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The Surface Tension of Solutions of Electrolytes as a Function of the Concentration. I. A Differential Method for Measuring Relative Surface Tension

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Introduction

Most salts may be classified among the "capillary-inactive substances" which give solutions having a surface tension slightly greater than that of pure water and which are negatively adsorbed in the surface layer within the range of concentration hitherto investigated. Measurements by many early investigators have shown that the surface tension–concentration curves are approximately linear and that the slope and curvature are less influenced by the individuality and valence type of the salt than the corresponding curves for most other properties of solutions of electrolytes.

The first careful work on dilute solutions (less than 0.2 *N*) appears to have been done under the supervision of Heydweiller by two of his pupils, Gradenwitz and Kleine, who used the capillary rise method. Heydweiller has assembled and critically analyzed the data available up to 1910.[1]

If Quincke's law, which may be expressed $\sigma_c/\sigma_0 = 1 + kc$, were really valid, then $(\sigma_c - \sigma_0)/\sigma_0 c = k$ should be a constant independent of the concentration. Heydweiller found, however, that for many salts $(\sigma_c - \sigma_0)/\sigma_0 c$ decreases rather sharply with rising concentration in the dilute range (below 0.2 *N*), passes through a flat minimum, and then rises slowly for concentrated (above about 2 *N*) solutions. Heydweiller suggests that the attractive forces between adjacent ions of opposite charge will cause an increase in the surface tension. He says, "The effect of ions on the surface tension is to be ascribed in greatest part to the electrical forces of their charges."

Schwenker[2] has measured the surface tension of still more dilute (0.015 *N* up to 0.15–0.18 *N*) solutions of lithium, sodium and potassium chlorides at 0° by measuring the vertical force necessary to pull a horizontal wire out of the solution. His surface tension–concentration curves for these three salts are identical at the lower concentrations within his experimental error and have the same downward curvature at low concentrations which Heydweiller found to be characteristic of solutions of electrolytes. Schwenker regards this characteristic behavior to be in accord with Lenard's theory that the surface layer of water at a water–air interface is electrically negatively charged and that there is a positively charged layer at a lower depth.[3]

Wagner,[4] and later Onsager and Samaras,[5] have applied the Debye–Hückel theory of interionic attraction to the problem and reached the conclusion that the electric forces between the ions must cause a deficiency of ions in the surface layer and an increase of the surface tension. They derived the following equation for dilute aqueous solutions of uni-univalent electrolytes

$$\sigma_c/\sigma_0 = 1 + \frac{79.517}{D\sigma_0} c \log \frac{1.143 \times 10^{-8}(DT)^3}{c} \qquad (1)$$

where *D* is the dielectric constant of water and *T* the absolute temperature. It should be noted that this equation contains no parameters which are selected to fit the data, and also that it contains no quantities which are dependent on the particular salt or ions present. This equation, therefore, predicts that all uni-univalent salts should give identical surface tension–concentration curves, at least through the range of concentrations for which the authors would claim that their equation is valid. The available experimental data show that in the relatively high concentrations for which reliable data are available the curves are approximately, but not exactly, identical. The Onsager–Samaras equation predicts that the limiting slope at zero concentration should be plus infinity and have a very sharp negative curvature in the extremely dilute range. Data at sufficiently low concentrations to test this conclusion are not available. According to this equation, within the experimentally accessible range the surface tension–concentration curve should have a gentle positive but decreasing slope, which is qualitatively in accord with the data. The equation predicts that the relative surface

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(1) A. Gradenwitz, Diss., Breslau, 1902; *Physik. Z.*, **3**, 329, (1902); A. Kleine, Diss., Munster, 1908; A. Heydweiller, *Ann. Physik*, [4] **33**, 145–185 (1910).

(2) G. Schwenker, *ibid.*, [5] 11, 525 (1931).

(3) P. Lenard, *ibid.*, [4] **47**, 463 (1915).

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

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

tension should reach a maximum at $c = 0.54$ with the low value of only 1.0033. The available data give no indication that there is a maximum in the surface tension curves near half normal, or at any other concentration, and values much above the computed maximum have been observed for many salts. It is, therefore, evident that there have been terms omitted in the derivation of this equation which become significant substantially below half normal. Although in the derivation of their equation Onsager and Samaras limited themselves to uni-univalent salts, the available data indicate that the influence of valence on the surface tension is much less than on most other properties of electrolytes.

The object of this investigation is to study the relative surface tension of solutions of electrolytes as a function of concentration and nature of the salt, with special attention to very dilute solutions. Since we are interested in the interpretation of the data from the point of view of the interionic attraction theory of Debye, we are interested primarily in the conditions after equilibrium between the thermal and electrical forces has been established. We, therefore, desire to measure the static rather than the dynamic surface tension. Since the surface tension of solutions of salts differs only slightly from that of pure water (less than 3% for normal solutions), a higher order of precision will be needed to secure significant results for dilute solutions than has hitherto been obtained with any of the methods. For the theoretical purposes which interest us an accurate knowledge of surface tension relative to that of pure water will suffice and absolute values are not needed. This simplifies the experimental problem greatly. The capillary rise method seemed to be the most promising. We undertook, therefore, to modify the technique of this method to make it a differential method of sufficient precision for our purposes.

A Differential Method of Determining the Surface Tension of Solutions Relative to that of the Pure Solvent

In its fundamentals the capillary rise method of determining the absolute surface tension of a liquid consists in measuring the vertical difference in height between a meniscus in a narrow cylindrical tube, whose radius is determined independently, and in a connecting tube which is so wide that it has a flat surface at the center, together with an independent determination of the density of the liquid. The surface tension is then computed from the equation

$$\sigma = \frac{rhg(D - \beta)}{2} \cos \theta \qquad (2)$$

where r is the radius of the narrow tube at the level of the meniscus, h is the capillary rise measured above a connecting free surface of infinite extent, g is the acceleration of gravity, D is the absolute density of the liquid, and β is the density of the gas phase (air plus water vapor) at the temperature and the barometric pressure prevailing when the experiment is made, and θ is the angle of contact. For water and aqueous solutions in glass or silica tubes θ is zero if the surfaces are really clean. An approximate value of the capillary rise is obtained by measuring the difference in elevation between the lowest points in the menisci in the narrow and wide tubes. The true capillary rise, h, is then obtained by applying a correction for the liquid in the upper and lower menisci by Rayleigh's[6] formula. When necessary, subscripts are used to distinguish between the capillary rise for a solution, h_c, and that of pure water, h_0.

The density can be determined easily within 0.001% and the value of the acceleration of gravity can be regarded as known, so that the accuracy of the result depends on the unavoidable experimental errors in determining r and h.

The radius of the capillary has usually been computed from measurements of the length of a weighed drop of mercury in the capillary. This requires the assumption that the capillary is a true right circular cylinder, whereas even the best capillary obtainable may be more or less elliptical and conical. Irregularities in the walls of the tube may cause optical distortion of the image and thus cause an error in the measurement. The capillary rise is found by measuring the elevation of the upper and lower meniscus on a vertical scale by means of a cathetometer. This reading on the meniscus in the capillary tube is comparatively easy, but it is much more difficult to obtain an accurate reading on the meniscus in the wide tube. The apparent readings are influenced by the adjustment of the illuminating device, the length of the focus, and the possible optical distortion of the image due to irregularities of the walls of the wide tube. Moreover, vibrations of the surface are apt to be disturbing.

