

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

A Theory of Surface Tension of Aqueous Solutions

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Introduction

It is the purpose of this paper to show that by making use of a modified form of the Langmuir hyperbolic adsorption equation, of a modified form of the Langmuir concept of a monolayer of pure water on the surface of salt solutions, and of a new hypothesis concerning the number of locations on the water surface available for adsorption of negative ions, it is possible to derive a general equation for the surface tension of salt solutions which is capable of reproducing the remarkable results of Jones and Ray, which reduces under the appropriate conditions to the well-known Szyszkowski equation for fatty acids and under other conditions to an equation applicable to sucrose solutions.

Onsager and Samaras,⁴ Oka,⁵ Ariyama,⁶ and Belton⁷ all predict at the lowest concentration an increase of surface tension with increase of salt concentration.

Surface tension ratios, σ/σ_0 , where σ is the surface tension of the solution and σ_0 , that of pure water, calculated from the Onsager-Samaras equations for 1-1 and 2-2 electrolytes at 25° are plotted in Fig. 1 as a function of the total ion concentration along with Jones and Ray's data for cesium nitrate, potassium chloride and potassium sulfate solutions, as well as for sucrose solutions. At the lowest concentrations, where one would expect the Onsager-Samaras theory to be most accurately valid, there is a pronounced disagreement between the experimental results

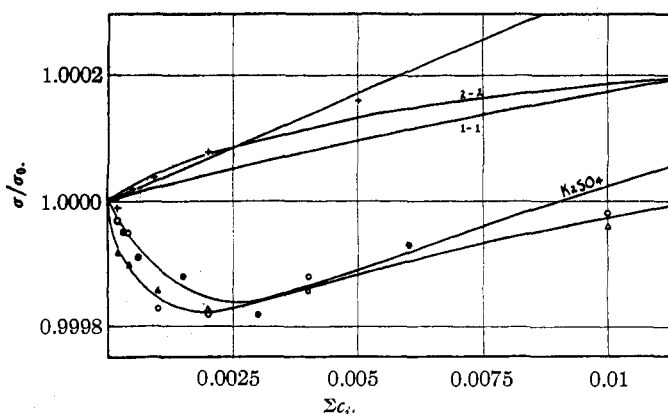


Fig. 1.—Comparison of Jones and Ray's data with Onsager-Samaras theory: circles, KCl; triangles, CsNO₃; solid circles, K₂SO₄; crosses, sucrose.

The recent accurate work of Jones and Ray¹ demonstrates that the surface tension of salt solutions at 25° first decreases with increase of concentration, passes through a minimum at a concentration of about 0.001*c* and then increases as the concentration is raised so that at concentrations above 0.005 to 0.01*c* the surface tension of the solution is greater than that of the pure solvent. For this unexpected effect, which we shall call the *Jones effect*, there is at present no adequate theory since the early theory of Langmuir² and the more recent theories of Wagner,³

and theory, the theory predicting a positive slope for the surface tension-concentration curve (these curves will be called hereafter S. T. C. curves) in contrast to the large negative slope of the experimental curve. At the lowest concentrations, therefore, the Debye-Wagner-Onsager-Samaras conceptions and theory need to be replaced by ideas and equations capable of explaining the negative slope and minimum in the S. T. C. curve.

For concentrations above the minimum it may be that the Onsager equations are applicable over a limited concentration range, but there are no data at present which prove that change of valence of the ions can change the S. T. C. curves in the manner shown in Fig. 1.

The Adsorption of Negative Ions.—The main idea, and one similar to the early conclusions of Langmuir and Harkins,⁸ on which the treatment of this paper is based, is that the forces in the first adsorption layer are much more important for the understanding of the Jones effect than the weaker, relatively long range mirror-image forces

(4) L. Onsager and N. N. T. Samaras, *J. Chem. Phys.*, **2**, 528 (1934).

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

(6) K. Ariyama, *Bull. Chem. Soc. Japan*, **12**, 32, 38 (1937).

(7) J. W. Belton, *Trans. Faraday Soc.*, **33**, 1449 (1937).

(8) In the well-known paper of Harkins, Davies and Clark, *THIS JOURNAL*, **39**, 541 (1917), the following significant statement is made, "surface tension phenomena in general are dependent upon the orientation and packing of molecules in surface layers."

(1) Grinnell Jones and W. A. Ray, *THIS JOURNAL*, **59**, 187 (1937).

(2) I. Langmuir, *ibid.*, **39**, 1896 (1917).

