

NRL Report 6583

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Surface Potentials of Aqueous Electrolyte Solutions

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Surface Potentials of Aqueous Electrolyte Solutions

N. L. JARVIS AND M. A. SCHEIMAN

*Surface Chemistry Branch
Chemistry Division*

October 10, 1967



**NAVAL RESEARCH LABORATORY
Washington, D.C.**

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ABSTRACT

The effect of added electrolytes on the surface potential of water was determined using the radioactive electrode technique. Changes in surface potential, ΔV , were found to vary from +64 mV for Na_2SO_4 at 1.8m to -180 mV for NaCNS at 7.5m. The Group IA chlorides in water gave surface potential differences that decreased in the order $\text{K}^+ = \text{NH}_4^+ > \text{Na}^+ > \text{Li}^+$, and the surface potentials of the Group IIA cations decreased in the order $\text{Ba}^{++} > \text{Sr}^{++} > \text{Mg}^{++}$. At a constant anion concentration of 2m the surface potential differences due to the sodium salts were in the order $\text{SO}_4^- > \text{CO}_3^- > \text{CH}_3\text{COO}^- > \text{Cl}^- > \text{NO}_3^- > \text{Br}^- > \text{I}^- > \text{CNS}^-$. In general the anion with the smaller hydration energy gave the greatest decrease in surface potential. The magnitude of each surface potential change, however, does not appear to be a simple function of the hydration energy or of some related property. The surface potential changes must involve the orientation and structure of the water molecules at the water/air interface, which may be only partially dependent upon the ionic properties as determined in bulk solution.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

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SURFACE POTENTIALS OF AQUEOUS ELECTROLYTE SOLUTIONS

INTRODUCTION

The presence of dissolved inorganic electrolytes can have a marked influence on both the surface tension (1,2) and surface potential (3-5) of water. The effect of inorganic salts on surface tension has received considerable attention, but little has been published regarding changes in surface potential with salt concentration. The surface tension of an aqueous electrolyte solution is known to increase linearly with concentration, except perhaps at very low concentrations, where Jones and Ray (1) reported an apparent surface tension minimum. As was pointed out by Langmuir (6), on the basis of the Gibbs adsorption equation, the increase in surface tension indicates a deficiency of solute in the surface layer. Langmuir concluded that a layer of pure solvent about 4Å thick will be present at the surface of a KCl solution. Subsequent calculations by Goard (7) and Harkins and coworkers (8,9) substantiated this value and further indicated that for chlorides of the Group IA cations the thickness of this pure solvent layer will decrease from 5Å for 0.1M solutions to almost 3Å for 2M solutions.

Wagner (10), Onsager and Samaras (11), and Schmutzer (12) attempted theoretical explanations of the negative surface excess based on the presence of an "image force" near the boundary between the two dielectrics, water and air. The results were found to be in approximate agreement with experimental data for some 1:1 electrolytes and gave a calculated 4.1Å-thick solute-free layer at the surface of a 0.02M solution. It was assumed in their analyses that different univalent salts, added in equivalent amounts, caused about the same increase in surface tension. Experimental evidence, however, shows that significant differences do exist between the surface tensions of many 1:1 electrolytes, particularly at higher solution concentrations. No theory has been proposed that will satisfactorily explain these differences or predict the surface tensions of aqueous solutions of multivalent ions.

The surface potential values reported to date for electrolyte solutions (3-5) are generally in poor agreement. The data of Frumkin (3) and Randles (5), however, do agree that the surface potentials of a series of anions decrease, i.e., become more negative, in the order $F^- > Cl^- > Br^- > NO_3^- > I^- > ClO_4^- > CNS^- > PF_6^-$. The specific properties of the anions responsible for these changes in potential of the water/air interface have not been clearly established. Haydon (13) suggested that the most acceptable general explanation for these results must be based on a consideration of the water structure, as influenced by the ions and the proximity of the interface. This must include a contribution due to the oriented solvent dipoles as well as to any electrokinetic potential established at the interface. To this end Randles (5) noted a correlation between the magnitude of the surface potential difference and the "real" hydration energies of the cation and anion. Randles further attempted a quantitative explanation of his surface potential data, but he found very poor agreement between his theory and the experimental results. Because of the complexity of an aqueous interface, an accurate prediction of the surface potentials of electrolyte solutions will indeed be difficult to achieve.

