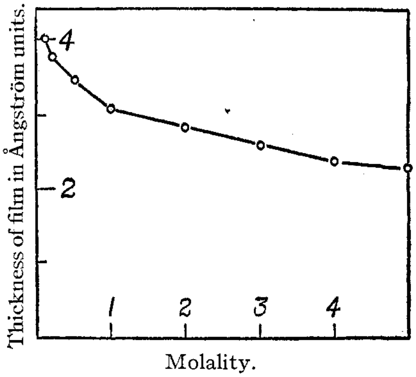

Fig. 1.—Thickness of the film of water on sodium chloride solutions of different concentrations (molalities).

The usefulness of this assumption in connection with such films as those of oleic and stearic acids suggests that it be adopted for the consideration of the film of water on a salt solution. Fig. 1 plots the variation of this "thickness" of the water film as a function of the concentration of the salt solution. In calculating the thicknesses it was assumed that the film consists of water alone, and that the concentration of the salt solution just underneath this film is the same as that of the solution in bulk. Even if the values obtained represent only apparent thicknesses, they are of great interest, for the following reasons.

1. The thickness of the film of water as thus calculated is close to a linear dimension of a water molecule. Thus, the apparent thickness of the film is from 2.3 to 4.2 Å., while the cube root of the volume occupied by one molecule of the formula H_2O in the liquid, is 3.1 Å. Thus, the film appears to be monomolecular.

2. The thickness of the film of water decreases as the concentration of the sodium chloride in the solution increases. Between 1 and 4 moles concentration of salt to 1000 g. of water this decrease is apparently linear, although the accuracy of the experimental work, while evidently of a high order, is not sufficient to make this certain.

It is evident that as the fugacity of the salt increases with increasing molality, the ions of the salt drive themselves closer and closer to the surface. This may be accomplished by a change in the orientation of the water molecules, or by a penetration of the ions between them. It may be noted that a marked change in the slope of the line which gives the thickness of the water film occurs at 1 *M*, which is very close to the position of the minimum activity coefficient for sodium chloride in its aqueous solution.

Experimental Methods and Data

In order to determine the adsorption of sodium chloride at the surface of its aqueous solution by the use of Gibbs' equation for adsorption, it is essential to have highly accurate values of the surface tensions of such solutions. These were determined by the drop-weight method as used by Harkins and Brown,[1] by means of which the experimental error may by careful work be reduced to about 0.05%. Practically all of the surface-tension data obtained before 1916 as recorded in the literature are greatly in error; nevertheless, the mean values given by Heydweiller[2] in 1910 do not differ from ours by more than 0.4%, which is a good agreement. However, his values for any one concentration differ considerably, so much as to make the slope of the surface tension-concentration curve uncertain, and this slope is used in the calculation of the thickness of the film or of the adsorption of the salt.

The new surface-tension values for aqueous sodium chloride solutions to a molality of 5.5 are given in Table I and Fig. 2.

The table shows that Δ' is much more constant than Δ. The activity coefficients at low concentrations are obtained from the measure-

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[1] Harkins and Brown, This Journal, **41**, 499 (1919).

[2] Heydweiller, *Ann. Physik*, [4] **33**, 154 (1910).

TABLE I

SURFACE TENSIONS OF SODIUM CHLORIDE SOLUTIONS

Radius of tip used, 0.24456 cm. Temperature, 20°

Molality	Normality	Activity coefficient	Density	Wt. of one drop, G.	f (r/a)	Surface tension	$\Delta \times 10^2$	$\Delta'^{a} \times 10^2$
0.00	0.00					72.80		
.2010	.2	0.751	1.00675	0.071962	0.62737	73.17	2.53	2.54
.5053	.5	.688	1.01876	.072472	.62725	73.71	2.47	2.50
1.0204	1.0	.650	1.0385	.073224	.6269	74.515	2.31	2.36
2.0988	2.0	.614	1.06984	.074902	.6265	76.27	2.32	2.39
3.1920	3.0	.714	1.1152	.076604	.6259	78.08	2.27	2.42
4.3628	4.0	.790	1.1507	.078476	.6255	80.02	2.27	2.47
4.9730	4.5	.848	1.1679	.079507	.62547	81.09	2.29	2.53
5.5410	5.0	.874	1.1947	.080508	.62505	82.17	2.38	2.57

[a] Freundlich ["Kapillarchemie," **1923**, p. 79] gives 2.28 × 10^{-2} for Δ' as calculated from the data of Heydweiller. Wagner [*Physik. Z.*, **25**, 474 (1924)] has calculated the value of Δ' as 2.10 at 0.2 *M*, which is considerably lower than the value derived by experiment.

