Thermodynamic Quantities of Surface Formation of Aqueous Electrolyte Solutions X. Aqueous Solution of 2:1 valence type salts

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Abstract

The behaviors of a series of calcium halides and of alkali earth metal chlorides in the air/water surface region were studied in comparison with those of alkali metal halides by measuring the surface tension increments of solutions. The effect of salts with divalent cation on the surface tension increments is pronounced than that of uni-univalent salts, but there are some similarities between these two types. It seems that the anions cause a marked effect on surface tension which is proportional to the magnitude of hydration in the bulk water. We also observed the decrease in the entropy change of surface formation with increasing concentration. The importance of electrical double layer at the surface was discussed in relation to these surface tension increments.

Key words: surface tension; electrolyte solutions; electrical double layer
Introduction

With few exceptions, the addition of ionic solute such as simple electrolytes into pure water would cause an increment in the surface tension ($\gamma$) of the solutions. Since this increment in $\gamma$ is a linear function of the concentration of solution ($m$), the value of the slope $d\gamma/dm$ of this linear relation have been used in an attempt to specify possible reasons that explain the observed individuality in the surface tension increments. There are two interesting points, i.e., finding a phenomenological rule for predicting the magnitude of $d\gamma/dm$ for the electrolytes of the same valence type and of different valence types, respectively. In an early review, Randles mentioned that ions of the same charge exhibit specific differences at high concentration region and there is a correlation with the lyotropic series [1]. In fact, theoretical considerations that an ion in a surface region is repelled from the surface will account for the difference in ion-water interaction [2, 3]. After the review of Randles, there is some unequivocal evidence that the hydration force of anions shows a significant effect on the increments of surface tension [4, 5]. Compared to anions, the hydration of cations appears to be less significant for the value of $d\gamma/dm$ in so far as the same valence type is concerned. However, the numerical values of $d\gamma/dm$ for 1:1 type electrolytes, evaluated from different kinds of measurements and different authors, involve considerable variation that are less satisfactory to explain a correlation with the hydration force of cations.

For high valence type electrolytes, as predicted by theory that Coulombic force may explain the surface tension increments, there seems to be no doubt that $d\gamma/dm$ of electrolytes with divalent and trivalent cation yield about twice and triple the magnitude
of that observed for univalent cation [6]. However, it is still uncertain whether their anion plays a significant effect on surface tension of solutions than cation or not.

In the last paper of this series, we have reported the experimental results of the effect of ammonium cations on the surface tension of solutions and emphasized the interactions between anions and cations in the electrical double layer [7]. This will inevitably lead to an increment of surface tension even though the concentration of ions in the surface region is limited. In this experimental work, then, we are intended to show how the forces between the ions of unsymmetrical valence type of salts influence the surface tension increments.

Materials and method

Calcium chloride (99.99%), calcium bromide (99.98%), Calcium iodide (99.95%), calcium nitrate (99%), barium chloride (99.999%), copper sulfate (99.995%), and nickel sulfate (99.99+%) are of Sigma-Aldrich and used without further purification. Water was doubly distilled from dilute alkaline permanganate solution. Surface tension was measured by the drop volume method which has proved useful through this series of measurements on the electrolyte solutions [7]. Measurements were made using glass dropping tips. The diameter of the tip was calibrated by measuring the surface tension of pure water 71.96 mN m\(^{-1}\) at 25 °C. The densities of aqueous solutions were measured using a vibrating tube density meter (Anton Paar DMA 60-602). The precision of the evaluated surface tension data was better than 0.05 mN m\(^{-1}\).
Results and discussion

The surface tensions of aqueous solutions of CaCl$_2$, CaBr$_2$, CaI$_2$, and Ca(NO$_3$)$_2$ were measured in the concentration range from 0 to 1 mol kg$^{-1}$, except CaBr$_2$ (0 to 0.33), and at temperatures ranging from 15 to 35°C. In addition, $\gamma$-versus-$m$ relations of the aqueous solution of BaCl$_2$, CuSO$_4$, and NiSO$_4$ were obtained at 25°C up to 1 mol kg$^{-1}$. In Fig. 1 and 2, we have plotted $\gamma$ against $m$ and $T$, respectively, for calcium chloride to show that $\gamma$-versus-$T$ and $\gamma$-versus-$m$ relations are satisfactorily represented by straight lines as well as those of uni-univalent salts. Table 1 shows the coefficients of the regression lines,

$$\gamma = \gamma^0 + \left(\frac{d\gamma}{dm}\right)_{T,P} m,$$

(1)

and the standard error of the estimate of $\gamma$ on $m$ for aqueous solutions of these salts, respectively.
Figure 1. Surface tension of calcium chloride solutions as a function of concentration. Temperatures of solutions are, from bottom to top, 35.0, 32.5, 30.0, 27.5, 25.0, 22.5, 20.0, 17.5, and 15.0 °C, respectively.