(3) C. Wagner, *Physik. Z.*, **25**, 474 (1924).

discussed by Onsager and Samaras. Below quantitative comparisons of these two types of forces are given after the method of estimating the adsorption energies has been explained, and it will be seen that the experimental data of Jones and Ray are consistent with the idea of a single adsorption layer largely determining the behavior in dilute solutions.

Jones and Ray¹ advance tentatively the theory that their effect is caused by the interaction between ions and water dipoles, saying "if we add a salt to water in such great dilution that the interionic forces are negligible, there must nevertheless be a disturbance of the normal arrangement of the water molecules in the vicinity of the ions. The electric forces between the water dipoles would oppose this disturbance and tend to thrust the disturbing ions out into the surface, thus causing positive adsorption." But the principles of electrostatics teach us⁹ that the interaction between ions and the water dipoles produces a repulsion from the surface and therefore negative adsorption. When it is remembered that bringing an ion from a vacuum into water liberates an enormous amount of energy from 60 to 90 or more kcal. per gram ion,¹⁰ it is difficult to understand how ions could be forced into the surface.

Accepting the correctness of Jones and Ray's data, it is necessary in developing a theory of surface tension to invent not only some explanation for the adsorption of ions at the interface, but also a mechanism by which this positive adsorption comes to an end at a concentration of about 0.001*c*, and negative adsorption begins. It would appear that this mechanism must involve ion-dipole interactions, since there is nothing in the Debye interionic attraction theory which could possibly explain the reversal in adsorption at 0.001*c*. The mechanism should depend largely on the properties of the solvent, because the Jones effect appears to be the same in magnitude and direction for all inorganic salts so far studied, but it must depend upon some abnormal property of the solvent, inasmuch as stated above the result of the usual or average ion-dipole interaction is to force the ion from the surface, or, better, to attract it to the interior of the liquid. The property of the solvent of which

we find necessary to assume the existence is the special orientation or grouping of water molecules in a limited number of locations or "active spots" on the water surface, and in such configuration that *negative* ions will be attracted to these spots from the interior of the solution, *i. e.*, a configuration with the proton ends of several contiguous surface water molecules pointing inward. The reason for specifying negative ions will be given below. We do not assume that these active spots are fixed in one place but appear from time to time at different points in the surface. Liquid water, thanks to the work of Stewart¹¹ and others and to the calculations of Bernal and Fowler and of Debye,¹² is now known to have a definite structure which differs from that of the solid chiefly in that it is a function of time. Frumkin¹³ first advanced the idea that a certain unspecified number of water molecules were oriented with their proton ends inward and Ariyama¹⁴ recently has made use of the same idea in developing a theory for the surface tension of inorganic acids. From the quantitative application of this postulate as given below, it is necessary that there be about four "active" spots for every 100,000 water molecules, a number that certainly seems to be within the realm of possibility, and a number that is the same for all data published by Jones and Ray. The chief difficulty with this hypothesis lies in the application of the law of mass action to the equilibrium between the water molecules in the active groups and the other water molecules of the surface layer and to the equilibrium between negative ions in the solution and those adsorbed on the active spots. If the adsorbed negative ions combine with these water groups and remove them from the water group-water equilibrium, then more active spots should appear on the surface, allowing more negative ions to be adsorbed. In this way the number of active spots becomes a function of the concentration of the negative ions in the solution. Since, however, the quantitative test of the theory shows no detectable variation of the number of active spots with increase of concentration up to 0.02*c*, we are forced to the conclusion that either the law of mass action cannot be applied to the reaction between the chloride ions and the water groups of the active spots or that

(9) See, for example, R. W. Gurney, "Ions in Solution," University Press, Cambridge, 1938, p. 8.

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

(11) G. W. Stewart, *Phys. Rev.*, **35**, 1426 (1930); **37**, 9 (1931).

(12) P. Debye, *Chem. Rev.*, **19**, 171 (1936).

(13) A. Frumkin, *Z. physik. Chem.*, **111**, 190 (1924).

(14) K. Ariyama, *Bull. Chem. Soc. Japan*, **12**, 109 (1937).

there is some other factor such as an electrical effect causing saturation of the surface at 0.001*c*. We shall discuss this point below; here we adopt as the main hypothesis of this paper the assumption of a limited number of surface locations on which negative ions can be adsorbed; the mathematical treatment given below does not depend upon the mechanism by which these active spots are produced but only on their existence.