In addition to the difficulty inherent in interpreting surface potential data, several questions have been raised (4,14) regarding the surface potential method used by Frumkin and Randles. The method they employed was essentially that of Kenrick (15), which measures the potential difference between two flowing liquid surfaces. Randles had the aqueous electrolyte solution flow down the inner surface of a glass tube while the

reference liquid, 1M NaCl, flowed from a fine glass tip, in the form of a jet, down the axis of the tube. In the present study the surface potentials of a variety of inorganic electrolytes were measured by the ionizing electrode method, similar to that proposed by Guyot (16). These results are compared with the previous data of Frumkin and Randles.

EXPERIMENTAL DETAILS

The ionizing electrode used in this study consisted of a series of thin polonium 210 strips attached to the face of a 2 in. by 2 in. brass plate. The electrode was mounted approximately 1 cm above the substrate liquid. A calomel electrode with a saturated KCl salt bridge was used as the reference electrode in the substrate. The sensitivity of the experimental apparatus was better than ± 1 mV. With the exception of NaI and NaCNS the salts used in this investigation were all Reagent Grade chemicals. NaCl, NaNO₃, Na₂SO₄, KCl, KI, NH₄Cl, and MgCl₂ were from the Baker Chemical Company; NaBr, Na(C₂H₃O₂), LiCl, MgSO₄, (NH₄)₂SO₄, BaCl₂, SrCl₂, Mg(NO₃)₂, and Ca(NO₃)₂ were from the Fisher Scientific Company. The NaI was U.S.P. Grade from Fisher, and NaCNS was C.P. Grade from Baker Chemical. All solutions of these salts were prepared in triply distilled water, the final two distillations being from an all-quartz apparatus. For the distilled water the pH was normally between 5.6 and 5.8. The pH values of the ionic solutions were not determined as functions of concentration.

The salt solutions were poured into shallow glass dishes and placed beneath the polonium electrode. The dishes were 1.8 cm deep and 16 cm in diameter, and the edges were lightly coated with paraffin to make them hydrophobic. A small Teflon-coated magnetic stirring bar was placed in the bottom of each dish to assure a uniform solution concentration. The primary difficulty encountered in making the surface potential measurements was the rather large amount of surface-active organic contamination that was present in almost all of the salts. Several procedures were used in an attempt to remove this contamination. Aqueous solutions of several of the electrolytes were percolated through Pyrex adsorption columns containing activated adsorbents such as Florisil or charcoal. The salts NaI, NaBr, and LiCl were recrystallized several times prior to use. Some of the salts such as NaCl were heated in a furnace to near their melting points to remove the trace organic matter. Each of these procedures was only partially successful.

It was finally determined that the surface-active contaminants could best be controlled by surface chemical techniques. Saturated solutions of the salts were prepared, and the high salt concentration effectively "salted out" much of the less soluble surface-active material. Each solution was then poured into a shallow glass dish until the liquid level was well above the waxed rim. The surface potential of a contaminated solution changed rapidly with time as the contaminating organic material was adsorbed at the interface. Often within minutes the surface potential would change as much as a 100 mV. Waxed glass barriers were then used to sweep the adsorbed material to one side of the dish, where it could be removed with an aspirator. After repeating the sweeping procedure several times, until the initial surface potential values were reproducible, it was assumed that the interface immediately after sweeping was relatively free of contamination. The change in surface potential with concentration was then determined by successive dilutions of the saturated solution, and finally by extrapolating the surface potential to zero concentration. The potential between the electrode and water at zero concentration did not indicate the actual potential of a water surface, since the potential of the reference ionizing electrode was unknown. The reported surface potentials are the differences between the potentials extrapolated to zero concentration and those measured at each given solution concentration. To reduce the possibility of contamination all surface potential measurements were carried out in an enclosed Lucite glove box, at a temperature of $20^\circ \pm 0.2^\circ\text{C}$.

The surface tension of each salt solution was also determined as a function of concentration. The measurements were made using a Cenco-duNouy ring tensiometer with a precision of approximately ± 0.1 dyne/cm. In these experiments the surfaces of the salt solutions were again cleaned with the movable barrier to remove the adsorbed surface-active contaminants. The surface tension measurements were made at $25^\circ \pm 1^\circ \text{C}$.

