[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Surface Tension of Solutions of Electrolytes as a Function of the Concentration II*

BY GRINNELL JONES AND WENDELL A. RAY

The first paper of this series[1] described a modification of the capillary rise method of measuring the surface tension of aqueous solutions relative to that of pure water, which makes it a differential method and permits greater precision in relative measurements than had been attained before. Data on the surface tension of aqueous solutions of three salts (potassium chloride, potassium sulfate, and cesium nitrate) were given. These measurements of capillary rise were interpreted as showing that the first trace of these salts when added to water causes a decrease in the surface tension and, therefore, according to the Gibbs theorem, must be adsorbed in the surface layer. The surface tension–concentration curves go through a rather sharp minimum at low concentrations (about 0.001 molar). These phenomena hitherto had not been observed for any capillary-inactive salt. At higher concentrations, our observations on these three salts show that the surface tension becomes greater than that of water and the surface tension–concentration curves have a positive slope, which means negative adsorption in the surface layer, and become approximately linear but have a slight downward curvature at moderate concentrations and a slight upward curvature at high concentrations. Our curves within this higher range of concentration have the shape which has long been known to be characteristic of "capillary-inactive" salts.

Solutions of sucrose on the other hand do not show the minimum in the surface tension–concentration curves but have a positive slope throughout and therefore must be negatively adsorbed at all concentrations.

Onsager and Samaras[2] have derived an equation for the surface tension of solutions of uni-univalent electrolytes as a function of the concentration, based on the Debye theory of interionic attraction, but this equation does not give a minimum in the curve at low concentrations. Recently Malcolm Dole[3] has proposed an hypothesis for the mechanism of the adsorption of salts at extreme dilution which ascribes the dominant role to the negative ions and has derived an equation which gives a minimum at low concentrations.

Bikerman[4] has developed a theory for the minimum in the surface tension–concentration curve which ascribes a significant role to an ionic double layer in the water or solution near the surface. He estimates the potential across this layer for our reference water to be 0.090 volt.

After the experiments reported in this paper had been completed and this paper was in galley proof form, Irving Langmuir[5] suggested a different interpretation of our experimental observations. According to Langmuir's theory the film of liquid which wets the capillary above the meniscus is not merely a few molecules thick and entirely negligible in comparison with the radius of the capillary, as had been assumed by all experimenters previously, but may be several hundred ångströms thick, and the thickness of the wetting film is greater for water than for a solution of an electrolyte. Langmuir's theory leads to an equation giving the thickness of the film as an explicit function of the zeta potential at the interface between the wall of the capillary and the water or solution, and of the temperature and the concentration of the solution and of the capillary rise (which of course is dependent on the radius of the capillary and on the surface tension of the liquid). If these parameters are all known with sufficient precision and if the theory is correct, it would be possible to compute the thickness of the film for each case and therefore to estimate the error, if any, due to our assumption that the effective radius of the capillary is identical for the solution and for the water used as a reference substance. If it can be established that the wetting film for the reference water is about 250 ångströms thicker than the wetting film of a 0.001 N salt solution, then our observations of capillary rise could be accounted for without inferring that there is a minimum in the surface tension–concentration curve.

---

*Original manuscript received August 8, 1938.

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

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

[3] M. Dole, THIS JOURNAL, **60**, 904 (1938).

[4] J. J. Bikerman, *Trans. Faraday Soc.*, **34**, 1268 (1938).

[5] Irving Langmuir, *Science*, **88**, 430 (1938); *J. Chem. Phys.*, **6**, 894 (1938).

The publication of these papers by Langmuir induced us to delay the publication of this paper until the question could be studied further theoretically and experimentally. A paper analyzing the Langmuir theory has been published recently.[6] In order to evaluate the integration constant of the fundamental differential equation Langmuir makes the assumption that the derivative of the potential with respect to the distance from the wall of the capillary, $\partial\psi/\partial x$, becomes zero at the solution–air interface. This assumption is unproven and questionable because it requires that there shall be no excess of positive or negative ions at the solution–air interface. The theory thus ascribes a dominant role in determining the thickness of the wetting film to the charge and potential at the glass (or silica)–solution interface but definitely postulates the absence of any effect of a charge or potential at the solution–air interface.