If this hypothesis is correct, negative ions will be adsorbed at the surface until all the active spots (on the time average) are occupied; at this point, approximately, the S. T. C. curve should go through its minimum. At higher concentrations no more negative ions can become adsorbed, but will be repelled from other places in the surface layer by virtue of the mirror-image forces discussed by Wagner, Onsager and Samaras or by other repulsive forces existing in the first adsorption layer, as postulated by Langmuir. Therefore, these ideas can be tested experimentally by seeing if the minimum in the S. T. C. curve occurs at the same concentration of negative ions for all salts.¹⁵ This is true for all the data published by Jones and Ray (KCl, CsNO₃, K₂SO₄ solutions), and for considerably more data on various valence-type salts as yet unpublished (BaCl₂, LaCl₃, LiF, KClO₃, etc., solutions).¹⁶ Thus it appears that the experimental data are consistent with the main assumption of this paper.

At concentrations above the minimum it may well be that the slope of the S. T. C. curve is determined completely by the mirror-image forces and screening effects considered by Onsager and Samaras, but here the concentration is comparatively so large that it is questionable whether Onsager's equation is applicable. Instead we shall make use of the Langmuir concept of a surface film of pure water from which all ions are rigidly excluded (except at the active spots), but as will be pointed out below the Langmuir theory has to be modified to include in the surface film more than one layer of water molecules.

Mathematical Development.—A statistical treatment of these ideas leads to the following hyperbolic equation for θ , the fraction of active spots covered

(15) More precisely the theory requires that the concentration of negative ions multiplied by the thickness of the surface layer be the same for all salts at the minimum. The surface layer thickness does not vary much, however, from salt to salt.

(16) Grateful appreciation is expressed to Professor Jones and Dr. Ray for making available their data in advance of publication.

$$\theta = \frac{c\nu_-t/1000}{ae^{W-/RT} + c\nu_-t/1000} \quad (1)$$

where *c* is the concentration in moles per liter, ν_- the number of negative ions one molecule of the salt dissociates into, *a* the number of active spots in units of moles per sq. cm., *W*—the adsorption potential of negative ions per mole, and *t* the thickness of the surface adsorption layer in cm. To simplify the succeeding equations we shall replace *t*/1000 by *k*. Eq. (1) is so similar to the adsorption equation derived by Langmuir for gases (except for the constant terms) that a repetition of its derivation here is unnecessary.

The excess number of moles of negative ions adsorbed per sq. cm., Γ_- , is given by the equation

$$\Gamma_- = a\theta - c\nu_-k \quad (2)$$

which on introduction of the value of θ becomes

$$\Gamma_- = c\nu_-k \left[\frac{a(1 - e^{W-/RT}) - c\nu_-k}{ae^{W-/RT} + c\nu_-k} \right] \quad (3)$$

Eq. (3) is necessarily different from that previously given by Langmuir for the adsorption of fatty acids. In the case of positive ions we shall assume first that the surface boundary is electrically neutral, that an equivalent quantity of positive ions are adsorbed along with the negative ions, and second that the fraction of surface covered, θ , is determined solely by the concentration of negative ions (as emphasized above). For the adsorption of positive ions we have, then

$$\Gamma_+ = a\theta \frac{\nu_+}{\nu_-} - c\nu_+k, \text{ and} \quad (4)$$

$$\Gamma_+ = c\nu_+k \left[\frac{a(1 - e^{W-/RT}) - c\nu_-k}{ae^{W-/RT} + c\nu_-k} \right] \quad (5)$$

The Gibbs adsorption theorem is

$$d\sigma = -\sum_i \Gamma_i RT \frac{dc\nu_i f_i}{c\nu_i f_i} \quad (6)$$

where *f* is the activity coefficient. Neglecting activity coefficients for the moment and setting Γ_{H_2O} equal to zero (which we have already implicitly done by calculating the adsorption according to Eqs. (2) and (4)), we have on combining (3), (5) and (6)

$$d\sigma = -RTk(\nu_- + \nu_+) \left[\frac{a(1 - e^{W-/RT}) - c\nu_-k}{ae^{W-/RT} + c\nu_-k} \right] dc \quad (7)$$

a differential equation which as one can readily see gives a negative value for $d\sigma/dc$, the slope of the S. T. C. curves, at the lowest concentrations (finite when *c* = 0), a value of zero for the slope when $a(1 - e^{W-/RT})$ is equal to $c\nu_-k$ and a positive slope at all higher concentrations. Eq.