RESULTS

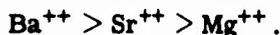
The surface potentials due to the electrolytes are plotted in Figs. 1a and 1b as a function of concentration (moles of salt/kg of water). In most cases the concentration range extends approximately to saturation. Data for at least two, and in some cases three, independent runs are plotted. The wide range of surface potentials for the various electrolytes, from -180 mV for NaCNS at 7.5m to $+64$ mV for Na_2SO_4 at 1.8m, demonstrates the marked effect that rather concentrated inorganic electrolytes can have on the electrical properties of a water surface. These results are in moderately good agreement with those of Frumkin (3) in those cases where the same compounds were studied. Frumkin did not report surface potentials for a range of concentrations for most of the electrolytes, rather he listed the values at one and two mole equivalents of anion per liter. He did find that the potential of a water surface decreased when KI, NaI, NaNO_3 , KCl, NaCl, NH_4Cl , or LiCl were the solutes, although his reported surface potential values at a concentration of 2m were from 2 to 15 mV more negative than those given in Fig. 1a. For the electrolytes $(\text{NH}_4)_2\text{SO}_4$ and Na_2CO_3 the present data are about 7 mV more positive at equivalent concentrations. The largest difference was for Na_2SO_4 , which Frumkin reported $\Delta V = +2.5$ mV at a concentration of one mole of anion, compared to $+35$ mV in Fig. 1a. The surface potentials given in Fig. 1a for KI agree within 5 mV with similar measurements reported by Randles (5), up to a concentration of 3m. The general agreement between the results of the present study and those of Frumkin and Randles indicates that the two experimental methods are indeed measuring the same surface phenomenon. The differences observed could easily arise from impurities present in the reagents. It is also possible that pH changes will influence surface potential and that impurities in the reagents will modify the solution pH.

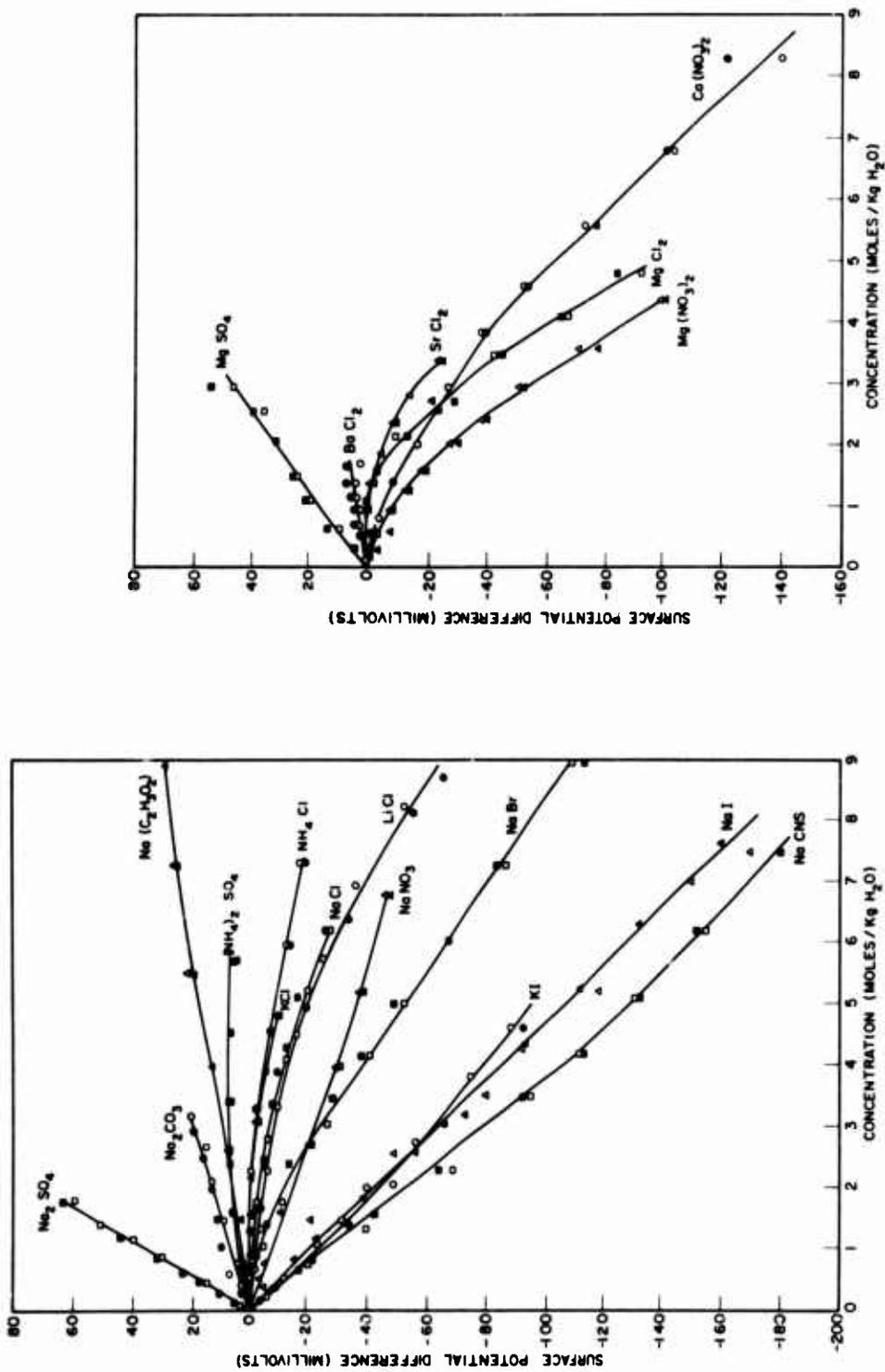
In addition to the doubts expressed by Koefoed (14) regarding the flowing jet method of measuring surface potential, it should be noted that with the flowing jet one actually measures the potential of a freshly formed surface, whereas the radioactive electrode method measures the potential of a surface that is at least several seconds old. If the level of contamination is very low, the flowing jet method may have an advantage, for there would be little time for the contaminants to diffuse into the flowing interface. On the other hand, if the concentration of contamination is such that some should adsorb at the surface of the flowing water, there would be no way to estimate its contribution to the measured potential. In the radioactive electrode method contamination can easily be detected and at least temporarily removed by sweeping the surface.