The computation of the thickness of the wetting film, Δr, by Langmuir's theory requires a knowledge of the zeta potentials, which are presumably functions of the temperature, the chemical nature and the concentration of the electrolyte, the nature of the capillary, and perhaps even its previous history. Even if Langmuir's theory is correct in principle, the zeta potentials are not known with sufficient precision to permit reliable calculations of the thicknesses of the films which would be needed to compute the corrections to be applied to the experimental data.

The mathematical development of the theory might be modified so as to take into account the potential at the air–solution interface but unfortunately the evaluation of such potentials is even more difficult experimentally than the evaluation of the potential at the glass–solution interface; the data available in the literature are probably even less reliable than the measurements of zeta potentials.

Langmuir stated that the addition of 10^{-6} M thorium ion would reduce the zeta potentials nearly to zero and predicted that it would thereby eliminate the apparent minimum in the surface tension–concentration curves. It was found experimentally that although 10^{-6} M thorium did not eliminate the decrease in the apparent surface tension completely, it did in fact reduce the magnitude of the effect and there were indications that a higher concentration of thorium might fulfill the prediction, which gives strong support to the theory in principle. Finally, it was found that a fourfold variation in the specific conductivity of the reference water between the limits of 0.37×10^{-6} and 1.67×10^{-6} did not influence the capillary rise, which is difficult to reconcile with the theory.

Recently Dole and Swartout[7] have developed the ring method so that it gives relative measurements which appear to be reliable to within 0.002%. Their measurements of the surface tension of potassium chloride solutions agree quite well with ours over the entire range up to 1 N, including the minimum in the curve at about 0.001 N. Their value for the relative surface tension at 0.001 N is even somewhat lower than ours. Their results, unless some source of error can be demonstrated in their method, adds a strong argument against Langmuir's suggestion that our experimental observations on capillary rise can be accounted for without drawing the conclusion that there is a minimum in the surface tension–concentration curve.

We are still open-minded as to the validity of Langmuir's theory but believe that a definite clear-cut decision requires more reliable data as to zeta potentials than are now available. A substantial improvement in the technique of measuring zeta potentials will be needed to settle the question. This problem is being studied in this Laboratory and hopeful progress has been made but it will be some time before the results will be ready for publication. The papers referred to and additional references contained therein should be consulted for a more detailed discussion of the historical and theoretical background of the problem.

The purpose of the present investigation was to determine whether or not it is a general rule that salts which are "capillary-inactive" at moderate concentrations have a minimum in their surface tension–concentration curves and are therefore "capillary-active" at sufficiently low concentrations, and also to follow these curves nearly to saturation. Since most properties of salt solutions are greatly dependent on the valence-type, we have selected barium chloride, lanthanum chloride, potassium ferricyanide and potassium ferrocyanide as good examples of salts having either a polyvalent cation or anion. Lithium

---

(6) Grinnell Jones and L. D. Frizzell, *J. Chem. Phys.*, **8**, 986 (1940).

(7) Malcolm Dole and J. A. Swartout. THIS JOURNAL, **62**, 3039 (1940).

fluoride and cesium iodide were chosen because they differ greatly in ionic size and in hydration. Potassium chlorate was selected for study because Heydweiller[8] states that most chlorate solutions wet glass so poorly that the capillary rise method cannot be used. We have not confirmed this observation. Potassium chlorate solutions behave normally in our quartz apparatus and we have had no difficulty in wetting either Pyrex glass or soft glass with a nearly saturated solution of potassium chlorate. Potassium thiocyanate was selected partly because of the great influence of the thiocyanate ion on the interfacial tension and on the electrocapillary phenomena at a mercury–water interface[9] and partly in response to a request of Malcolm Dole who, in a private letter, predicted that this salt would be unusually effective in giving a depression in the surface tension–concentration curve. This prediction was based largely on the inferences from the measurements of Frumkin,[10] which he interprets as showing that the surface layer of a solution of an electrolyte at an air interface is negatively charged with respect to the interior in nearly all cases, and that the magnitude of the potential difference depends greatly on the particular negative ion present.