Extreme care is required to reduce the combined effect of the errors in the radius and capillary rise to 0.1%, and it is doubtful if anyone has succeeded in reducing them below 0.05%.

We have devised a modification of the usual procedure which makes it a differential method for measurements of the surface tension of solutions relative to that of the pure solvent and practically eliminates the two greatest sources of error in the older technique.

Errors due to deviation of the capillary tube from a true right circular cylinder and to inaccuracy in the determination of the radius of the capillary are completely eliminated by bringing the meniscus of the solution and of pure water to the same part of the capillary tube, designated by a suitable permanent mark, and then determining the difference in capillary rise in the wide tube.[7] By dividing the expression for the surface tension of the solution, σ_c, by that of the pure solvent, σ_0, the radius of the capillary and the acceleration of gravity are eliminated entirely.

The difficulties of measuring the height of the meniscus in the wide tube by a cathetometer are avoided entirely by

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[6] Lord Rayleigh, *Proc. Roy. Soc.* (London), **A92**, 184 (1915).

[7] This device has been used by Gradenwitz and Kleine.[1]

a modification of the procedure which permits the difference in capillary rise of solution and of solvent to be computed from data obtained by weighing.

The new differential capillarimeter is in principle suitable for any solvent, but up to the present time we have used it only with aqueous solutions and, since the properties of water influence or control some of the details, we shall in the following discussion assume that the solvent is water.

Derivation of the Equation for the Computation of the Relative Surface Tension of Solutions from the Experimental Data

The differential capillarimeter is shown in Fig. 1. It consists of a fine capillary tube of vitreous silica of radius r (r is 0.0136 cm. in our instrument) sealed to a wide tube which has been ground and polished internally to a true right circular cylinder of radius R (R is 2.1489 cm.). The empty instrument is weighed and then mounted vertically in a thermostat at 25.00°. Pure water is added to the instrument in an amount which will bring the meniscus in the capillary to the reference mark M. The volume of the water is then designated as V_0. The vertical height between the lowest point in the meniscus in the capillary and the lowest point of the meniscus in the wide tube is then measured by a cathetometer which, after applying two small meniscus corrections explained below, gives the true capillary rise for water, h_0. The instrument is then removed from the thermostat and weighed with its contents, which, after subtracting the weight of the empty instrument and adding the vacuum correction, gives the true weight of water W_0. Let D_0 represent the absolute density of water. It is obvious that $V_0 = W_0/D_0$.

Then the instrument is emptied, dried and remounted in the thermostat and filled with the proper amount of solution containing c gram equivalents of salt per liter to bring the meniscus in the capillary again to the mark, M. The capillary rise is $h_c = h_0 + \Delta h$. It is not necessary to determine h_c by making measurements with the cathetometer and adding meniscus corrections, although this is sometimes done as a check. The instrument is then removed from the thermostat, dried externally and weighed with its contents, which, after subtracting the weight of the empty instrument and adding the vacuum correction, gives the weight of the solution W_c. The volume of the solution is V_c. The volume of the solution is obviously $V_c = W_c/D_c$ where D_c is the absolute density of the solution. The density is determined independently in a suitable pycnometer. Then we may write

$$\sigma = \frac{\sigma_c}{\sigma_0} = \frac{rg\ (D_c - \beta_c)h_c}{rg\ (D_0 - \beta_0)h_0} = \frac{(D_c - \beta_c)(h_0 + \Delta h)}{(D_0 - \beta_0)h_0} = \frac{D_c - \beta_c}{D_0 - \beta_0} + \frac{(D_c - \beta_c)\,\Delta h}{(D_0 - \beta_0)h_0} \qquad (3)$$

Since we bring the upper meniscus to the same part of the capillary for the solution and for water, the value of r cancels out and does not have to be known exactly.

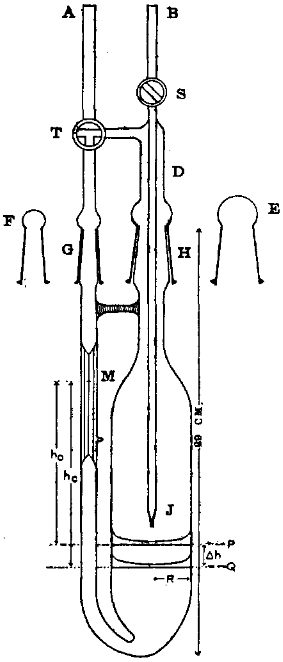

Fig. 1.—Silica capillarimeter.

Let W_0' and V_0' represent the weight and volume of water contained in the apparatus from the upper surface in the capillary to the level of a free surface of infinite extent which is assumed to be in hydrostatic equilibrium with the liquid in the instrument (P in the diagram), and let W_0'' and V_0'' represent the weight and volume between the meniscus in the wide tube and the level of the free surface (not the tangent to the lowest point of the meniscus). Then $W_0 = W_0' + W_0''$ and $V_0 = V_0' + V_0''$. The force of gravity on the liquid in the meniscus above the level of the free surface is balanced partly by the surface tension and partly by the buoyancy of the air. Therefore, we may write

$$W_0''g = D_0V_0''g = 2\pi R\sigma_0 + V_0''\beta_0 g \qquad (4)$$

$$V_0'' = \frac{2\pi R\sigma_0}{g(D_0 - \beta_0)} \qquad (5)$$

$$V_0' = V_0 - \frac{2\pi R\sigma_0}{g(D_0 - \beta_0)} = \frac{W_0}{D_0} - \frac{2\pi R\sigma_0}{g(D_0 - \beta_0)} \qquad (6)$$

and in an exactly analogous manner we may write for the solution

$$V_c' = V_c - \frac{2\pi R\sigma_c}{g(D_c - \beta_c)} = \frac{W_c}{D_c} - \frac{2\pi R\sigma_c}{g(D_c - \beta_c)} \qquad (7)$$

Since the wide tube is a true cylinder of radius, R, and is mounted vertically, we may write

$$\Delta V = V_0' - V' = \pi R^2 \Delta h \qquad (8)$$

$$\Delta h = \frac{1}{\pi R^2}\left\{\frac{W_0}{D_0} - \frac{2\pi R\sigma_0}{g(D_0 - \beta_0)} - \frac{W_c}{D_c} + \frac{2\pi R\sigma_c}{g(D_c - \beta_c)}\right\} \qquad (9)$$