The surface potentials of solutions of the Group IA chlorides were found to decrease in the order



The values for these chlorides are in good agreement with values reported by Randles (5), and they show the same decrease with increasing energy of cation hydration (17). The same trend was observed for the chlorides of the Group IIA cations in Fig. 1b, where the cations having the greatest energy of hydration again gave the lowest potential. The surface potential decreased in the order





(b) Electrolytes with divalent cations

(a) Electrolytes with monovalent cations

Fig. 1 - Surface potential difference vs solution concentration for aqueous solutions of inorganic electrolytes

Even though different ΔV values were observed for the various chloride salts, it appears as though the cations studied to date have a less pronounced effect on surface potential than the anions. This is apparent in Fig. 2, which shows the surface potentials of the chloride salts plotted as a function of the chloride concentration. At a 3m concentration the ΔV 's of all the chlorides fell within a range of 14 mV, while at 1m they were grouped within a span of only 4 mV, hardly more than the precision of the experimental technique. Only at the higher concentrations, above 4 or 5m, did the cations appear to have a marked effect upon surface potential.

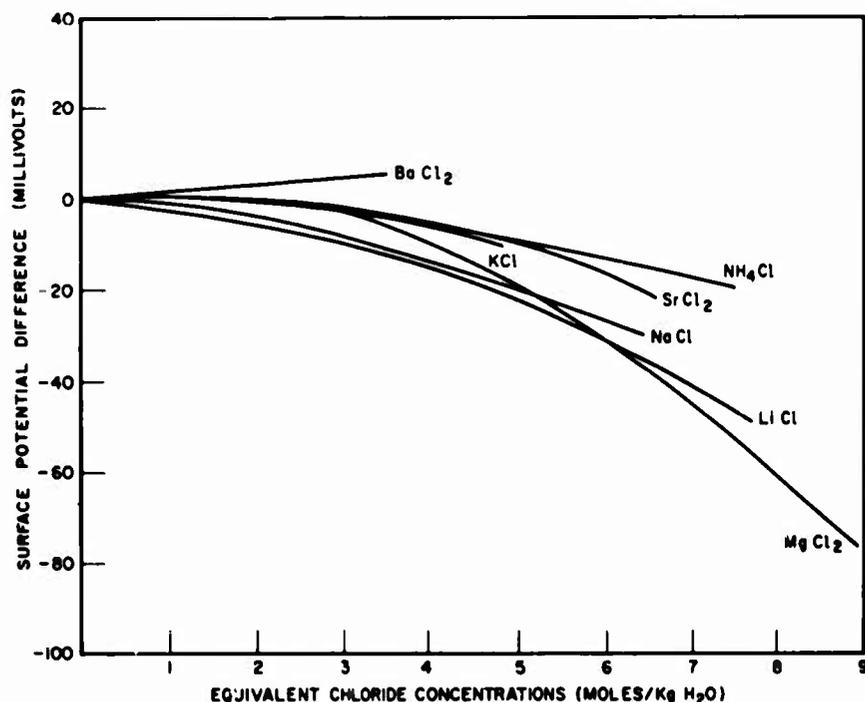
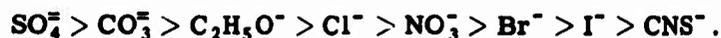
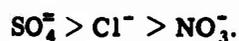