Experimental Procedure

The procedure in preparing the solutions and in measuring their relative surface tension and density was the same as that described in detail in our first paper. Further experience with our differential method did not reveal any source of error which had hitherto been overlooked. Each of the salts was carefully purified and dried in a suitable atmosphere (air, or oxygen-free nitrogen, or hydrogen chloride followed by air or nitrogen, depending on the salt used). Measurements of the relative surface tension were made on at least two samples of each solution and the results obtained rarely differed by more than two thousandths of one per cent. All measurements were made at 25.00°. The density, $Dc = D^{25}_{4}$, of each solution was determined in three Ostwald pycnometers of about 50-cc. capacity. The results obtained with the three pycnometers usually checked within five parts in a million. The concentration, c, is expressed in gram molecules per liter.[11] The results are recorded in Table I.

TABLE I

APPARENT RELATIVE SURFACE TENSION OF SOLUTIONS AT 25°

c	D_c	σ_c/σ_0	$(\sigma_c - \sigma_0)/c\sigma_0$
Lithium Fluoride			
0.00010	0.997078	0.99994	−0.6
.00020	.997079	.99992	− .4
.00050	.997088	.99988	− .24
.00100	.997094	.99988	− .12
.00200	.997118	.99992	− .04
.00500	.997206	1.00000	+ .000
.01000	.997348	1.00026	+ .026
.02000	.997630	1.00056	+ .028
.03000	.997902	1.00086	+ .0287
Potassium Chlorate			
0.00010	0.997078	0.99992	−0.8
.00020	.997084	.99987	− .65
.00050	.997113	.99984	− .32
.00100	.997150	.99984	− .16
.00200	.997224	.99986	− .07
.00500	.997456	.99998	− .004
.01000	.997840	1.00011	+ .011
.02000	.998601	1.00022	+ .011
.05000	1.000898	1.00066	+ .013
.10000	1.004702	1.00132	+ .0132
.20000	1.012280	1.00254	+ .0127
.50000	1.034786	1.00558	+ .0112
Cesium Iodide			
0.00010	0.997101	0.99995	−0,5
.00020	.997119	.99986	− .7
.00050	.997183	.99984	− .32
.00100	.997288	.99987	− .13
.00200	.997474	.99991	− .045
.00500	.998101	.99998	− .004
.01000	.999100	1.00010	+ .010
.02000	1.001118	1.00038	+ .019
.05000	1.007179	1.00101	+ .0202
.10000	1.017258	1.00193	+ .0193
.20000	1.037389	1.00361	+ .0181
Potassium Thiocyanate			
0.00020	0.997086	0.99992	−0.4
.00050	.997105	.99989	− .22
.00100	.997125	.99986	− .14
.00200	.997170	.99980	− .10
.00500	.997310	.99986	− .028
.01000	.997548	1.00002	+ .002
.02000	.998025	1.00013	+ .0065
.05000	.999444	1.00037	+ .0074
.10000	1.001795	1.00079	+ .0079
.20000	1.006472	1.00144	+ .0072
2.50000	1.020367	1.00284	+ .00568
4.99937	1.043164	1.00575	+ .00575
.00000	1.087862	1.01322	+ .00661
.99412	1.216271	1.05202	+ .01042
Barium Chloride			
0.00005	0.997083	0.99990	−2.0
.00010	.997089	.99985	−1.5
.00025	.997113	.99984	−0.64

---

(8) A. Heydweiller, *Ann. Physik*, **4**, 33, 148 (1910).

(9) H. Freundlich, "Kapillarchemie," Akademische Verlagsgesellschaft, Leipzig, 4th ed., Vol. I, 1930, p. 414; M. Gouy, *Ann. chim. phys.*, [7] **29**, 169 (1903).

(10) Frumkin, *Z. physik. Chem.*, **109**, 34 (1924). Similar conclusions have been drawn from other evidence by H. A. McTaggart, *Phil. Mag.*, [5] **27**, 297 (1914), and by Lenard and his pupils (see reference 16 of the first paper).

(11) It should be noticed that in our first paper c was defined as gram equivalents per liter. This change in the definition seemed to be advisable because it makes it easier to use the data in testing the Dole equation.