Making this substitution in equation (3) gives

$$\sigma = \frac{\sigma_c}{\sigma_0} = \frac{D_c - \beta_c}{D_0 - \beta_0} + \frac{(D_c - \beta_c)}{(D_0 - \beta_0)}\frac{\Delta h}{h_0} = \frac{D_c - \beta_c}{D_0 - \beta_0} + \frac{(D_c - \beta_c)}{(D_0 - \beta_0)\,\pi R^2 h_0}\left\{\frac{W_0}{D_0} - \frac{2\pi R\sigma_0}{g(D_0 - \beta_0)} - \frac{W_c}{D_c} + \frac{2\pi R\sigma_c}{g(D_c - \beta_c)}\right\} \qquad (10)$$

Then a purely algebraic and rigid transformation remembering that $r = 2\sigma_0/gh_0(D_0 - \beta_0)$ gives the equation

$$\sigma = \frac{\sigma_c}{\sigma_0} = \left\{\frac{D_c - \beta_c}{D_0 - \beta_0}\right\}\left\{1 + \frac{1}{\pi R^2 h_0 (1 - r/R)}\left(\frac{W_0}{D_0} - \frac{W_c}{D_c}\right)\right\} \qquad (11)$$

It should be noted that this equation does not involve any assumption that the reservoir is so wide that the capillary rise in this tube is negligible, nor does it contain any assumption that the meniscus in the wide tube has the same shape for the solution and for water. If the derivation is carried through with these assumptions the result is the same, except that the factor $(1 - r/R)$ in the denominator of the second term is missing.

Precision Analysis

For the purpose of precision analysis it is more convenient to write equation (11) in the equivalent form

$$\sigma = \frac{\sigma_c}{\sigma_0} = \frac{D_c - \beta_c}{D_0 - \beta_0} + \frac{(D_c - \beta_c)}{(D_0 - \beta_0)}\frac{(W_0 D_c - W_c D_0)}{\pi R(R - r)h_0 D_0 D_c} \qquad (12)$$

For all the cases reported below, the first term in equation (12), $(D_c - \beta_c)/(D_0 - \beta_0)$ is greater than 1 and less than 1.15. The second term is negative in all cases yet encountered and much smaller (the greatest numerical value so far experienced is 0.06338 for 3 N potassium chloride) and may, therefore, be regarded as a correcting term. It is, therefore, obvious that the accuracy of the final result will depend directly upon the accuracy of the determination of the densities of our solutions and that the quantities which are involved as factors of the second term do not have to be known with as great accuracy as the densities. Since in our instrument r/R is 0.00633, the final result will be very little influenced by an error in r.

D_0, β_c, β_0 and π may be regarded as known without significant error, but all of the other quantities appearing in the equation are determined by experiment and are subject to experimental errors which may influence the accuracy of the computed relative surface tension. From the principles of partial differentiation we may write

$$\Delta\sigma = \frac{\partial\sigma}{\partial D_c}\Delta D_c + \frac{\partial\sigma}{\partial W_0}\Delta W_0 + \frac{\partial\sigma}{\partial W_c}\Delta W_c + \frac{\partial\sigma}{\partial h_0}\Delta h_0 + \frac{\partial\sigma}{\partial R}\Delta R + \frac{\partial\sigma}{\partial r}\Delta r + \frac{\partial\sigma}{\partial T}\Delta T + \frac{\partial\sigma}{\partial(r_c/r_0)}\Delta\frac{(r_c)}{(r_0)} \qquad (13)$$

Although equation (12) does not contain the temperature, T, explicitly, σ is a function of the temperature, and therefore to obtain a complete differential equation the term $\partial\sigma\Delta T/\partial T$ must be added. In the derivation of equation (12) it was assumed that the solution and water are brought to the same part of the capillary so that $r_c = r_0$. The error caused by a failure to meet this condition perfectly in the experiments is represented by the term $\partial\sigma\Delta(r_c/r_0)/\partial(r_c/r_0)$.

The problem now is to carry out the differentiation indicated in equation (13) and to substitute actual numerical data for each algebraic symbol in the total differential equation. In Table I we have used the data for three different solutions of potassium chloride selected to be typical of a dilute solution, an intermediate solution, and a very concentrated solution to compute the experimental errors in the measured quantities, D_c, W_0, W_c, h_0, R and r, which would each separately cause an error of 0.001% in the relative surface tension for an instrument for which h_0 = 10.834 cm., R = 2.1489 cm. and r = 0.0136 cm.

TABLE I

PRECISION ANALYSIS

	0.001 N KCl	0.1 N KCl	3 N KCl	
D_c	0.997116	1.001787	1.12808	G./ml.
W_0	84.9947	84.9947	84.9795	G.
W_c	85.0318	85.7047	106.1728	G.
D_c	+0.0000064	+0.0000064	+0.0000064	G./ml.
W_0	+ .00155	+ .00155	+ .00137	G.
W_c	− .00155	− .00155	− .00155	G.
h_0	+ .5	+ .055	+ .0038	Cm.
R	+ .05	+ .0054	+ .00017	Cm.
r	− .1	− .0108	− .00033	Cm.

The foregoing table, interpreted in the light of our experience with the method, shows that the accuracy of the result will probably be chiefly influenced by the errors in W_0 and W_c because it is difficult to determine them experimentally within 0.0015 g. It should, however, be noted that any systematic error in W_0 is likely to be duplicated in W_c and hence these errors are likely to compensate each other. The quantity D_c ranks next in its probable influence on the result because it is difficult to determine the density of a solution within 6 parts in a million, although by using large pycnometers (50 cc.) results can be duplicated within this limit. The combined effect of these errors should not exceed 0.003% with our apparatus. On the other hand, it is experimentally easy to determine h_0, R and r within the limits required of them except that for the most concentrated solutions the determination of R commences to become critical. The experimental error in R may be about 0.0001 cm. The radius of the capillary, r, is computed from the capillary rise with water, and the error in r depends mainly on the error in the value σ_0 selected from the literature for the calculation. An error of about 2.5% in the assumed value of σ_0 would be needed to cause an error of 0.00033 cm. in r and hence an error of 0.001% in the relative surface tension of a 3 N potassium chloride solution. Since σ_0 is probably known within 0.1%, errors due to r are insignificant in all the cases yet investigated.

The absolute surface tension of water at 25° changes 0.22% per degree, which would require that the temperature should be fixed within 0.0045° in order to fix the absolute surface tension within 0.001%. Since it is probable that the absolute surface tension of solutions varies with the temperature nearly the same as water, it follows that the temperature coefficient of the relative surface tension of solutions to that of water is presumably much smaller than the figure given above, so that a substantially greater error than 0.005° in our temperature scale could be tolerated. Since we had available a very good thermometer having a scale of 6 cm. per degree, which had been calibrated at the Bureau of Standards, we are confident that the working temperature of our thermostat was so near to 25.00° that no significant error is involved. A more dangerous source of error would be a variation of the temperature of the thermostat during the interval between the measurements on water and on the solutions. Our thermostat was good enough so that the maximum variation ever observed was safely within the tolerable limit of 0.004°.

The foregoing analysis also assumed that the radius of the tube is the same for the solution and for water. Since the position of the meniscus when the capillarimeter is filled may differ from the reference mark by ±0.001 cm., a variation of radius of 0.001% over a range of 0.002 cm. or 0.5% per cm. might cause an error of 0.001% in the relative surface tension. It is believed that our capillary is uniform within this tolerance (see page 192).

