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<td>Author(s)</td>
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Thermodynamic Quantities of Surface Formation of Aqueous Electrolyte Solutions VIII. Aqueous Solutions of Sulfates Salts.

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We measured here surface tension of the aqueous solutions of alkali metal sulfate, magnesium sulfate, and magnesium nitrate with an expectation that the effect of sulfate salts on the air/water surface differs from that of typical electrolyte because of their peculiar results of surface potential data. The results show that the slope of surface tension – concentration curves of sulfate salts depends to some extent upon cations while that of alkali metal nitrate gives almost the same magnitude. In order to make comparison with salts of different valence types, we used the ratio of surface excess density to bulk concentration of a salt as an index of surface activity of the salt. It was shown that the surface activity of a salt largely dependent upon its valence type as well as its specific property of anion.

Key words: surface tension; electrolytes
INTRODUCTION

According to a series of thermodynamic studies on the adsorption at interfaces given by Motomura et al. [1, 2], the change in the surface tension (γ) of an aqueous solution of electrolyte which dissociates completely into ν⁺ cations and ν⁻ anions is given as a function of temperature (T), pressure (p) and concentration (m) so that

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

where \( \Delta s \) and \( \Delta v \) are the entropy and the volume of surface formation, and \( f_\pm \) is the mean activity coefficient. Here, \( \Gamma^H \) is the surface excess density of the electrolyte and there are equalities that

\[ \Gamma^H = \Gamma^H_+/\nu_+ = \Gamma^H_-/\nu_- . \]

The subscripts + and – refer to ionic constituents cations and anions, respectively. At constant temperature and pressure, the surface tension of an electrolyte solution usually increases linearly with concentration corresponding to the negative value of \( \Gamma^H \). This change in \( \gamma \) with \( m \) is primarily dependent on the valence types but characteristic of each electrolyte. For 1 : 1 type sodium salts, we can see that the plots of \( d\gamma/dm \) against the enthalpy change, corresponding to the transfer of ions from gas phase to the solution [3], lie on a single curve and that the magnitude of \( d\gamma/dm \) is remarkable for the salts with highly hydrophilic anions [4]. It can be seen, however, that in a series of salts with common anion the relationship between \( d\gamma/dm \) and the enthalpy change of hydration differ in magnitude and tendency from those of the salts with common cation. Indeed, each of alkali metal nitrates shows nearly the same value of \( d\gamma/dm \) [5]. By means of the surface potential measurement for simple electrolyte solutions, Jarvis and Scheiman also pointed out that the anions primarily determine the sign and the magnitude of the
potential [6]. They suggested that there is a preferential accumulation of anions at the surface and the cations are attracted by this layer of anions. The agreement between the results of two different methods indicates that the difference in the significance of anions and cations is caused by the same surface phenomena which accompany the formation of electrical double layer at the surface. From these considerations, it is clear that, although the relation between the magnitude of $\gamma'/dm$ and the enthalpy of hydration of salts seems to be related to satisfactory a figure of specificity of 1:1 electrolytes, we have to extend the discussion thermodynamically to include the possible interactions of ions and water in the double layer.

Surface potential values of a series of sodium salts reported by Jarvis and Scheiman [6] decreased in the order $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{Br}^- > \text{I}^-$. The same trend was reported for salts of magnesium as $\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$. They reported that sulfate ion, whose energy of hydration is most remarkable among these ions, gave the highest and positive surface potential while the other ions reveal negative potential. The surface tension of the aqueous solution of sulfate salts has been given repeatedly. However, we believe that the data are insufficient to confirm the peculiar behavior of sulfate salts, because we have yet to specify how the valence type of salts acts upon the changes in the surface tension of solution. In order to develop our study to the salts of multivalent ions, we are now inclined to study the aqueous solution of sulfate salts whose surface potential is inverted with the chloride or nitrate.