TABLE I (*Concluded*)

c	D_c	σ_c/σ_0	$(\sigma_c - \sigma_0)/c\sigma_0$
.00050	.997159	.99982	− .36
.00100	.997262	.99984	− .16
.00250	.997527	.99994	− .024
.00500	.997989	1.00016	+ .032
.01000	.998917	1.00047	+ .047
.02500	1.001665	1.00126	+ .0504
.05000	1.006231	1.00254	+ .0508
.10000	1.015324	1.00484	+ .0484
.25000	1.042414	1.01117	+ .04468
.50121	1.087294	1.02174	+ .04337
1.00800	1.176471	1.04440	+ .04405
Lanthanum Chloride			
0.00005	0.997082	0.99985	−3.0
.00010	.997091	.99984	−1.6
.00025	.997127	.99981	−0.76
.00050	.997184	.99985	− .30
.00100	.997307	.99987	− .13
.00250	.997645	1.00004	+ .016
.00500	.998216	1.00028	+ .056
.01000	.999354	1.00068	+ .068
.02500	1.002767	1.00176	+ .0704
.05000	1.008404	1.00324	+ .0648
.10000	1.019614	1.00625	+ .0625
.25000	1.052910	1.01496	+ .05984
.50000	1.107596	1.03045	+ .06090
1.00000	1.214554	1.06733	+ .06733
Potassium Ferricyanide			
0.000033	0.997080	0.99994	−1.8
.000067	.997085	.99993	−1.1
.000167	.997102	.99992	−0.48
.000333	.997130	.99990	− .30
.000667	.997190	.99991	− .13
.001667	.997374	1.00004	+ .024
.00333	.997675	1.00014	+ .042
.00667	.998279	1.00053	+ .079
.01667	1.000078	1.00126	+ .0756
.03333	1.003044	1.00235	+ .0705
.06667	1.008935	1.00430	+ .0645
.16667	1.026357	1.00986	+ .0592
.33333	1.054853	1.01875	+ .05625
.66667	1.110314	1.03847	+ .05770
1.00000	1.164128	1.06172	+ .06172
1.16667	1.190499	1.07469	+ .06402
Potassium Ferrocyanide			
0.00005	0.997087	0.99992	−1.6
.00010	.997095	.99987	−1.3
.00020	.997128	.99984	−0.8
.00050	.997200	.99994	− .12
.00100	.997325	1.00003	+ .03
.00200	.997582	1.00014	+ .07
00500	.998340	1.00048	+ .096
.01000	.999581	1.00090	+ .090
.02000	1.002054	1.00169	+ .0845
.05000	1.009358	1.00376	+ .0752
.09940	1.021195	1.00672	+ .0676
.19881	1.044523	1.01232	+ .06195
.50058	1.112837	1.02953	+ .05899

Interpretation of the Data

In view of the doubt in our minds whether or not a wetting film correction should be applied to our data and the impossibility of computing this correction until more reliable measurements of zeta potentials can be made, we have decided to publish our results on many additional salts as originally obtained and calculated without any correction being applied to them. These "apparent relative surface tensions" can then be corrected later, if necessary, when more reliable zeta potentials are available. Equation (11) of our first paper can be modified so that it reads

$$\frac{\sigma_c}{\sigma_0}\left(\frac{r - \Delta r_0}{r - \Delta r_c}\right) = \left\{\frac{D_c - \beta_c}{D_0 - \beta_0}\right\}\left\{1 + \frac{1}{\pi R^2 h_0(1 - r/R)}\left(\frac{W_0}{D_0} - \frac{W_c}{D_c}\right)\right\}$$

where r is the actual radius of the dry capillary, Δr_0 the thickness of the film for the reference water and Δr_c is the thickness of the film for the solution. If later information makes it possible to compute the Δr_0 and Δr_c reliably, a correction to these "apparent relative surface tensions" can be made. It seems improbable that these corrections will amount to more than 0.03%.

The results as recorded in Table I are computed without applying any correction for the possibly varying wetting film in accordance with Langmuir's theory and therefore may be tentatively designated as "apparent relative surface tension." Since Langmuir's correction, if applicable, will affect the reference water chiefly it will probably raise all of the values for the apparent relative surface tension by a small amount. Such a correction might eliminate the minimum in the surface tension curve but would not appreciably affect the shape of the curve above the minimum. Subject to this reservation the implications of the data will be discussed as if the minimum is real.

The densities of the solutions of all of the salts can be expressed by means of equations of the form suggested by Root[12] over the entire range of concentrations studied (up to 5 normal in one case) with an average deviation between the observed and calculated values of less than 0.001%. The values of the parameters were computed by the method of least squares. The equations thus obtained are as follows:

For $LaCl_3$ $D^{25}{}_4 = 0.997074 + 0.229398c - 0.011911c^{3/2}$

---

(12) W. C. Root, THIS JOURNAL, 55, 850 (1933).