The advantages of our differential method over the old method are shown by a similar analysis of the formula

$$\sigma = \frac{\sigma_c}{\sigma_0} = \frac{g(D_c - \beta_c)h_c r_c}{g(D_0 - \beta_0)h_0 r_0}$$

On differentiating with respect to each of the experimentally determined quantities and substituting the numerical data for the 0.001, and 0.1 and 3 N potassium chloride solutions in this equation, it appears that the requirements for precision are nearly independent of the concentration and, therefore, a detailed table is omitted. These calculations show that an error of 0.000010 g./ml. in D_c, an error of 0.00011 cm. in either h_c or h_0 will each cause an error of 0.001% in the relative surface tension. Although D_c can be determined within this tolerance, the probable error in h_c and h_0 is many times the safe limit. By comparison with the table given above it will be noted that the new method is more dependent on errors in D_c than the old, but that is of minor importance because, if unlimited amounts of solutions are available, the densities can be determined with sufficient accuracy. On the other hand, the influence of errors in h_0 is reduced greatly in the new method, especially at low concentrations, and the necessity of determining h_c is eliminated. Moreover, the old method, in which no effort is made to bring the meniscus to exactly the same part of the capillary, requires the assumption that $r_c/r_0 =$ 1.00000 over the working range of the capillary which may amount to 2 cm., whereas the new method only requires that the radius of the capillary shall be constant within 0.001% over a range of only 0.002 cm.

The Capillarimeter and its Accessories.—The capillarimeter (Fig. 1) has graduation marks, 0.1 mm. apart, engraved on the capillary tube. A segment of this tube was ground off to give a flat polished strip and the marks were cut on this surface by the use of a fine diamond point operated by a dividing engine. These marks were so fine as to be invisible to the naked eye, but were correspondingly sharp when viewed under the microscope. They were not visible when the tube was immersed directly in the water of the thermostat; this was remedied by enclosing the capillary tube in another tube, the intervening space being filled with hydrogen for better thermal conductivity. The wide tube of the capillarimeter before fabrication was ground and polished inside and outside to true coaxial right circular cylinders in order to permit an accurately reproducible vertical mounting of the instrument and to avoid optical distortion. The external and internal diameters of this tube were measured with a micrometer before fabrication and found to be 5.0126 and 4.3004 cm., respectively, with a maximum variation at any place of ±0.00013 cm. After the construction of the complete instrument the external diameter was again measured by the micrometer and found to be unchanged within the working range.

A special holder, equipped with precision levels and leveling screws, was constructed which ensured that the capillarimeter could be mounted in a definite reproducible vertical position inside a water thermostat which was maintained at 25 ± 0.003°. The levels of the menisci were measured by observation through a window of optically plane glass by means of a special cathetometer, whose vertical scale was calibrated by comparison with a standard Invar scale provided with a Bureau of Standards certificate. To improve the definition of the menisci an adjustable blackened metal screen with horizontal slits as used by Richards and Coombs[8] was installed behind the menisci. A window of frosted glass in the back wall of the thermostat permitted adequate illumination.

The internal radius of the wide tube and of the capillary were determined after the construction of the instrument. The capillarimeter in its vertical mounting inside the thermostat was filled with sufficient water to bring the menisci within the working range. After waiting forty minutes for temperature equilibrium the heights of the menisci were measured. A weighed quantity of water of about 30 g. was then added and the measurements repeated. Three such independent determinations, covering approximately the same working range, gave as computed values of the radius of the wide tube 2.14882; 2.14892; and 2.14883; average 2.1489 cm. This figure is believed to be more reliable than the figure 2.1504 cm. obtained with a micrometer before the construction of the instrument.

As a result of many readings the observed or apparent capillary rise for water at 25° was taken as 10.8293 cm. between the lowest level of two menisci. This figure must be corrected[9] by +0.00453 cm. for the liquid in the upper meniscus; and by +0.00068 cm. for the elevation of the lowest part of the meniscus in the wide tube above the level of an infinite connecting surface; giving 10.8345 cm. as the true capillary rise. Hence the internal radius of the capillary at the point M (or more accurately at a level about 0.0045 cm. above M where the gas–liquid interface becomes vertical) is computed to be 0.01361 cm., by the use of equation (2), assuming[10] that $\sigma = 71.97$ for pure water at 25, and that at Cambridge the acceleration of gravity is 980.4.

Similar measurements, made at intervals along the capillary near the mark, M, show that the radius changes by 0.26% of itself per centimeter of length. If we always bring the water and solutions to be compared within 0.001 cm. of the mark, which is possible experimentally, the error in the relative surface tension due to conicality of the capillary tube would be less than 0.001%, which is negligible.

Purification of Materials and Preparation of Solutions.—The impurities most to be feared are capillary active substances, especially traces of grease and oils. Any relaxation in extreme care to maintain perfect cleanliness is apt to be followed promptly by erratic results. The capillarimeter, solution flasks, delivery tubes and all glassware were cleaned by exposure to a hot mixture of concentrated sulfuric and nitric acids, and finally thoroughly rinsed with water. This process was repeated whenever there was the slightest indication of imperfect drainage.

Richards and Carver[11] have published results indicating the effect of dissolved air is to lower the surface tension of water at 20° by about 0.03%. This difference, however, is about their limit of error and may not be significant. It seemed impractical to carry out all of our measurements *in vacuo*. Since we are interested in relative results and since the effect of dissolved air, if any, would probably be very nearly the same for solutions and for water, we decided to make all measurements on water and on solutions which were saturated with air.

The water used was freshly distilled conductivity water. It was collected in large bottles and shaken to saturate it with air, then blown by filtered compressed air through a sintered Jena Glass filter into a "water tower" which served as a storage reservoir. It was made of Pyrex, was 1 meter high, and 8 cm. in diameter. The water was stored here overnight to permit capillary active substances to rise to the surface and any dust particles to settle out. The water was then withdrawn when needed through a tube from the interior of the reservoir. The cock which controlled the outflow was ungreased and so well ground that no lubricant except water was needed. When water was withdrawn, suitable adapters were used to guide the water into the solution flasks or into other receptacles. The development of this device for protecting the water from capillary substances or dust greatly improved the reproducibility of the results.

The purest potassium chloride which could be purchased was recrystallized twice with centrifugal drainage and fused in platinum. A saturated solution of this salt gave no color with phenolphthalein. Potassium sulfate was prepared and tested in an exactly similar manner, except that it was not fused but was heated to redness in platinum. The cesium nitrate was made from the mineral pollucite by Professor Brainerd Mears and was a part of the same material already used for viscosity measurements in this Laboratory. Sucrose was obtained from "rock candy," since our previous experience showed that this variety contains less electrolyte than sucrose from any other source. The carefully selected crystals were then placed in platinum Gooch crucibles in a centrifuge

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[8] T. W. Richards and L. B. Coombs, THIS JOURNAL, **37**, 1656 (1915).