$$\Delta = \frac{\gamma_m - \gamma_o}{\gamma_0 \, m} \qquad \Delta' = \frac{\gamma_N - \gamma_o}{\gamma_0 \, N}$$

ments on the lowering of the freezing point of sodium chloride solutions by Harkins and Roberts,[3] at higher concentrations by Jahn,[4] and at high concentrations by Rodebush.[5] The calculations agree very closely

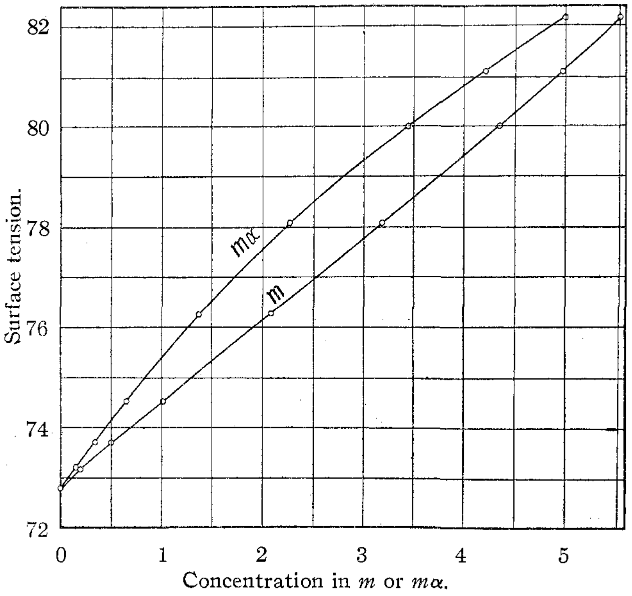

Fig. 2.

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[3] Harkins and Roberts, THIS JOURNAL, **38**, 2676 (1916).

[4] Jahn, *Z. physik. Chem.*, **66**, 144 (1905); **59**, 33 (1907).

[5] Rodebush, THIS JOURNAL, **40**, 1204 (1918).

with those made by Lewis and Randall,[6] since they were made by their method.

The figure indicates that the relation between surface tension and molality (moles per 1000 g. of water) is nearly linear, but the relation between surface tension and concentration in moles per liter (molarity) is even closer to linear, as is indicated by the fact that Δ' is much more constant than Δ, and the curvature exhibited at small molalities in Fig. 2 almost entirely disappears if the molarity is plotted on the X-axis. Each plotted value represents the average of from three to seven closely agreeing separate determinations of the surface tension.

Preparation of Sodium Chloride

Pure sodium chloride was prepared as follows from Baker and Adamson's C. P. sodium chloride and partly from Kahlbaum's salt. The salt was dissolved in distilled water and reprecipitated with hydrogen chloride. As much of the mother liquor was removed as was possible by filtering with suction. This product was heated to dryness at a temperature somewhat below fusion and dissolved in twice distilled water. About three-fourths of the salt was reprecipitated by evaporation, the mother liquor removed by filtering with suction and the product washed with an approximately 1:1 water-alcohol mixture until the wash water was neutral to litmus. The pure white salt was then thoroughly dried close to the temperature of fusion.

An Accurate Adsorption Equation

Gibbs' equation for adsorption may easily be given the following exact and general form.

$$u = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \, ln \, a}\right)_{T,\,A} \tag{1}$$

If an electrolyte dissociates into ions, $a_{\pm}$, the mean activity of the ions may be defined by the equation, $a_{\pm} = a^{1/\nu}$ or $a = a_{\pm}^{\nu}$, so for electrolytes (1) becomes

$$u = -\frac{1}{\nu RT}\left(\frac{\partial \gamma}{\partial \, ln \, a_{\pm}}\right)_{T,\,A} \tag{2}$$

or, since $a_{\pm} = \alpha m_{\pm}$,

$$u = -\frac{1}{\nu RT}\left[\frac{\partial \gamma}{\partial \, ln \, (\alpha m_{\pm})}\right]_{T,\,A} \tag{3}$$

which may be put in the form

$$u = -\frac{\alpha m_{\pm}}{\nu RT}\left[\frac{\partial \gamma}{\partial \, (\alpha m_{\pm})}\right]_{T,\,A} \tag{4}$$

Since in a solution of sodium chloride and most other salts $\left[\frac{\partial \gamma}{\partial (\alpha m_{\pm})}\right]_{T,\,A}$ is positive, the salt is negatively adsorbed, or withdrawn from the surface. If it is assumed that the surface film is pure water, and that the concentration of the solution inside this film is uniform, then the thickness t of the film may be calculated. If it is assumed that the density of the water in the film is the same as that of pure water, the relation is very simple and $t = 1000u/m$, if ρ for water $= 1$

[6] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923, p. 351.

or

$$t = -\frac{1000\ \alpha}{\nu RT}\left[\frac{\partial\gamma}{\partial\ (\alpha m_{\pm})}\right]_{T,\ A} \tag{5}$$