For $BaCl_2$ $D^{25}{}_4 = 0.997074 + 0.184762c - 0.006758c^{3/2}$

For $KClO_3$ $D^{25}{}_4 = 0.997074 + 0.077010c - 0.00224c^{3/2}$

For KSCN $D^{25}{}_4 = 0.997074 + 0.047936c - 0.0018093c^{3/2}$

For LiF $D^{25}{}_4 = 0.997074 + 0.02647c - 0.0072c^{3/2}$

For CsI $D^{25}{}_4 = 0.997074 + 0.202610c - 0.00232c^{3/2}$

For $K_3Fe(CN)_6$ $D^{25}{}_4 = 0.997074 + 0.182105c - 0.015075c^{3/2}$

For $K_4Fe(CN)_6$ $D^{25}{}_4 = 0.997074 + 0.25168c - 0.028877c^{3/2}$

The last column in Table I gives the value of $(\sigma_c - \sigma_0)/c\sigma_0$ which should be a constant if there were a simple linear relationship between surface tension and concentration as was suggested by Quincke long ago. As will be seen, the actual relationship is much more complicated than this.

The most striking feature of the new data is that all eight salts are like the three for which data are presented in our first paper in that the first addition of salt causes a decrease in surface tension and there is a minimum in the surface tension–concentration curve at a low concentration of the order of 0.001 *N*. These eleven salts must, therefore, in accordance with the Gibbs theorem, be positively adsorbed in the surface layer for very dilute solutions. Since all eleven salts which have been studied show this behavior without exception and since the salts were purposely chosen to differ greatly among themselves in valence-type, in size of the ions, in degree of hydration, and in complexity, the probability that this is a general characteristic property of salts is enormously increased by our new data. If exceptions are found in the future, it seems probable that the exceptional behavior can be correlated with some other special or unusual property such as a low degree of ionization. At all concentrations above the minimum, the slope of the surface tension–concentration curves is positive, which means that the surface layer is depleted of salt. This negative adsorption is at least qualitatively in accord with predictions based on the Debye theory of interionic attraction. At the minimum in the curve, there is neither positive nor negative adsorption, which means that there is a balance between the forces causing positive adsorption at extreme dilution, and the interionic forces which draw the ions away from the surface. These opposing forces are evidently very different functions of the concentration. The former are dominant at extreme dilution (under about 0.001 normal) and the latter become more effective at higher concentrations.

The depth of the minimum does not vary greatly among the eleven salts studied. It is least for potassium ferricyanide, about 0.01% less than that of water, and greatest for potassium thiocyanate, about 0.02% less than that of water.

The typical shape of the surface tension–concentration curve is quite complicated. It has a steep negative initial slope, then passes through a sharp minimum at about 0.001 molar and then becomes approximately linear with a positive slope and a positive curvature. The surface tension becomes equal to that of water at about 0.005–0.006 molar for uni-univalent salts (except for potassium thiocyanate at about 0.009 molar) and at lower concentrations for salts containing a polyvalent ion. There is a point of inflection below 0.02 molar, followed by a slight negative curvature. Although it is difficult to locate the point of inflection very definitely because the curvature on both sides is so slight, in nearly all cases it seems to be below the concentration at which the surface tension becomes equal to that of water. Before a maximum appears, if the salt is sufficiently soluble, there is another point of inflection followed by a positive curvature at high concentrations. It is evident that a function adequate to express the curve accurately must have a quite complicated form.