MATERIALS AND METHOD
Lithium sulfate (Sigma), potassium sulfate (Sigma), cesium sulfate (Alfa Aesar), magnesium sulfate heptahydrate (Sigma), and magnesium nitrate hexahydrate (Sigma) were of purity of >99.99% 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 been used through this series of measurements on the electrolyte solutions. Measurements were made using glass dropping tips. The diameter of the tip was calibrated by measuring the surface tension of pure water at 25 °C, 71.96 mN m⁻¹. 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 tension of aqueous solutions of Li₂SO₄, K₂SO₄, Cs₂SO₄, Mg(NO₃)₂, and MgSO₄ were measured in the temperature range of 15 to 35 °C at 2.5 °C intervals and concentration range of 0 to 1 mol kg⁻¹ except K₂SO₄ and Mg(NO₃)₂. For potassium sulfate of low solubility, measurements were made up to 0.6 mol kg⁻¹. For the aqueous solution of magnesium nitrate the surface tension was measured only at 25 °C. Under our experimental conditions, the γ-versus-T plots can be represented by linear plots. Figure 1 shows examples of such plots for the aqueous solutions of lithium sulfate observed at fixed concentrations. The all linear plots appear to be nearly parallel in the figure, since the change in the magnitude of the slopes of these γ-versus-T plots are very limited. For a large number of salts, the γ-versus-m plots can be represented accurately by a linear relation. Table 1 shows the coefficients of the regression lines,
\[ \gamma = \gamma^0 + \left( \frac{d\gamma}{dm} \right)_{T,P} m, \]  

(2)

and the standard error of the estimate of \( \gamma \) on \( m \) for aqueous solutions of \( \text{Li}_2\text{SO}_4, \text{K}_2\text{SO}_4, \text{Cs}_2\text{SO}_4, \text{MgSO}_4, \) and \( \text{Mg(NO}_3)_2 \) respectively.

Since the experimentally determined \( \gamma \)-versus-\( m \) relations for solutions containing a single electrolyte can be practically represented by a straight line, the magnitude of \( d\gamma / dm \) has been conveniently treated as an empirical parameter in the discussion of the specific properties of ions or salts. Each salt has a characteristic value of this parameter which depends on temperature. In Fig. 2, we have plotted the magnitude of \( d\gamma / dm \) against temperature. In general, the curve for a solution of a single electrolyte increases with increasing temperature and is concave upward. Exceptional examples are found in systems containing mixtures of ions of incompletely dissociated electrolyte such as aqueous solution of sodium carbonate and in the system of two simple salts mixtures such as sodium chloride and sodium iodide, where the value of \( d\gamma / dm \) decreases with increasing temperature [7]. By means of these facts, we are able to remark that the curves with positive slope shown in Fig. 2 represent a characteristic manner of a single salt solution free from inorganic contaminations. These curves show another two characteristic aspects of sulfate salts. First, there is no relationship between the magnitude of \( d\gamma / dm \) and the position the metal occupies in the periodic table. Secondly, there are large spaces between the curves on the figure when we compared with those of nitrate or chloride salts [5, 7]. As shown in the figure, the difference between \( \text{Na}_2\text{SO}_4 \) and \( \text{Cs}_2\text{SO}_4 \) is 0.58 mN m\(^{-1}\) mol Kg\(^{-1}\), while we observed only 0.18 mN m\(^{-1}\) mol kg\(^{-1}\) between \( \text{LiCl} \) and \( \text{CsCl} \) [8]. Further, the values for \( \text{LiNO}_3, \text{NaNO}_3, \) and \( \text{KNO}_3 \) are given as 1.14, 1.13, and 1.10 mN m\(^{-1}\) mol Kg\(^{-1}\), respectively [5]. It seems
likely that the remarkable dependence of \( \frac{d\gamma}{dm} \) upon cations will prove to be in agreement with the results of the surface potential measurements obtained by Jarvis and Scheman [6]. They have shown that the changes in surface potential with concentration for \( \text{Na}_2\text{SO}_4 \) are positive, while those for chloride or nitrate are negative.

The magnitude of \( \frac{d\gamma}{dm} \) of alkali metal sulfate is larger than that of chlorides or nitrates. For magnesium salts, however, it decreases in the order \( \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-} \), in contrast to the decreasing order of surface potential \( \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- \). The magnitude of magnesium sulfate \( 1.67 \text{ mN m}^{-1} \text{ mol Kg}^{-1} \) is nearly identical to that of \( 1:1 \) alkali metal chlorides and is almost half of that of magnesium chloride [8]. There is no adequate explanation by which this small value of magnesium sulfate may be predicted.