[9] These corrections were computed by the equations given by Lord Rayleigh. Lord Rayleigh, *Proc. Roy. Soc.* (London), **A92**, 184 (1916).

[10] "I. C. T.," Vol. IV, p. 447.

[11] T. W. Richards and E. K. Carver, THIS JOURNAL, **43**, 846 (1921).

and washed with conductivity water to rinse off the surface and then dried in a vacuum at a temperature of 50°. The electrical conductivity of solutions of this sucrose was so low as to prove that the electrolyte present as an impurity was less than 0.001% and, therefore, negligible for our purposes.

All solutions were prepared by the weight method with extreme care to prevent contamination by capillary active substances. All weighings were corrected to vacuum, and the concentration in gram molecules per liter at 25° computed by the aid of the density which was determined for each solution. The density determinations were made by the use of three Ostwald pycnometers of slightly more than 50 cc. capacity. The results obtained with these three instruments usually checked within five parts in a million.

Capillarimetric Procedure.—Comparative measurements were made on the solutions and on water with every detail of manipulation, except the addition of salt, and of measurement as nearly identical as possible. The capillarimeter was cleaned, weighed, and hung in the thermostat in the proper position and the height of the reference mark on the fixed vertical scale measured. After standing for several hours to permit capillary-active substances, if present, to come to the surface, slightly less than the required amount (about 85 cc.) of water (or solution) was transferred to the capillarimeter through a tube containing a sintered Pyrex filter. The water (or solution) was brought to 25.00° before making the transfer to avoid condensation in the upper part of the capillarimeter and suitable precautions taken to deliver the water (or solution) to the lower part of the capillarimeter without spattering and the delivery tube was withdrawn without touching the neck of the capillarimeter and thereby wetting it. The cross head filled with water (or solution) from S to J was then placed in position, as shown in Fig. 1. After waiting about thirty minutes for temperature control, the liquid was sucked up into the capillary by opening the cock, T, and applying gentle suction at A. The meniscus was allowed to fall until it reached its position of rest and then observed through the telescope. Water (or solution) was then added drop by drop from J until the meniscus, when falling, came to rest within 0.001 cm. of the reference mark. Then, after the proper quantity of water had been added, the level of the lowest point of the meniscus in the capillary with reference to the mark, M, and to the fixed scale was measured and recorded. Then the level of the lowest point of the meniscus in the center of the wide tube was measured with reference to the fixed scale. The cross head of the capillarimeter was then removed, replaced by the caps (F and E, Fig. 1), and the capillarimeter removed from the thermostat, carefully dried externally, and weighed on a large Troemner balance against a suitable counterpoise. The balance was sensitive to 0.1 mg. but the results were not reproducible better than 1–2 mg.

The entire operation was then repeated as exactly as possible, using a solution instead of water. The measurement of the actual capillary rise for the solution is not needed for the calculations of the results, and was sometimes omitted when pressed for time, but often made as a check.

It is well known that solid surfaces become coated with a greasy film when exposed to air for a short time.[12] In order to allow all traces of capillary active substances which might be introduced in this manner to rise to the surface, all of the solutions were made up in much larger quantities than were required for the measurements and allowed to stand undisturbed in closed flasks for from six to eighteen hours before use. Only the interior fractions taken from near the bottom were employed in the actual surface tension measurements.

In order to test the effectiveness of this method, three solutions of approximately 0.001 molar potassium sulfate were made up in three different ways. The first solution was prepared from a sample of salt which was weighed in a platinum boat, then ignited to a red heat and dissolved as soon as it had cooled; the second solution was prepared from a sample which was exposed to the laboratory air for twenty-four hours without a cover; while the third solution was prepared from a sample of salt which was deliberately contaminated with olive oil, by wetting the salt with a solution of olive oil in ethyl ether. The ether was allowed to evaporate leaving about 0.2 mg. of oil on the surface of the crystals. The surface of this solution was obviously greasy. Two determinations of relative surface tension were made on each of these solutions, the first after standing for six hours, and the second after standing for eighteen hours. The results are shown in the following table.

	Soln. I	Soln. II	Soln. III
6 hours old	0.99983	0.99986	0.99986
18 hours old	.99983	.99987	.99985

All three solutions had the same surface tension within the experimental error, which proves that the technique of withdrawing the solution from the interior was adequate to prevent errors due to accidental contamination of the salt by dust carrying capillary active substances.

Experimental Data

In order to illustrate the concordance which can be obtained with the new differential method the data are given in full for 0.05 *N* potassium chloride. Two different solutions were prepared, as shown in the upper part of Table III. This also shows the values for h_0 and W_0 determined on the same day and with the same reference mark. Each solution was used for two entirely independent experiments in the capillarimeter as is shown in the lower part of the table. The following figures were used in computing the results: $D_0 = 0.997074$; $\beta_c = \beta_0 = 0.00117$; $R = 2.1489$ cm.; $r = 0.013607$ cm.; $1 - r/R = 0.993671$.

In order to save space in printing the data are given in more abbreviated form in Tables III, IV and V. The figures for the relative surface tension are the averages of at least two independent experiments. The greatest deviation for any solution was only 0.005% and the average deviation was only 0.002%.

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(12) Lord Rayleigh, *Phil. Mag.*, [5] **33**, 220 (1892); I. Langmuir, *Trans. Faraday Soc.*, **15**, Part 3, 67 (1920).

TABLE II

INTERPRETATION OF EXPERIMENTAL DATA

KCl, g.		3.5366		3.5365	
Solution, g.		948.211		948.186	
D_c		0.999442		0.999434	
		.999442		.999432	
		.999447		.999438	
D_c average, g./ml.		.999444		.999435	
c, g.-mol./liter		.050000		.050000	
$(D_c - \beta_c)/(D_0 - \beta_0)$		1.002380		1.002371	
Apparent capillary rise for water		10.8281		10.8280	
Corr. upper meniscus		+ 0.00453		+ 0.00453	
Corr. lower meniscus		+ .00068		+ .00068	
	h_0, cm.	10.8333		10.8332	
$\pi R^2 h_0(1 - r/R)$		156.165		156.162	
Apparent weight water		84.9265		84.8946	
Corr. to reference mark		− 0.0029		+ 0.0290	
Vacuum correction		+ .0896		+ .0895	
	W_0, g.	85.0132		85.0131	
Apparent weight solution		85.2755	85.2746	85.2869	85.2912
Corr. to reference mark		− 0.0029	− 0.0015	− 0.0145	− 0.0174
Vacuum correction		+ .0896	+ .0895	+ .0892	+ .0888
	W_c, g.	85.3622	85.3626	85.3616	85.3626
Apparent cap. rise		10.8170	10.8180	10.8180	10.8179
Corr. upper meniscus		+ 0.00453	+ 0.00453	+ 0.00453	+ 0.00453
Corr. lower meniscus		+ .00068	.00068	.00068	.00068
	h_c, cm.	10.8222	10.8232	10.8232	10.8231
$W_0/D_0 - W_c/D_c$		− 0.1470	− 0.1474	− 0.1473	− 0.1483
$(W_0/D_0 - W_c/D_c)/\pi R^2 h_0(1 - r/R)$		− .000941	− .000944	− .000943	− .000959
σ_c/σ_0		1.001437	1.001434	1.001426	1.001410
	Average		1.00143		