Fig. 2 - Surface potentials of various chloride salt solutions as a function of chloride concentration (mole-equivalents of Cl^- per kg of water)

The relative importance of the anions in determining the surface potential of an electrolyte solution is further reinforced by observing the differences in surface potential of a series of sodium salts. At a constant anion concentration of 2m their surface potentials cover a range of over 100 mV. The surface potentials decrease in the order



In contrast with the cations the anions with the smaller hydration energies apparently give the lowest surface potentials. The same general trend was observed for salts of Mg^{++} , whose surface potentials also decreased in the order



It is also observed in Fig. 1 that all of the electrolytes containing SO_4^{2-} gave rise to positive surface potentials.

From the results it appears probable that the effect of an ion upon surface potential is related in some manner to the structure of the water molecules in the ionic co-sphere, as influenced by ionic charge and ionic radius. Randles showed this by plotting ΔV against the differences in "real" hydration energies of the ions in the electrolytes. Many ionic properties such as hydration energy, ionic entropy, ionic mobility, temperature coefficient of ionic mobility, the well-known B-coefficient of viscosity, and the so-called structure-making or structure-breaking properties of ions in solution were shown by Gurney (18) to be closely related to each other. In Fig. 3 the surface potentials of several electrolytes at a 1m concentration are plotted against the differences between the individual ion entropies as given by Powell and Latimer (19). The solid line shows the correlation for the chloride salts.

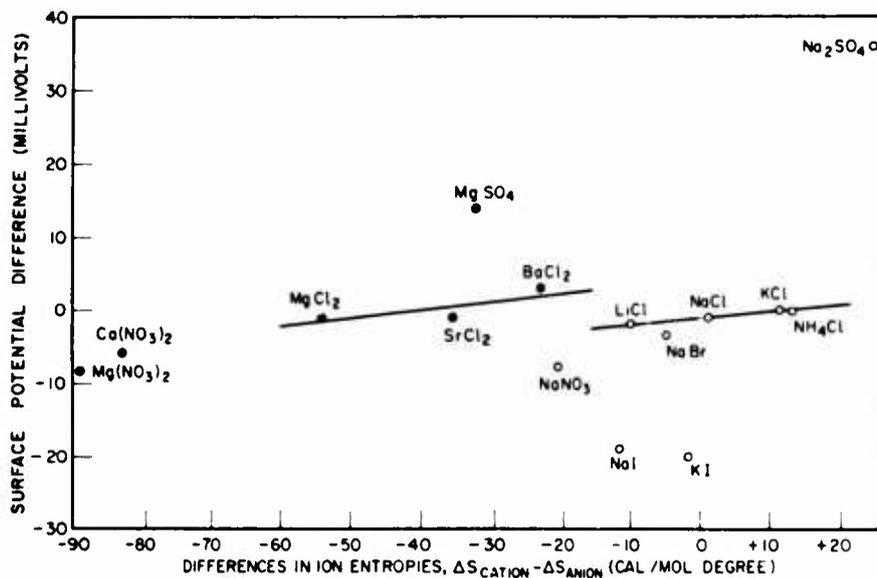


Fig. 3 - Surface potentials of electrolyte solutions as a function of the difference between cation and anion entropies (for 1m solutions)

The ionic properties mentioned are determined in bulk solution where the anions and cations are uniformly distributed and are subjected to a more or less symmetrical force field. At the interface the anions and cations may not be uniformly distributed, and it is obvious that the forces operating on a molecule near the surface will be unsymmetrical. Weyl (20), Good (21), and Fletcher (22) have all argued that the water molecules at the water/air interface have a preferential orientation, with the oxygen atom outermost and the protons more or less directed toward the interior of the liquid. A result of this orientation is the establishment of an electrical double layer at the surface, with the outermost portion of the double layer being negative and the innermost part being positive. With the positive portion of the double layer directed into the solution, one might expect a preferential accumulation of the anions near the interface.