Figure 2. Surface tension of calcium chloride solutions as a function of Temperature. The concentration of solutions are, from bottom to top, \( m = 0.0, 0.117, 0.196, 0.279, 0.387, 0.472, 0.597, 0.685, 0.757, 0.908, 0.989 \) mol kg\(^{-1}\), respectively.

From the beginning of the study of the surface of simple salt solutions, numerical values of \((d\gamma /dm)\) has been used as an empirical parameter characteristic of each salt or group of salts. The value roughly 1.5 mN m\(^{-1}\) mol\(^{-1}\) Kg of \((d\gamma /dm)\) is common for
uni-univalent electrolytes, and about twice of this value is generally adapted for salts of
divalent cations [6]. Early works are reviewed by Randles, who described the Onsager
and Samaras' image force theory, and summarized that equivalent concentrations of
many different salts of the same valence type gave almost identical increments of
surface tension at sufficiently low concentration region [1]. He also noticed that as the
concentration increases, ions of the same charge exhibit specific differences and there is
a correlation with the lyotropic series. This outline of the surface properties of solutions
of electrolytes have been reported repeatedly [8-10]. Most of them are argued using a
limited number of salts, but Weissenborn and Pugh measured a large number of salts
such as chloride, sulfates, and nitrates. They suggested that the cations of different
valence types which are strongly hydrated have high values of $d\gamma/dm$ and the magnitude
being dependent on the extent of hydration. Our results for the bi-univalent salt
solutions show certainly larger values than those of uni-univalent salt solutions.
However, it is a matter of our primary concern to ascertain whether the extent of
hydration of 2:1 electrolytes affect on the surface tension increments in a similar
manner observed for 1:1 electrolytes.

Comprehensive investigations of the effect of salts on the surface tension were
mainly developed on uni-univalent salts. Johansson and Eriksson pointed out that
specific anion effects are to a large extent decisive for the surface tension increments [8].
In the previous reports for alkali metal chloride [11] and sodium halides solutions [12],
we have confirmed this pronounced effect of anions by plotting the $d\gamma/dm$ against
hydration enthalpy $\Delta H_h$. For the purpose of illustrating the similarity and difference
between 1:1 and 2:1 type electrolytes, these plots are reproduced in Fig. 3 together with
those for 2:1 type given in Table 1. The values of $\Delta H_h$ were taken from the textbook by Marcus [13]. We note immediately the similarity in nature of the curves. The order of magnitude of the anion contribution is the same order as indicated by their magnitude of hydration, Cl$^-$ > Br$^-$ > NO$_3^-$ > I$^-$, and the cation contribution appears less pronounced than the anion.

Figure 3. Plot of $d\gamma/dm$ against enthalpy of hydration for uni-univalent (upper) and di-univalent (lower) electrolytes at 25 °C.
Fig. 3 illustrates one more interesting point. The slopes of lines of \( \frac{d\gamma}{dm} \) versus \( \Delta H_h \) for calcium and sodium halides, respectively, appear to be roughly the same, but the line connecting the former salts cannot be extrapolated to that of the latter salts. Then, before proceeding to more detailed consideration of 2:1 type, let us outline the influence of valence type upon surface tension increments. In Fig. 4, a number of salts of different valence types are plotted against the \( \Delta H_h \) in order to visually recognize how the extent of hydration affect upon the surface tension increments. It appears that each electrolyte spreads out across the entire graph and exhibits pronounced individual differences, corresponding to the valence type. This figure illustrates three important points. First, the symmetrical valence type shows roughly the same magnitude, but smaller than unsymmetrical 2:1 and 1:2 types. Considering that the anions have a decisive effect on the increment of surface tension, the difference in magnitude of \( \frac{d\gamma}{dm} \) between 1:2 type sulfates and 2:2 type sulfates seems to be remarkable. Second, the 2:1 and 1:2 type salts show nearly the same magnitude even though their anions are very different each other. Finally, it seems difficult to show a simple line on this graph which describes a single factor corresponding to the magnitude of surface tension increment. However, the above three feature suggests the possibility that an interesting view on the surface tension increments will be found if we use the total number of moles of ions \( \hat{m} \) instead of the total number of moles of a salt \( m \). Indeed, when Fig. 4 is reconstructed using \( \frac{d\gamma}{d\hat{m}} \) as the vertical axis, each valence types group is arranged parallel to the abscissa. It seems probable from this relationship that the apparent increments in surface tension of electrolyte solution depend primarily upon the number of ions in the solution irrespective to the signs and magnitudes of charges. This outline about valence types
indicates that the use of Fig. 3 has advantage in considering the relationship between hydration and the specific increments of surface tension of a salt.