TABLE III

RELATIVE SURFACE TENSION OF POTASSIUM CHLORIDE SOLUTIONS AT 25°

c	D_c	σ_c/σ_0	$(\sigma_c - \sigma_0)/c\sigma_0$
0.000100	0.997078	0.99997	−0.3
.000200	.997081	.99995	− .3
.000500	.997094	.99983	− .32
.001000	.997117	.99982	− .18
.002000	.997161	.99988	− .06
.005000	.997306	.99998	− .04
.010000	.997540	1.00013	+ .013
.020000	.998018	1.00047	+ .023
.050000	.999440	1.00143	+ .0286
.10000	1.001787	1.00273	+ .0273
.20000	1.006456	1.00514	+ .0257
.50000	1.020275	1.01197	+ .02354
.99996	1.042865	1.02299	+ .02299
1.99908	1.086749	1.04531	+ .02266
2.99647	1.129252	1.06894	+ .03453

TABLE IV

RELATIVE SURFACE TENSION OF POTASSIUM SULFATE SOLUTIONS AT 25°

c	D_c	σ_c/σ_0	$(\sigma_c - \sigma_0)/c\sigma_c$
0.000200	0.997088	0.99995	−0.25
.000400	.997100	.99991	− .20
.001000	.997140	.99988	− .12
.002000	.997202	.99982	− .09
.004000	.997349	.99993	− .018
.010000	.997773	1.00019	+ .019
.020000	.998478	1.00058	+ .029
.040000	.999880	1.00110	+ .0275
.10000	1.004043	1.00262	+ .0262
.19993	1.010886	1.00460	+ .0230
.40015	1.024412	1.00850	+ .0212
1.00142	1.063920	1.01956	+ .0195

TABLE V

RELATIVE SURFACE TENSION OF CESIUM NITRATE SOLUTIONS AT 25°

c	D_c	σ_c/σ_0	$(\sigma_c - \sigma_0)/c\sigma_c$
0.000100	0.997088	0.99992	−0.8
.000200	.997101	.99990	− .5
.000500	.997138	.99986	− .28
.001000	.997212	.99983	− .17
.002000	.997361	.99986	− .07
.005000	.997791	.99996	− .008
.010000	.998509	1.00013	+ .013
.020000	.999944	1.00046	+ .023
.050000	1.004258	1.00118	+ .0236
.10001	1.011430	1.00217	+ .0217

Interpretation of the Data

The densities of these three salts can be expressed over the entire range studied by equations having the form suggested by Root.[13]

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[13] W. C. Root, THIS JOURNAL, 55, 850 (1933).

For KCl: $d^{25}{}_4 = 0.997074 + 0.0480688c - 0.002283c^{3/2}$
For K_2SO_4: $d^{25}{}_4 = 0.997074 + 0.070994c - 0.004240c^{3/2}$
For $CsNO_3$: $d^{25}{}_4 = 0.997074 + 0.143708c - 0.000477c^{3/2}$

These equations agree with our data over the entire range studied and with the average deviations of less than 0.001%. This confirms previous experience in this Laboratory as to the usefulness of the Root equation.

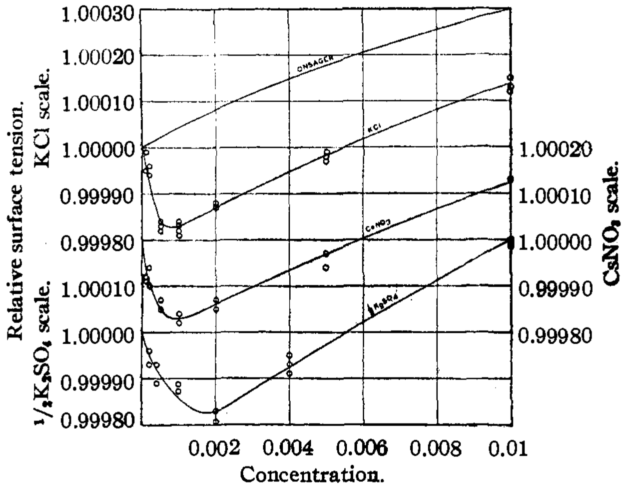

Fig. 2.

Within the ranges of concentration which have been studied by earlier experimenters, our data on the relative surface tension show the characteristics which Heydweiller has found to be typical of solutions of strong electrolytes; namely, $\sigma - c$ curves which are approximately linear with a gentle positive slope, but with a slight downward curvature which is especially pronounced in the dilute range (below 0.1 *N*), followed by an upward curvature in concentrated solutions (above 2 *N*) (see Figs. 3, 4 and 5). A comparison of the last column in our tables with the corresponding figures in the papers by Heydweiller and of Schwenker shows a marked similarity.

The most interesting and novel result of these measurements is that at extreme dilutions (less than about 0.006 *N*) the solutions of the three salts studied have a smaller surface tension than pure water, although above this lower limit the surface tension is greater than that of pure water and the surface tension–concentration curves show that these salts may be regarded as typical "capillary-inactive" substances.

The minimum surface tension which has been observed is not quite 0.02% less than that of pure water and occurs at about 0.001 *N*. In spite of the fact that the observed decrease is so small we believe that it is real and not due to experimental error. Figure 2 shows graphically the results of the separate experiments. Their averages only are given in the tables of numerical data. The concordance of the separate data, together with the precision analysis given above, make it seem probable that the error in the average for any concentration is not more than 0.002%. At the minimum in the surface tension the depression is, therefore, about nine times the probable error in the data. Moreover, the data give smooth curves which are similar for the three salts.

If the observed depression in surface tension is real, it follows from the well-known Gibbs theorem that at extreme dilutions these salts must be positively adsorbed in the surface layer, whereas above some lower limit of concentration (from 0.001 to 0.002 normal) there must be a deficiency in the surface layer or negative adsorption.

It would, of course, be premature to generalize from observations on three salts only that all salts will cause a diminution in surface tension and be positively adsorbed in the surface layer at sufficiently low concentrations. We intend to extend the experimental investigation to other salts of varied valence types and to study the influence of variations in the temperature and solvent. Since, however, the only three salts studied give similar curves, we shall assume tentatively that the phenomenon is general for aqueous solutions and discuss its implications on this assumption.

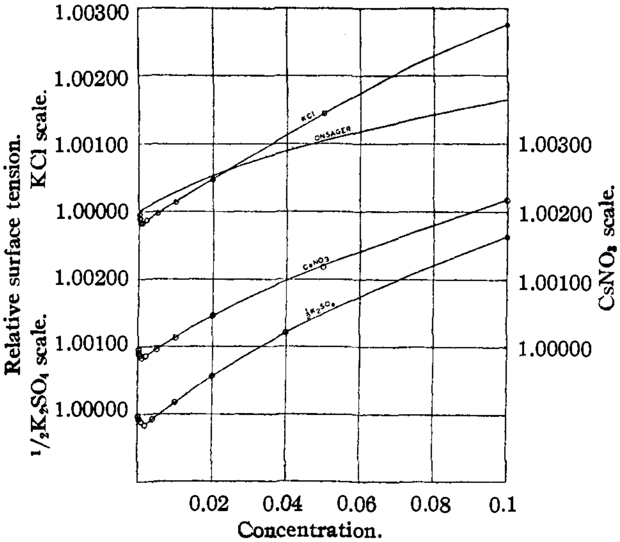

Fig. 3.