For a di-ionic salt such as sodium chloride $a_{\pm} = a^{1/2} = m$, so Equation 5 becomes

$$t = -\frac{1000\ \alpha}{2RT}\left[\frac{\partial\gamma}{\partial\ (\alpha m)}\right]_{T,\ A} \tag{6}$$

SYMBOLS

u = adsorption of solute in moles per sq. cm. of surface
m = moles per 1000 g. of solvent, or the molality
a = activity of solute
$a_{\pm}$ = geometrical mean of the activity of the ions of the solute
α = the activity coefficient of the salt, $= \frac{a_{\pm}}{m\ (\nu_{+}{}^{\nu_{+}}\ \nu_{-}{}^{\nu_{-}})} .1/\nu$
ν = the number of ions per formula weight into which the salt dissociates = 2 for NaCl
A = the area of the surface of the solution
γ = the surface tension of the solution
T = temperature
t = thickness
ρ = density
$m_{\pm}$ = geometrical mean of the molalities of the ions

The Adsorption of Sodium Chloride or of Water

The values obtained for the thickness of the water film at each concentration are given in Table II.

TABLE II

THICKNESS OF THE MONOMOLECULAR FILM OF WATER ON SOLUTIONS OF SODIUM CHLORIDE

Soln., M	0.1	0.2	0.5	1.0	2.0	3.0	4.0	5.0
Thickness of films, Å	4.00	3.76	3.45	3.25	2.82	2.57	2.35	2.30

The last two columns of Table I show that the increase in the surface tension produced by the salt, if divided by either the molality or the molarity of the solution, reaches a minimum at about 1 M, which is in agreement with the work of Heydweiller.[2] Thus, this minimum nearly coincides, in the case of sodium chloride, with the minimum in the activity coefficient of the salt, and the effect of these two minima is a rapid change in the slope of the curve of Fig. 1 at this concentration.

From the results of the work of various observers Langmuir[7] has calculated the thickness of the water film on potassium chloride solutions. While the thickness thus found is of the order of a linear dimension of a water molecule, the experimental values differ so greatly that only an approximate estimate could be made. He concluded that the thickness is constant, with a value of 3.3 from the data of one observer, 4.24 from those of another and intermediate values from those of the others.

[7] Langmuir, THIS JOURNAL, **39**, 1848 (1917).

As has been stated, the volume occupied by a molecule of the formula H_2O corresponds to that of a cube of 3.09×10^{-8} cm. edge, which is not far from the mean value of the thickness of the water film obtained from our results. It would be easy to say that on dilute solutions the water molecules stand with their longest axis perpendicular to the surface, while on more concentrated solutions the ions of the salt diffuse closer to the surface, and thus force the longer axis into a horizontal position. This picture is undoubtedly too simple, but it may be that this occurs to some extent.

On the whole, the thinness of the water film suggests that the layer of water on a hydrated ion in sodium chloride is not in general more than one molecule thick on the side of the ion toward the surface. It seems probable that the water molecules involved are of the type of H_2O, but the evidence is not sufficiently exact to indicate that molecules of the type $(H_2O)_2$ are not involved. If a water surface at 20° is kept in a vacuum, 7 million molecules jump out each second from the area occupied by a single molecule,[8] so at equilibrium an enormous number of molecules jump out from, and jump back into, this area. However, the time required for the orientation of a molecule of this type is so minute that at any instant the percentage of more or less oriented molecules is probably high.

The high surface tension of the more concentrated salt solutions may be partly due to the forcing of the water molecules into such position that the portions which give the weakest fields cannot occupy the whole outer surface. In the case of sodium chloride solutions the closer approach of the ions to the outer surface is probably one of the predominant factors, and the increase in their concentration another.

Summary

1. A cube of edge 3.09×10^{-8} cm. or 3.09 Å. has the same volume as is occupied by a molecule of H_2O in water. The apparent thickness of the water film on a solution of sodium chloride is 4.00 Å. at a concentration of 0.1 *M*, and falls to 2.30 Å. at 5 *M*. Thus the thickness is of the order of a linear dimension of a water molecule. This suggests that the film of water is monomolecular, and that the ions of the salt, Na^+ and Cl^-, in general keep buried beneath a monomolecular film of water. As the concentration of the salt increases, the diffusion pressure forces the ions closer and closer to the surface. To what extent this is due to a change in the orientation of the molecules of water, and to what extent the ions partly penetrate between the water molecules, is not indicated. It is pointed out that the phenomenon is highly kinetic, since 7 million molecules of water per second jump out from a water surface at 20° into a vacuum from an area equal to that of a single molecule (about 10 sq. Å. of

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[8] Harkins, "Colloidal Behavior" (edited by Bogue) McGraw-Hill Book Co., **1924**, p. 149.

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