(7) can be integrated easily between the concentration limits $c = c$ and $c = 0$ with the result

$$\sigma - \sigma_0 = RTk(\nu_- + \nu_+)c - \frac{aRT(\nu_- - \nu_+)}{\nu_-} \ln \left[1 + \frac{k\nu_- c}{ae^{W-/RT}} \right] \quad (8)$$

Calculations show that activity coefficients must be considered for 1-1 salts above $0.01c$ and for 2-1 salts above $0.002c$ so that before comparing (8) with the data the method for calculating the activity coefficient correction will be described.

The Activity Coefficient Correction.—The concentration terms of Eqs. (2) and (4) are concentrations and not activities; we shall assume, furthermore, that the concentration terms in the equation for θ , Eq. (1), do not require the activity coefficient correction. When it is realized that at such a low concentration as $0.0002c$, θ already is equal to 0.93 in the case of potassium chloride solutions and approaches unity as an upper limit, it becomes apparent that activity coefficients may be omitted from Eq. (1) even at the higher concentrations. We need, therefore, to consider only the error involved in omitting activity coefficients from the Gibbs equation. If we let $d\bar{\sigma}$ represent the increase in relative surface tension due to the activity coefficient correction, the differential equation for this correction can be written

$$d\bar{\sigma} = -\frac{RTk}{\sigma_0}(\nu_+ + \nu_-)c \left[\frac{a(1 - e^{W-/RT}) - c\nu_-k}{ae^{W-/RT} + c\nu_-k} \right] d \ln f_{\pm} \quad (9)$$

To integrate (9) it is necessary to express f_{\pm} as a function of the concentration. This was done readily by employing Hückel's partially empirical equation

$$\ln f_{\pm} = -\frac{H\sqrt{c}}{1+B\sqrt{c}} + Ec \quad (10)$$

but the integration yielded such an unwieldy equation that it was repeated neglecting the term $ae^{W-/RT}$ in the denominator of (9), obtaining thereby the much simpler result

$$\Delta\bar{\sigma} = k'E(1/2c - k'')c - \frac{k'H\sqrt{c}}{1+B\sqrt{c}}(c - k'') + \frac{2k'H}{B^2} [1/2(1 + b\sqrt{c})^2 - 2(1 + B\sqrt{c}) + \ln(1 + b\sqrt{c}) + 3/2] \quad (11)^{17}$$

where

$$k' = \frac{RTk(\nu_- + \nu_+)}{\sigma_0} \quad (12)$$

$$k'' = \frac{a(1 - e^{W-/RT})}{\nu_-k} \quad (13)$$

(17) Dr. Ray has succeeded in reducing (11) to a still simpler form which will be published shortly in collaboration with Professor Jones along with their new data.

In Table I activity coefficient corrections are given for potassium chloride based on activity data of Harned¹⁸ and for potassium sulfate based on activity data of Åkerlöf.¹⁹ These corrections were calculated from (11) using the constants a , W^- and k for the two salts as given in the next section.

TABLE I
CORRECTION TO THEORETICAL SURFACE TENSION VALUES DUE TO INTRODUCTION OF THE ACTIVITY COEFFICIENT

c	KCl		K ₂ SO ₄	
	f _±	Δσ̄	f _±	Δσ̄
0.001	0.996	0	0.889	0
.002	.953	0		0
.005	.929	0	.781	0.00003
.01	.903	-0.00002	.715	-0.00010
.02	.871	-0.00002		-0.00020
.05	.817	-0.00013	.504	-0.00089
.1	.771	-0.00034		-0.00214

The activity coefficients of Table I are defined in terms of moles per 1000 g. of water. We neglect the difference between this concentration unit and the unit used in this paper, moles per liter of solution.

Comparison with Experiment.—We already have mentioned how our Eq. (7) duplicates the initial negative slope of the S. T. C. curves, the minimum and the final positive slope. To test Eq. (8) quantitatively we follow Jones and Ray and write it in terms of relative surface tension, σ/σ_0

$$\frac{\sigma}{\sigma_0} = 1 + \frac{RTk(\nu_- + \nu_+)}{\sigma_0} c - \frac{aRT(\nu_- + \nu_+)}{\sigma_0\nu_-} \ln \left[1 + \frac{c\nu_-k}{ae^{W-/RT}} \right] \quad (14)$$

Of the constants in this equation, R , T , σ_0 , ν_- and ν_+ are known; the constant t , the thickness of the surface layer ($t = 1000k$), should be equal to 2.76 Å., the diameter of the water molecule, if the Langmuir hypothesis of a monofilm of pure water on the surface of a salt solution is correct. This thickness is quite inadequate to reproduce the data, however; instead it is necessary to consider the thickness of the surface film as the thickness of a monolayer of water molecules to which ions are adsorbed. Thus it is the thickness of a water molecule plus adsorbed ion rather than merely that of a water molecule which seems to determine the magnitude of the surface tension results. Since there is some uncertainty whether to take the thickness as being equal to the sum of the diameter of the