Figure 4. Comparison of the spectrum of (a) $\frac{d\gamma}{dm}$ and (b) $\frac{d\gamma}{d\dot{m}}$ of symmetrical valence types with those of unsymmetrical valence types at 25 °C. Salts labeled "1:1" and "2:1" are the same shown in Fig. 3. 1:2 type salts are Cs$_2$SO$_4$, K$_2$SO$_4$, Na$_2$SO$_4$, and Li$_2$SO$_4$ [14] from left to right, respectively. 2:2 type salts are MgSO$_4$ [14], CuSO$_4$, and NiSO$_4$ from bottom to top, respectively.

We again consider the curves shown in Fig. 3. We first note that the additivity rule observed for alkali metal halides will not be expanded to include halide ions of alkali
earth metal halides. For example, the difference in $d\gamma/dm$ between NaCl and NaI is 0.46, while that of CaCl$_2$ and CaI$_2$ is 0.71, respectively. Further, it seems probable that the $d\gamma/dm$ observed for alkaline earth metal halides is no more an additive property of the individual ions, because observed difference of 0.61 between CaCl$_2$ and Ca(NO$_3$)$_2$ is much smaller that of 1.11 between MgCl$_2$ and Mg(NO$_3$)$_2$. Secondly, the ability of divalent cations to effectively increase the surface tension is in the same order as indicated by their magnitude of hydration, Mg$^{2+}$ > Ca$^{2+}$ > Ba$^{2+}$. This order may be a specific behavior for alkaline earth chlorides of the 2:1 type, since the alkali metal chlorides are arranged in the reverse order to the hydration, Cs$^+$ > K$^+$ > Na$^+$ > Li$^+$. The most notable is the large spread of the points for divalent cations compared to the plotted points of univalent cations of 1:1 alkali metal chloride. Since the specific contribution to the $d\gamma/dm$ of 1:2 type alkali metal sulfates due to univalent cation appears to be explicitly present to a considerable magnitude, it may be necessary to consider the effect of asymmetry in charge on the surface tension increments.

According to a series of thermodynamic studies on adsorption at interfaces given by Motomura [15], variation in $\gamma$ for aqueous salt solution of a strong electrolyte which dissociates into $v_+$ cations and $v_-$ anions is given as a function of $T$, $p$ and $m$;

$$d\gamma = -\Delta s dT + \Delta v dp - \frac{(v_+ + v_-)RT\Gamma_{H}}{m} \left[ 1 + \left( \frac{\partial \ln f_{\pm}}{\partial \ln m} \right)_{T,p} \right] dm$$

where $\Delta s$ and $\Delta v$ referred to as the entropy and volume of surface formation, respectively, $\Gamma_{H}$ is the surface density of salt, and $f_{\pm}$ is the mean activity coefficient of the salt. For a salt which dissociate into $(v_+ + v_-)$ ions, total number of moles of
ions on molality scale and total number of moles of ions on surface excess scale are given
\[
\hat{m} = (\nu_+ + \nu_-)m = m_+ + m_-
\] (3)
and
\[
\hat{\Gamma}^H = (\nu_+ + \nu_-)\Gamma^H = \Gamma^H_+ + \Gamma^H_-,
\] (4)
respectively [16]. On substitution of these relation in Eq. 2,
\[
d\gamma = -\Delta s dT + \Delta v d\rho - RT \frac{\hat{\Gamma}^H}{\hat{m}} \left[ 1 + \frac{d \ln f_2}{d \ln \hat{m}} \right]_p d\hat{m} \] (5)
is obtained. Here \(\hat{\Gamma}^H/\hat{m}\) represents the hydrophilic properties of a salt, which satisfy the following equalities.
\[
\frac{\hat{\Gamma}^H}{\hat{m}} = \frac{\Gamma^H_+ + \Gamma^H_-}{m_+ + m_-} = \frac{\Gamma^H_+}{m_+} = \frac{\Gamma^H_-}{m_-} = \frac{\Gamma^H}{m}.
\] (6)
Fortunately, numerical values of this ratio at infinite dilution can be used to evaluate the hydrophilic properties of ions and salts as a kind of partition coefficient between surface and bulk solution, since it is possible to assume that the surface tension of solution can be extrapolated linearly to the dilute solution where the Kohrausch law is applicable. If we substitute molality in \(\Gamma^H/m\) by molarity, we can use label nm without change in ordinate scale within an acceptable error range. The magnitude of the 1:1, 1:2, 2:1, and 2:2 type salts are compared in Fig. 5, in which all salts are plotted in the range of 0.2 to 0.4 \(\mu\)kg m\(^{-2}\). Since plots are made using minus \(\Gamma^H/m\), the uppermost plot MgCl\(_2\) represents its remarkable hydrophilic behavior while the lowermost plot in the figure shows that the NaI is the most surface active among the salt shown in this figure. In comparing symmetric with unsymmetric valence type, this figure suffices to show that
the anions of former type are the major factor which causes the variation $\Gamma^{H}/m$ but both the anions and cations are important in the latter case.