Dole infers from his hypothesis that the minimum in the surface tension curve should occur at the same concentration of the negative ions for all salts. In order to test this inference, we have plotted (see Fig. 1) the data over the lower range of concentration with the relative surface tension as the ordinate and the concentration of the negative ion, $c\nu_-$, as abscissa. Here ν_- is the number of negative ions in the salt. In order to avoid confusion between the different curves, the origin has been shifted vertically by an amount corresponding to 0.01% for each successive salt. As will be seen, for nine of the eleven salts the minimum occurs at about the same concentration ($c = 0.001$) in accordance with Dole's hypothesis, but two salts, potassium thiocyanate, and potassium ferrocyanide, are exceptions to the rule. These exceptions perhaps can be explained by the different slopes of the ascending branches of the curves. Potassium thiocyanate is the most effec-

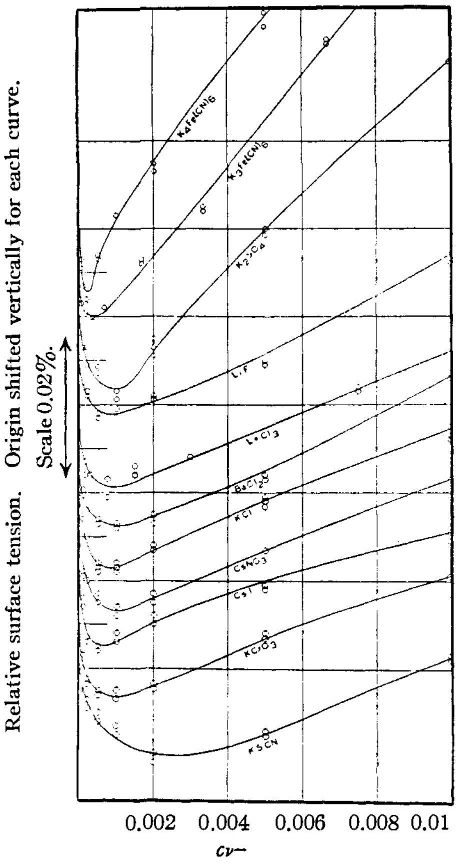

Fig. 1.

tive of all of the salts yet studied in depressing the surface tension. It gives the deepest minimum (about 0.02%) which occurs at about 0.0025 molar. This is the highest concentration yet observed for the minimum, and the surface tension does not again become equal to that of water until the concentration is about 0.009 molar, which is also the highest yet observed, and the slope of the ascending branch of the curve is the smallest of the eleven salts. On the other hand, the slope of the ascending branch of the curve for potassium ferrocyanide, when plotted in this manner, is steeper than for any of the other salts and this apparently gives a minimum at a lower concentration.

Neither the Onsager–Samaras nor the Dole equation is adequate to represent the whole curve. The Onsager–Samaras equation, which contains no parameters chosen to fit the data, gives a positive slope and a slight negative curvature characteristic of the intermediate range but it does not give the proper limiting slope at infinite dilution or the minimum in the curve. Moreover, it treats all uni-univalent salts as identical, whereas the different salts have an individuality which is experimentally demonstrated, although less pronounced than for most other properties of solutions of salts. The Onsager–Samaras theory evidently only takes into account a part of the forces which determine the surface tension of solutions of electrolytes.

Dole's three-parameter equation is much better at low concentrations. It gives a steep negative slope at extreme dilution, the sharp minimum at low concentrations and the ascending branch of the curve with a slight positive curvature. However, even when complicated by the activity correction[13] it does not give either of the two points of inflection which the real curve has.

We have attempted to combine the two equations on the assumption that each is part of the truth but is incomplete. The result is clearly an improvement over either one but the labor of computing the activity correction and the parameters by successive approximations is enormous. It seemed inadvisable to delay the publication of the data which have been obtained until such calculations could be extended to all of the salts which have been studied, especially as in some cases the data necessary to apply the activity correction

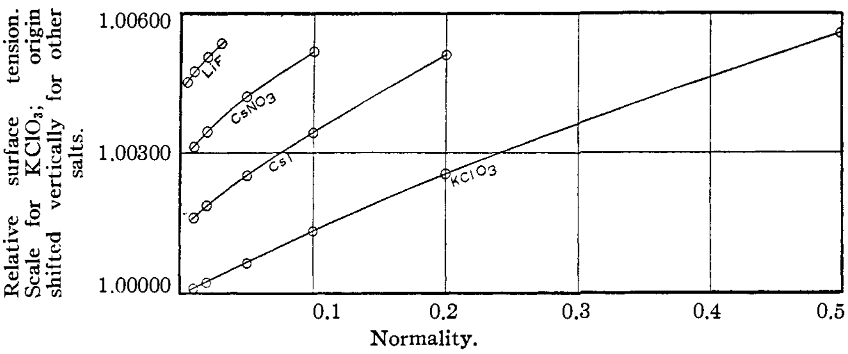

Fig. 2.