(18) H. S. Harned, THIS JOURNAL, 51, 416 (1929).
(19) G. Åkerlöf, *ibid.*, 48, 1160 (1926).

water molecule plus that of the negative ion or plus that of both the positive and negative ions and since nothing is known as to the exact orientation or position of the ions in the surface layer, values of t were chosen which gave the best fit over the rising, nearly linear part of the S. T. C. curve. In all cases, however, the value of t so chosen was of the expected order of magnitude. The value of a is found easily from the equation

$$a = c_m \nu_- k \tag{15}$$

where c_m is the concentration in moles per liter at which the minimum in the S. T. C. curve occurs. Eq. (15) readily follows from (7) on setting $d\sigma/dc$ equal to zero, the term $e^{W_-/RT}$ being small in comparison to unity. Knowing k and a , the remaining unknown parameter W_- is calculated from the equation

$$W_- = RT \ln \left[\frac{k\nu_- c_1}{a(e^{k\nu_- c_1/a} - 1)} \right] \tag{16}$$

where c_1 is the concentration at which the surface tension becomes equal to that of pure water after passing through the minimum.

After the unknown constants have been evaluated in this way, the activity coefficient correction is calculated from (11) and the constants redetermined. Table II contains the constants found by applying the above method to the data published by Jones and Ray.

TABLE II
CONSTANTS FOR EQUATION (14)

	a moles per sq. cm.	t	W_- cal./g. ion
KCl and CsNO ₃	7×10^{-14}	7 Å.	-2500
K ₂ SO ₄	8×10^{-14}	10 Å.	-1430

Using the constants of Table II, theoretical surface tension values were calculated for the salts listed and are shown by the solid lines of Figs. 2 and 3. Except for the measured surface

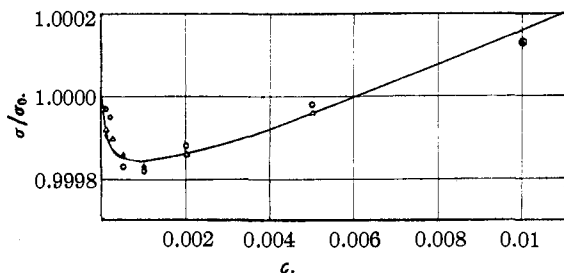


Fig. 2.—KCl circles, CsNO₃ triangles, solid line theory.

tension datum at the minimum for potassium sulfate solutions the theoretical calculations

agree with the data within the experimental limits of error up to $0.02c$. The fact that the constant a is practically the same for all three salts confirms our contention, in these few cases at least, that the concentration of the minimum in the S. T. C. curves is determined by the concentration of negative ions (compare Eq. 15). The values of t are reasonable and of the right order of magnitude; for example, the diameter of the water molecule plus that of the chloride ion²⁰ is 6.4 Å. and t has a larger value for potassium sulfate, as one might expect.

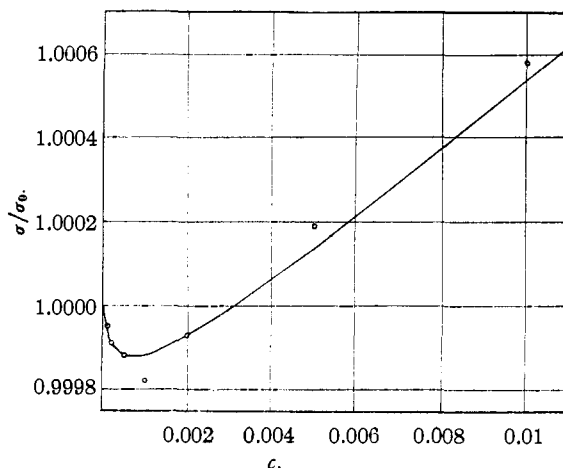


Fig. 3.—Comparison of theory and experiment for K₂SO₄ solutions.