So far as we know this depression of the surface tension and positive adsorption at low concentrations has never been observed at a liquid–gas interface for any salt which gives increased surface tension at moderate concentrations and, therefore, can be classed as a "capillary-inactive" substance in the sense that this term has been used in the literature. An analogous phenomenon, however, has been observed at the interface between aqueous solutions of salts and organic liquids. Eversole and Dedrich, and Dedrich and Hanson,[14] who used a drop weight method, have measured the effect of sodium formate and of sodium acetate on the interfacial tension between aqueous solutions of these salts and mineral oil, or toluene, or benzene. They found a minimum in the curves for all of the cases studied, except for sodium acetate solutions against mineral oil. In the case of sodium formate solutions the minimum was found at high concentrations (above 1 *N*). The minimum for the sodium acetate solutions was not located very definitely, but was evidently much lower and was placed by the authors at around 0.1 to 0.15 *N*. "An attempt to explain the effect of these salts has been made on the basis of the Langmuir theory of molecular orientation and the increased interionic attraction in the interface due to the dielectric constant gradient in the interfacial layer."

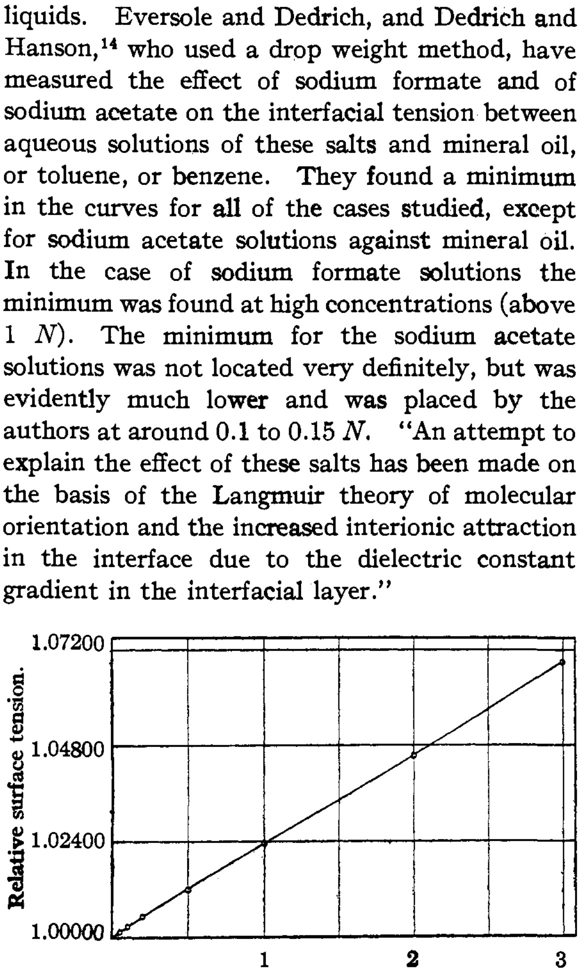

Fig. 4.

McTaggart[15] has found that a bubble of air suspended in water moves toward the cathode in an electric field, which he interprets as proving that the surface film of water at the water–air interface is negatively charged. Lenard and his students[16] have reached the same conclusion from experiments on electrical effects in waterfalls and sprays. McTaggart then finds that by the addition of minute traces of salts containing positive ions of high valency (aluminum nitrate, lanthanum nitrate, thorium nitrate) to the water the air bubble will then move cataphoretically to the anode.

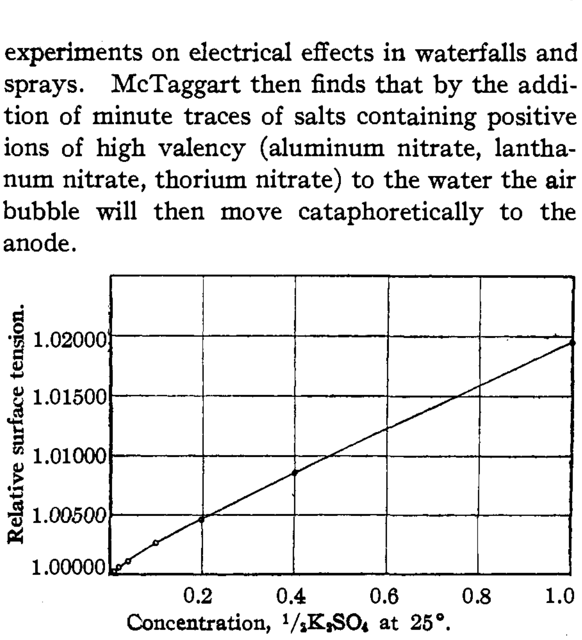

Fig. 5.

Freundlich, in a discussion of McTaggart's experiments on the cataphoresis of air bubbles says, "The fact that inorganic salts must here be assumed to be positively adsorbed does not appear to be in agreement with earlier experience. At all other interfaces, such as those of charcoal, glass, and oil, this assumption is justified, since they are actually positively adsorbed and lower the interfacial tension. At the interface water–air, however, they almost always raise the surface tension, and hence should be negatively adsorbed. This rise of σ refers, of course, to much more concentrated solutions. In such dilutions as come into question here a change in the surface tension cannot be established. It is not impossible that in this range of concentration the surface tension may be lowered by these electrolytes and positive adsorption take place, in accordance with the very general experience, that the first small amount of a foreign substance always causes a lowering of σ. The first gentle rise of the σ, c curve for inorganic salt solutions would thus be in the region of a minimum in the σ, c curve, only that this minimum, since it is very slight, cannot be measured."[17]

McTaggart's demonstration, however, that a trace of a salt containing a trivalent or tetravalent positive ion causes an air bubble to move to the anode merely proves that the surface film

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(14) W. G. Eversole and D. S. Dedrich, *J. Phys. Chem.*, **37**, 1205 (1933); D. S. Dedrich and M. H. Hanson, *ibid.*, **37**, 1215 (1933).

(15) H. A. McTaggart, *Phil. Mag.*, [5] **27**, 297 (1914).

(16) P. Lenard, *Ann. Physik*, [4] **47**, 463 (1915); W. Obolensky, *ibid.*, [4] **39**, 961 (1912); W. Busse, *ibid.*, [4] **76**, 493 (1925); A. Bühl, *ibid.*, [4] **83**, 1207 (1927); [4] **84**, 211 (1927); [4] **87**, 877 (1928).