---

[13] The activity correction may be computed by the formula

$$\Delta\bar{\sigma} = k'E\left(\frac{c}{2} - k''\right) + \frac{k'k''H\sqrt{c}}{1 + B\sqrt{c}} + \frac{2k'H}{B^3}\left[\frac{1}{2(1 + B\sqrt{c})} - \frac{1 + B\sqrt{c}}{2} + \ln(1 + B\sqrt{c})\right]$$

which is algebraically equivalent to Dole's equation (11), but has a form which is easier to use in practical computations. The symbols are defined in Dole's paper. The symbol b which appears in Dole's equation (11) is a misprint for B.

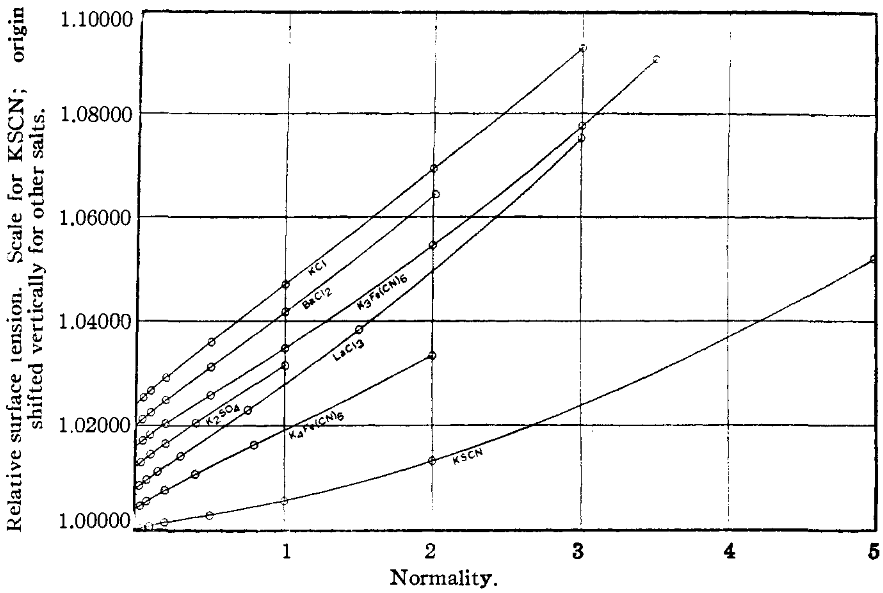

Fig. 3.

are not available, so that the results would not be really comparable. Moreover, the results so far obtained by this method of analysis are not sufficiently encouraging to justify the labor involved.

In Figs. 2 and 3 the values of the surface tension through the upper range of concentration are plotted as the ordinates against the normality of the solution, *i. e.*, the concentration divided by the valence of the polyvalent ion present, if any. In order to avoid confusion the origin for each salt is shifted vertically by 0.004%. Figures 2 and 3 differ in the scales used but both scales are altered proportionally so that the slopes on the two figures are comparable. The method of plotting against the normality was chosen instead of plotting against the concentration, c, or against $c(\nu_+ + \nu_-)$ because the use of the normality as the abscissa makes the slopes come out more nearly alike for the different salts. This fact may indicate that the forces which determine the surface tension in the upper range of concentration are mainly due to the electric charges on the ions. Surface tension is not a colligative property as required by Valson's rule.

Summary

1. The relative surface tensions of aqueous solutions of eight salts (barium chloride, lanthanum chloride, potassium chlorate, potassium thiocyanate, potassium ferricyanide, potassium ferrocyanide, cesium iodide and lithium fluoride) have been measured over a wide range of concentration at 25°.

2. Subject to a reservation discussed in the text, it is shown that these eight salts, like the three others previously studied, all cause a decrease in surface tension at extreme dilution and, therefore, according to the Gibbs theorem, must be positively adsorbed from very dilute solutions. It seems probable that all salts are "capillary-active" in sufficiently dilute solutions.

3. At moderate and high concentrations these salts all increase the surface tension and act like typical "capillary-inactive" salts.

4. The validity of the Onsager–Samaras and of the Dole equations for the variation of the surface tension with the concentration is discussed.

CAMBRIDGE, MASS. RECEIVED NOVEMBER 29, 1940