The adsorption potential, W_- , which is the work necessary to bring a mole of negative ions from the interior to the surface layer (the free energy of adsorption) is of the same order of magnitude as calculated by Langmuir for the lower molecular weight fatty acids. Langmuir's equation, valid in dilute solutions where the decrease in surface tension is directly proportional to the concentration and derived by a method involving the Boltzmann equation, is (in the nomenclature of this paper)

$$-W = RT \ln \left[1 + \frac{1000}{iRT} \left(\frac{d(\sigma_0 - \sigma)}{dc} \right)_0 \right] \tag{17}$$

Equation (17) readily follows from our equation (7) at low concentrations, but we did not use (17) to estimate W because of the difficulty in determining the slope at the lowest concentrations. The adsorption potentials given in Table II are of the opposite sign and roughly ten times greater than those predicted by the mirror-image equation used by Wagner and by Ousager

(20) J. E. Mayer and I. Helmholtz, *Z. Physik*, **75**, 19 (1932).

and Samaras in their theoretical treatments of surface tension. Using this equation and calculating the adsorption potential of the chloride ion in the surface layer we get only 222 cal. per gram ion. Thus, the energy liberated during the adsorption of the chloride ion outweighs considerably the energy absorbed due to the mirror image repulsion; our original postulate that the forces in the first surface layer predominate therefore seems to be substantiated.

In Fig. 4 the comparison between theory and experiment is extended up to a concentration of 0.1*c* using the constants found applicable to the very dilute range. The dotted line in this figure represents the theoretically calculated surface tension data corrected for variation of the activity coefficient, a correction which is in the right direction, but is not of sufficient magnitude to bring about agreement between the theory and the experimental results at the high concentrations. The wide divergence of the theory from the actual results at 0.1*c* and above may be due to a number of reasons, some of which are discussed in the next section.

In concluding this part of the paper we wish to point out that large organic ions or ions of intermediate size probably would be adsorbed at the surface in a different number of spots from the small inorganic ions; in other words, the constant *a* depends only to a first approximation purely on the solvent. We might expect a large change of *a* with change of solvent, but not much change with change of temperature.

Additional Implications and Applications of Theory.—Eq. (8) when derived for non-electrolytes is

$$\frac{\sigma}{\sigma_0} = 1 + \frac{RTkc}{\sigma_0} - \frac{aRT}{\sigma_0} \ln \left[1 + \frac{ck}{ae^{W/RT}} \right] \quad (18)$$

Sucrose molecules are known to be strongly hydrated, so that we can expect that the sucrose molecule would tend to bury itself in the interior of the solution, or in other words that *W* of Eq. (18) would be large and positive. If this is the case, (18) reduces to

$$\frac{\sigma}{\sigma_0} = 1 + \frac{RTkc}{\sigma_0} \quad (19)$$

as the surface tension equation for sucrose solutions. From the data of Jones and Ray, see Fig. 1, as applied to Eq. (19), we calculate *t* to be equal to 9.2 Å., which indicates that one should take as thickness of the surface layer the diameter of the water molecule, 2.76 Å., plus that of the

sucrose molecule, *ca.* 6 Å.²¹ Here it is again apparent that the monolayer of water theory of Langmuir needs to be modified to take into consideration also the diameter of the adsorbed molecule.

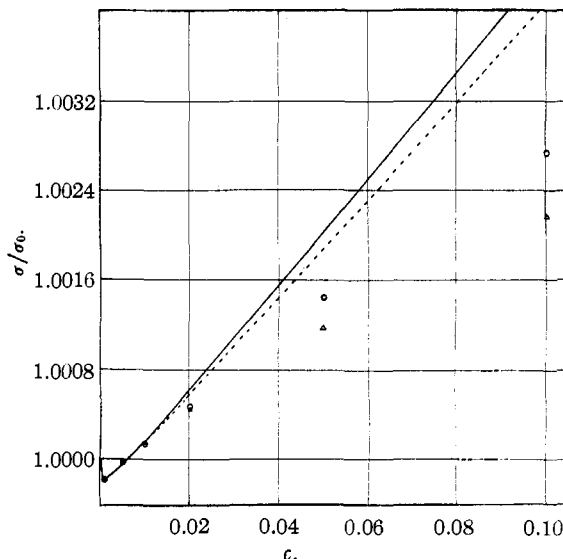


Fig. 4.—KCl circles, CsNO₃ triangles, solid line theory, dotted line theory corrected for variation in activity coefficients.

If practically the whole surface can adsorb molecules of solute, as is the case for the fatty acids, *a* will be large and Eq. (18) reduces to

$$\frac{\sigma}{\sigma_0} = 1 - \frac{aRT}{\sigma_0} \ln \left[1 + \frac{ck}{ae^{W/RT}} \right] \quad (20)$$

which is the well-known empirical equation of Szyszkowski.²² Langmuir many years ago showed that Eq. (20) reduced to an adsorption equation having the form of Eq. 1 (but not of Eq. 3 of this paper); he did not derive an expression for Szyszkowski's empirical constant in the logarithm term of Eq. (20) although his general conclusions regarding the Szyszkowski equation are exactly the same as those resulting from the theory of this paper.