When a simple electrolyte constituted of cations and anions is dissolved in pure water, parts of the ions adsorb at the air/water surface and the electrical double layer is formed by these ions depending on their affinity to the surface. At the beginning of the study of the adsorption of surface active molecules at the solution surfaces, the slope of the surface tension against concentration at infinite dilution was used as a quantitative measure of the surface activity of each solute [10, 11]. We believe that this idea would presumably apply to the adsorption of ions as well, as noted in our previous report [4]. Further we have shown that the magnitude of \( \Gamma^{\text{H}}/m \) helps us more adequately for expressing the surface activity than \( \frac{d\gamma}{dm} \) itself, because it is a kind of partition coefficient of the electrolytes between surface region and bulk solution. It is a constant at the fixed temperature and pressure for the dilute solutions where the activity coefficient can be assumed to be unity, and is a characteristic property for individual salt. For a salt which dissociate \( \nu_+ \) cations and \( \nu_- \) anions, the \( \Gamma^{\text{H}}/m \) is given as
\[
\frac{\Gamma^\text{II}}{m} = \frac{-1}{RT\left(v_+ + v_-\right)} \left(\frac{d\gamma}{dm}\right)_{T,p} \sqrt{1 + \left(\frac{\partial \ln f_+}{\partial \ln m}\right)_{T,p}}.
\]

Since we expect the electroneutrality in both the surface region and bulk solution, there are equalities,

\[
\frac{\Gamma^\text{II}}{m} = \frac{\Gamma^\text{II}_+}{m_+} = \frac{\Gamma^\text{II}_-}{m_-} = \frac{\Gamma^\text{II}_+ + \Gamma^\text{II}_-}{m_+ + m_-}.
\]

The magnitude of this ratio at infinite dilution provides information about the difference in the hydrophilic property of a salt between surface and bulk solution; that is a numerical index of the surface activity of solute species. For alkali metal sulfate, the comparison is illustrated graphically in Fig. 3, where the activity coefficients necessary to apply Eq. (3) are obtained from the textbook of Robinson and Stokes [12]. There are sharp decreases in the activity coefficients of these salts at low concentration range of this figure but the data are limited for accurate evaluation of the change in the slope, it must be noted that the calculations of the plots at low concentrations such as 0.1 mol kg\(^{-1}\) include more than 10% of error. At zero concentration we can not evaluate the surface activity values by the left side of Eq. (3), but right hand side of this equation provide the value as an extrapolated one to zero concentration. Since we have plotted minus \(\Gamma^\text{II}/m\) on the vertical axis, a curve with a positive slope shows that the surface activity of the salt decreases with increasing concentration and with increasing ion-ion interaction in the bulk solution. Evidently the plots for Cs\(_2\)SO\(_4\) increase progressively at low concentration above that for other salts, suggesting that the surface activity is less important than others. At higher concentration region of this figure, the surface activity increases in the order Cs\(_2\)SO\(_4\) < K\(_2\)SO\(_4\) < Na\(_2\)SO\(_4\) < Li\(_2\)SO\(_4\) in a similar manner observed for alkali metal nitrates and chlorides.
The surface activity of MgSO₄, MgCl₂, and Mg(NO₃)₂ have been evaluated by Eq. (3) and their values are plotted against concentration in Fig. 4. The plots increase sharply at low concentrations in the figure as the activity coefficient of the salts steeply decreases, passes through a maximum at about 0.2 mol kg⁻¹, and decreases gradually with concentration. Since the drops in the activity coefficient of 2:2 electrolytes are larger than that of 1:2 electrolytes, the increases of the plots of magnesium sulfate solutions are remarkable. These observations indicate that the surface activity of magnesium salts increases in the order SO₄²⁻ < Cl⁻ < NO₃⁻ at higher concentration range of the figure in agreement with the results of surface potential measurements. The sulfate ions are much hydrophilic than chloride ions at the concentration range in which the surface potentials of the solution have been measured. These considerations can be equally made by using the plot of ΓⅢ against concentration, but surface activity defined by Eq. (3) has advantages for the comparison of salts of different valence types. This can be easily shown by considering Eq. (4) for a salt of each valence type. If we define the ionic strength or mean molality of a salt in the surface region and take the ratio of it to that of the bulk, the numerical value will be equal to the ratio of ΓⅢ to m. The surface activity extrapolated to zero concentration can be used as one of the parameters to estimate the affinity of ions or salts to the surface.