![Figure 5](image)

Figure 5. Comparison of the surface activity of 1:1, 1:2, 2:1, and 2:2 valence type salts at 25 °C. The labels and units of these 4 axis are $-(\Gamma^{H}/m)/\mu\text{kg m}^{-2}$, respectively. Previously reported surface tension data used in this figure are taken from the references sodium halides [11, 12], sulfates [14], nitrates [17], and ammonium salts [7], respectively.

Figure 5 can be used to compare the adsorption of specific ions from different salt solutions, since we have the equalities shown in Eq. (6). When we suppose that vertical scale represents the value of $-\Gamma^{H}/m_{\text{Cl}^-}$, chlorine anion concentration at the surface which is in equilibrium with that in sodium chloride solution is pronounced than that which is in equilibrium with that in alkaline earth metal chloride solutions. The specific dependence of $\Gamma^{H}/m_+$ and $\Gamma^{H}/m_-$ upon ion pair is evident when we compare them in different salt solutions. Thermodynamics provides no explanation to satisfy our interest, but we suppose that the formation of double layer restricts free movement of ions in the surface region.
Figure 6. Entropy of surface formation of calcium chloride and calcium iodide solutions at 25°C.

The formation of electrical double layer in the surface region is always accompanied by the decrease in $\Delta s$ [18]. For sodium halides, the order of magnitude of this decrease is in the order NaI > NaBr > NaCl > NaF, and this lowering is greater the smaller the magnitude of $d\gamma/dm$ [12]. We suppose that the higher the amount of ions in the surface region, the larger the lowering in $\Delta s$. As shown in Fig. 5, the value of -0.38 for $\Gamma^H/m$ of CaCl₂ which is much smaller than that of -0.28 for CaI₂ indicate that calcium chloride is much more hydrophilic than calcium iodide. In comparing $\Gamma^H/m$ values of NaF (-0.36) and of CaCl₂ (-0.38), then it will be expected that the amount of calcium chloride in the surface region is too small to lead to the formation of double layer accompanying remarkable lowering in $\Delta s$. Figure 6 shows the plots of $\Delta s$ for CaCl₂ and CaI₂ calculated by using Eq. (2) and it is apparent that the $\Delta s$ for CaCl₂ decreases as same as for CaI₂ in contrary to our expectation. The $\Delta s$ versus $m$ relation
for MgCl₂ (-0.41) shows also a remarkable lowering in Δs [19]. We assume that this observation is the characteristic behavior of the salts of simple unsymmetrical valence type.

**Conclusion**

From consideration of the difference of valence type, it is possible to ascribe the surface tension increment to the total number of ions in solution irrespective of the signs and number of the valences. However, this result leads to only a rough indication of the surface tension increment caused by a salt, and it is important to note that the specific contributions of anions and cations in the surface region are clearly observed when we consider a group of salts of a given valence type. For a group of 2:1 type salts, characteristic contribution of cations is found, while significance of anions and their magnitude of hydration are clearly observed as has been reported for 1:1 type salts. In comparing salts of unsymmetrical valence type with those of symmetrical type, experimental results lead to the conclusion that we are not inclined to ascribe the surface tension increments to the interaction of ions to the solvent only. Interaction of ions of unsymmetrical valence type in the surface region is more remarkable than that of ions of symmetrical type.
REFERENCES