(17) H. Freundlich, "Colloid and Capillary Chemistry," Methuen Co., London, 1926, pp. 75 and 279–280.

becomes positively charged. It does not necessarily prove that the salt as a whole, or even the positive ion, is positively adsorbed in the surface. There might be a deficiency of both ions in the surface layer (negative adsorption and increased surface tension), but if there were a partial separation of the ions in the process with the negative ion being drawn into the interior more than the positive ion, there would be established an electrostatic double layer which would account for McTaggart's results.

It next became of interest to determine whether the observed decrease in surface tension at great dilutions is caused by ions only, or whether it will also be found in dilute solutions of non-electrolytes which are capillary inactive in the sense that they give a slight increase in surface tension and are not adsorbed in the surface at moderate concentrations. Sucrose is known to cause a linear increase in surface tension within the lower part of the range of concentration hitherto investigated, but accurate measurements at extreme dilution are not available. We, therefore, made measurements on sucrose solutions from 0.0002 to 0.005 molar, as shown below.

TABLE VI

RELATIVE SURFACE TENSION OF SUCROSE SOLUTIONS AT 25°

c	D_c	σ_c/σ_0
0.000200	0.997093	0.99999
.000500	.997132	1.00002
.001000	.997202	1.00004
.002000	.997329	1.00008
.005000	.997726	1.00016

These results are shown in Fig. 6.

The slight indicated decrease at 0.0002 molar is within the limit of experimental error and is not significant. The data show a linear increase in surface tension and, therefore, show that sucrose is negatively adsorbed even at these extreme dilutions. It seems probable, therefore, that the influence which causes the decrease in surface tension and positive adsorption for salts is dependent on the electric charges of the ions.

Our results on the surface tension of salts are not in accord with the Onsager and Samaras equation, especially as to the sign of the limiting slope at infinite dilution. The Onsager–Samaras equation predicts that the limiting slope should be plus infinity, whereas the data show a large negative slope at extreme dilutions. The systematic differences between the data and the equation are shown in Figs. 2 and 3. The experimental and theoretical curves cross each other and there is no maximum in the experimental curve.

An inspection of our curves indicates that the influence which causes the diminution of surface tension is of such a nature that it reaches a limiting or saturation value at an extremely low concentration (perhaps under 0.002 *N*) and is maintained, but not appreciably increased, at higher concentrations.

The effect of the interionic attraction which is treated by Onsager and Samaras and which causes an increase in surface tension is of minor importance in the dilute range but increases approximately linearly with the concentration and becomes dominant above about 0.006 *N*.

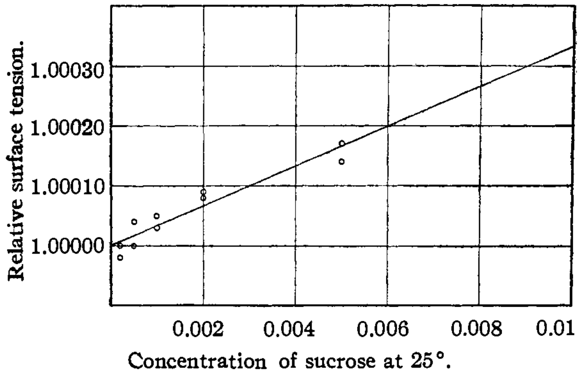

Fig. 6.

Onsager and Samaras in the derivation of their equation consider only the electric forces between the ions, but they do not consider the electric forces between the ions and the water molecules considered as electric dipoles. The electric forces between the dipolar water molecules must tend to maintain a systematic or ordered arrangement. A fairly detailed theory as to the nature of this ordered arrangement has been worked out by Bernal and Fowler.[18] 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. In view of the electrically unsymmetrical character of the water molecules, this force may well be different for positive and negative ions, thus accounting for the effects described

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

by McTaggart and by Lenard and his students. Since the cohesion, and therefore also the surface tension, of water is probably largely due to the electric forces between the dipoles, a disturbance of the normal electric distribution may cause a diminution of the surface tension.

As the solution becomes more concentrated (about 0.01 N or above), the mutual attraction between ions of opposite polarity becomes stronger than the forces between the ions and the water molecules and causes negative adsorption and an increase in surface tension in the manner discussed by Onsager and Samaras. We may conclude, therefore, that the treatment of Onsager and Samaras is over simplified and thus fails to give a complete and accurate result.

Summary

1. A modification of the capillary rise method of measuring the surface tension of solutions relative to that of the pure solvent, which makes it a differential method and substantially improves the accuracy of the results, is described.
2. The relative surface tension of aqueous solutions of potassium chloride, potassium sulfate, and cesium nitrates has been determined at 25° from 0.0001 N up to 3, 1 and 0.1 N, respectively, and of sucrose solutions from 0.0002 molar up to 0.005 molar.
3. These three salts all increase the surface tension of water from 0.01 N up to the highest concentration studied and give surface tension–concentration curves which are typical of strong electrolytes that are capillary inactive and negatively adsorbed in the surface layer.
4. At extreme dilutions (below about 0.006 N) all three salts cause a decrease in surface tension and are, therefore, positively adsorbed in the surface layer at concentrations below that giving the minimum (about 0.001 N) of the surface tension.
5. Sucrose gives a linear surface tension–concentration curve with no change in the sign of the slope at extreme dilutions.
6. The data are not in accord with the Onsager–Samaras equation for the surface tension as a function of the concentration.
7. The influence which causes diminished surface tension and positive adsorption at extreme dilution is ionic in character and probably due to an interaction between the ions and polarized water molecules.

CAMBRIDGE, MASS. RECEIVED JULY 29, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Action of Elementary Fluorine upon Organic Compounds. III. The Vapor Phase Fluorination of Hexachloroethane

BY WILLIAM T. MILLER, JR., JOHN D. CALFEE AND LUCIUS A. BIGELOW

Previous papers in this series[1] have described the fluorination of certain organic compounds dissolved in carbon tetrachloride, using, however, an open type of generator as the source of the halogen. This earlier procedure had two disadvantages, since the fluorine produced was contaminated with other gases, and also reacted to a considerable extent with the solvent. More recently, we have designed a new closed generator[2] capable of delivering fluorine 94–99% pure, and in addition have considered it desirable to avoid the use of solvents altogether. The present paper describes the vapor phase fluorination of hexachloroethane over a copper gauze catalyst. It is probable, of course, that the reaction took place at the surface of the metal, which acquired a thin coating of copper salts during the process, and cupric fluoride may have been the immediate fluorinating agent. However, the change did not occur rapidly at ordinary temperatures, and the gauze was not greatly attacked over a considerable period of time, even when heated. So far as the writers are aware, no similar, direct, vapor phase fluorination of an organic compound containing more than one carbon atom has as yet been reported, in which definite chemical individuals have been formed.

The procedure employed in this fluorination was exceedingly simple. The sample was placed in a horizontal tube, between two copper gauze rolls, suitably heated. The fluorine, diluted with nitrogen, was introduced at the center of one of

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(1) THIS JOURNAL, 55, 4614 (1933); 56, 2773 (1934).

(2) Miller and Bigelow, *ibid.*, 58, 1985 (1936).