Coming back now to ionic solutions we find possible confirmatory evidence for our theory in the work of Frumkin,²³ who measured the relative total potential drop across various air-solution interfaces. His results showed that among inorganic solutions negative ions were

(21) See G. L. Clark, "Applied X-Rays," 2d ed. McGraw-Hill Book Co., New York, N. Y., 1932, p. 318.

(22) B. von Szyszkowski, *Z. physik. Chem.*, **64**, 385 (1908).

(23) A. Frumkin, *Z. physik. Chem.*, **109**, 34 (1924); **111**, 190 (1924).

chiefly responsible for the changes in observed e. m. f.; that change of positive ion had little if any effect upon the e. m. f. He concluded that at the air-water interface there was "directed" ionic adsorption of the Harkins-Langmuir type, with the negative ion next to the interface and the positive ion farther away from the boundary in the interior of the solution.

The potential differences across the boundary measured by Frumkin increased with increase of concentration. This latter fact indicates that our treatment of W_- as being constant is only correct to a first approximation. Actually we should expect the adsorption potential of negative ions to depend upon the electric field at the interface, the latter to depend upon the concentration and therefore the adsorption potential should depend upon the concentration. In an earlier part of this paper it was pointed out that the number of active spots, a , should also vary with the concentration if the mass action law is applicable to the equilibria existing at the water surface. The minimum in the S. T. C. curve depends upon the factor $a(1 - e^{W_-/RT})$; if a increases with the concentration as predicted by mass action considerations, we may still get a minimum by virtue of W_- approaching zero because of the production of the negative electric potential at the boundary. Fortunately these two uncertainties act to offset each other so that it is perhaps by a balancing of these two additional effects that our simple Equation (8) is valid in dilute solution.²⁴

At higher concentrations it is possible that the decline in the factor $(1 - e^{W_-/RT})$ would no longer neutralize the increase in a so that (8) would give too high surface tension values; to this explanation might also be added the statement that our assumption that no ions at all could penetrate into the surface layer except at the location of the active spots breaks down in concentrated solutions where there will be in solution ions having high enough energies to become adsorbed at the surface.

Finally, in concluding this paper we wish to point out the negative charge acquired by air bubbles, oil drops, glass and quartz particles, etc., when in water, as evidenced by ζ -potential measurements may be explained by the ad-

sorption of negative ions at the water interface as postulated above.²⁵

Summary

By postulating, first, that the surface forces in the first adsorption layer predominate over the relatively weak, long-range forces calculated from the mirror-image equation; second, that negative ions are adsorbed at the boundary in a limited number of locations; and, third, that at all other locations both positive and negative ions are completely excluded from the first adsorption layer, it has been possible to develop a theory of surface tension with the following results:

1. A general equation for the variation of surface tension with change of concentration has been derived, namely

$$\sigma - \sigma_0 = RTk(\nu_- + \nu_+)c - \frac{aRT(\nu_- + \nu_+)}{\nu_-} \ln \left[1 + \frac{k\nu_-c}{ae^{W_-/RT}} \right]$$

2. The empirical constant a which is the number of surface adsorbing spots per sq. cm. is given by the equation

$$a = c_m k \nu_-$$

where c_m is the concentration at the minimum of the surface tension, and the constant W_- , the adsorption potential, is given by the equation

$$W_- = RT \ln \left[\frac{k\nu_-c_1}{a \left(e^{\frac{k\nu_-c_1}{a}} - 1 \right)} \right]$$

where c_1 is the concentration at which the relative surface tension becomes equal to unity after passing through the minimum.

3. The equation for the correction due to a consideration of activity coefficients has been derived. This correction is negligible at concentrations below $0.005c$.

4. The new equation has been tested with the data of Jones and Ray for strong electrolytes and shown to be valid up to a concentration of $0.02c$.

5. The theory predicts that the minimum in the surface tension-concentration curve occurs at the same concentration of negative ions of inorganic salts. This prediction is in harmony with the experimental data.

(25) Brief mention should be made of the recent measurements of A. W. Evans, *Trans. Faraday Soc.*, **33**, 794 (1937), on the interfacial tension between aqueous solutions of strong electrolytes and *n*-hexane. He finds a minimum in the S. T. C. curves for lithium chloride and sodium hydroxide solutions, but the data, due to experimental difficulties, are not accurate enough to apply the theory of this paper.