It will be of interest to compare the surface activity of 1:2, 2:1, and 2:2 electrolytes reported here with that of 1:1 alkali metal halides. In order to compare the surface activity of these salts graphically, limiting values of −ΓⅢ/m at zero concentration are plotted on the vertical axes of Fig. 5. On the middle axis, the values of 1:1 electrolytes have plotted for comparison but those of alkali metal chlorides and nitrates except
sodium salts are not shown to avoid overlapping with sodium chloride and sodium nitrate. The first plot from the bottom shows that sodium iodide is the most hydrophobic one among the plotted salts. The most hydrophilic salt is magnesium chloride, but the magnesium sulfate is much hydrophilic one at higher concentration as shown in Fig. 4. The pronounced variation observed in the values of sulfate salts is illustrated graphically on the left side axis but there is no way to confirm if this cation-dependent property is a peculiar one for sulfate salts or general property of 1:2 electrolytes. The magnesium nitrate and chloride are more hydrophilic than corresponding sodium salts, and the difference in surface activity between magnesium nitrate and chloride is much larger than that of sodium salts. It seems likely that sulfate salts and magnesium salts are more hydrophilic than 1:1 salt, but the behavior of magnesium sulfate is similar with 1:1 salt. In spite of the limitation of the experimental data, it should be remarked at this point that the surface activity of a salt largely dependent upon its valence type rather than its specific property of anion.

In studying the entropy change of surface formation of 1:1 electrolyte, we have noted that the negative slope of the $\Delta s$ versus $m$ curves decreases in the order NaI > NaBr > NaCl > NaF which is in the reverse order to the hydrophilic property of the salts [7]. For sodium nitrate we also observed a clear decrease in the $\Delta s$ with increasing bulk concentration, since the surface activity of NaNO$_3$ is intermediate in magnitude between that of NaBr and NaI. The decrease in the $\Delta s$ of sulfate salts is of the same order as that observed for sodium nitrate, but it is difficult to arrange them in the order of the magnitude because of the overlapped plots of them. For this reason, the slope of $\Delta s$ versus $m$ plots is evaluated by the relation
\[
\frac{d}{dT} \frac{d\gamma}{dm_s} = \frac{d}{dm_s} \frac{d\gamma}{dT} = -\frac{d}{dm_s} \Delta s. \tag{5}
\]

The values of \(d(\Delta s)/dm\) for Li_2SO_4, Na_2SO_4, K_2SO_4, and Cs_2SO_4 evaluated from the slope of plots illustrated in Fig. 3 are -0.0072, -0.011, -0.011, and -0.028, respectively. It is evident that there is no relationship between these values and surface activity of 1:2 sulfate salts. The value -0.013 is obtained for magnesium sulfate. This value is much larger than that of lithium sulfate whose surface activity is nearly the same with that of magnesium sulfate.

The above considerations about the surface activity of salts lead to the conclusion that the sulfate salts are less hydrophobic than nitrate salts and show same order of magnitude as chloride salts. If we assume the effect of charge number of the ions cancel between numerator and denominator of Eq. (4), the distinctions and similarities in surface activity between salts of different valence type may be explained by the structure of electrical double layer formed in the surface region.
REFERENCES


FIGURE READINGS

Figure 1. Surface tension of lithium sulfate solutions as a function of temperature. Molalities of solutions are, from bottom to top, 0.0, 0.101, 0.257, 0.424, 0.511, 0.634, 0.759, 0.900, and 1.00 mol kg\textsuperscript{-1}, respectively.

Figure 2. The \( \frac{d\gamma}{dm} \) of alkali metal sulfates, magnesium sulfate, and magnesium chloride as a function of temperature.

Figure 3. The surface activity of alkali metal sulfates as a function of concentration at 25 °C.

Figure 4. The surface activity of magnesium chloride, magnesium sulfate, and magnesium nitrate as a function of concentration at 25°C.

Figure 5. Comparison of the surface activity of 1:1, 2:1, 1:2, and 2:2 electrolytes. The unit of horizontal scales are \( -\left( \Gamma^H/m \right) / \mu\text{kg m}^{-2} \), respectively.
Figure 1.
Figure 2.
Figure 3.
Figure 4.
Figure 5.
### TABLE 1

Coefficients of the regression lines and standard error of estimate of $\gamma$ on $m$ (SE)

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Mg(NO$_3$)$_2$

| 25.0 | 71.94 | 1.95    | 0.022         |