(24) My colleague, Dr. A. A. Frost, has suggested that perhaps the adsorption of ions at the boundary is an adsorption on traces of impurities at the water surface rather than on the pure water surface.

6. For sucrose solutions the surface tension equation reduces to

$$\sigma - \sigma_0 = RTkc$$

which is in agreement with the data of Jones and Ray.

7. For the lower molecular weight fatty acids, the surface tension equation reduces to

$$\frac{\sigma}{\sigma_0} = 1 - B \log \left[1 + \frac{c}{A} \right]$$

which is the well-known empirical equation of Szyszkowski. The interpretation of the constants of the Szyszkowski equation resulting from the theory of this paper is closely similar to the conclusions of Langmuir published many years ago.

8. In very dilute solutions the surface tension

decreases linearly with the concentration. Over this range the adsorption potential can be calculated from the equation

$$-W = RT \ln \left[1 + \frac{1}{RTk} \left\{ \frac{d(\sigma_0 - \sigma)}{dc} \right\}_0 \right]$$

an equation resulting from the theory of this paper and being identical with a similar equation of Langmuir derived in a different way.

9. The adsorption potential for negative ions is negative, is about ten times greater in absolute magnitude than the positive adsorption potential calculated from the mirror-image equation and is of the same order of magnitude as the adsorption potentials found by Langmuir for fatty acids.

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The Ternary System Selenium Dioxide-Barium Selenite-Water at 0, 25, and 50°

BY JOSEPH L. NEAL, JR., AND C. R. McCROSKY

Although they have been known for over one hundred years, the salts of selenious acid have received comparatively little attention. Analyses and qualitative descriptive studies were made by Berzelius,¹ Muspratt,² Nilson,³ and Boutzourcano.⁴ Recently the solubilities in water and the transition points of the selenites of sodium, potassium,⁵ and ammonium⁶ have been studied. Quantitative solubility measurements upon the other selenites are entirely lacking. Such data are of interest in connection with certain efforts which are being made in this Laboratory to utilize these salts in analytical and preparative processes. As a step toward these ends, this report deals with the results of a study of the ternary system selenium dioxide-barium selenite-water at three temperatures. We hope later to present data for the corresponding systems of the other alkaline earth selenites.

Experimental

Materials.—Selenium dioxide was prepared by the oxidation of crude black selenium (supplied through the

courtesy of the United States Metals Refining Co.) with nitric acid, and purified by repeated sublimation.

Selenious acid was prepared by dissolving the purified dioxide in a small excess of hot water, cooling and inoculating, if necessary. The crystals were dried on a porous plate, without the use of a desiccant. An analysis of a typical lot showed SeO₂, 85.79%; calcd. 86.06%. The crystals are slightly hygroscopic. They were kept in amber glass containers and remained white or nearly so for months.

The starting material for the preparation of barium selenite was commercial barium carbonate. This salt was dissolved in nitric acid and recrystallized several times. The purified nitrate was treated with a slight excess of selenious acid, and the selenite precipitated by gradual addition of ammonia, at the boiling point. The precipitate was washed free of ammonia and dried on filter paper, which seems to have no reducing action on it. Analysis of a typical lot: SeO₂, 41.96%, calcd. 41.99%; BaO, 58.19%, calcd. 58.01%. Through the courtesy of Mr. Paul Keene of the Solvay Process Co., a spectrogram was obtained, which indicated the presence of calcium, copper, aluminum, iron, and magnesium to an extent of much less than 0.1% in any case. Qualitative tests by the Noyes procedure also showed less than 0.1% of nitrate, ammonium, and carbonate ions. Samples of this material were preserved in colorless glass containers for over two years without showing reduction. The portion used for solubility measurement on the pure salt was extracted with water for several weeks in a Soxhlet apparatus.

For the preparation of barium pyroselenite, the normal selenite was digested with an excess of selenious acid at about 50° for several weeks, to ensure complete conversion. The crystals were drained by suction, washed thoroughly

(1) Berzelius, *J. Chem. Phys.*, **23**, 309 and 430 (1818), and elsewhere.

(2) Muspratt, *J. Chem. Soc.*, **2**, 52 (1850).

(3) Nilson, *Regiae Societatis Scientiarum Upsaliensis, Nova Acta*, [3] **9**, fasc. 2, II (1875).

(4) Boutzourcano, *Ann. chim. phys.*, [6] **18**, 309 (1889).

(5) Janitzki, *Z. anorg. allgem. Chem.*, **206**, 49 (1932).

(6) Janickis, *ibid.*, **218**, 89 (1934).