Another difficulty in relating ΔV directly to the hydration properties of the electrolytes is our lack of information about the effect of the ions on the outermost layer of water molecules. In this respect it is difficult to determine what part of the surface potential signal may arise directly from the electrostatic forces associated with the ionic charge and hydration, and what part may be due simply to a change in the orientation of

the water dipoles in the vicinity of the ion. On the basis of the Helmholtz equation even a small change in the average orientation of the surface water molecules could be sufficient to cause the observed changes in surface potential. If the reorientation of the water dipoles does contribute significantly to ΔV , it could lead to an increase as well as a decrease in ΔV , thus accounting for the positive ΔV 's without having to postulate the preferential adsorption of cations into the surface region.

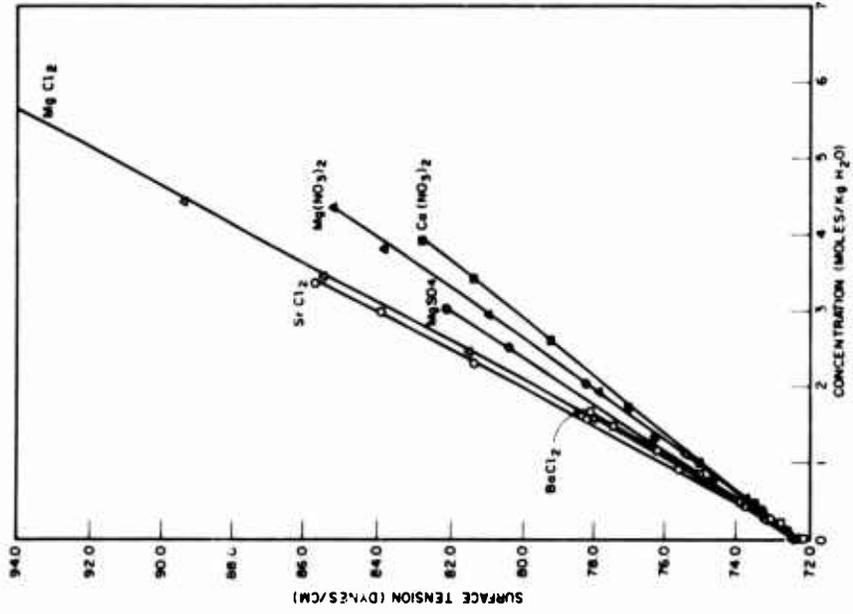
Very few experimental techniques are available for studying the surface properties of an aqueous electrolyte solution. In addition to surface potential, surface tension is the only technique that seems appropriate. Surface tension vs concentration curves are given in Fig. 4 for each of the electrolytes. A comparison of the data for the two techniques at an equivalent anion concentration of 2M is given in Fig. 5 and indicates that, if there is any correlation at all, the surface potential may in general become more positive for those electrolytes giving the greater increase in surface tension. At equivalent cation concentrations no trend at all was observed. Actually the poor correlation between surface tension and surface potential is not surprising. Even though both techniques are measuring properties of an interfacial phase, the properties are somewhat unrelated, one being the intermolecular forces of attraction and the other the electrical properties of the surface molecules.

Several investigators have applied the Gibb's equation to surface tension data such as these (6-9) and have calculated that a salt-free layer of water should exist at the surface of an electrolyte solution, the thickness of the layer decreasing with increasing concentration. At the surface of a 1 to 2M alkali chloride solution they estimate a salt-free layer of the order of 3Å deep. At solution concentrations of 5 to 6M the mole ratio of water to salt is small, on the order of only 10 moles of water to every mole of electrolyte. With each of the ions competing for available water very little salt-free water should be remaining at the interface, and the little that is remaining will be strongly associated with the ions immediately beneath. This is substantiated by the marked decrease in vapor pressure of strong electrolyte solutions. Even at these high electrolyte concentrations, however, it is doubtful that many unhydrated ions are penetrating the interface. At the higher solution concentrations the problem of determining the behavior of ions at interfaces is even further complicated by the fact that many electrolytes will not be completely dissociated, and many may also hydrolyze in aqueous solution giving rise to complex ions as well as OH^- and H^+ ions in solution.

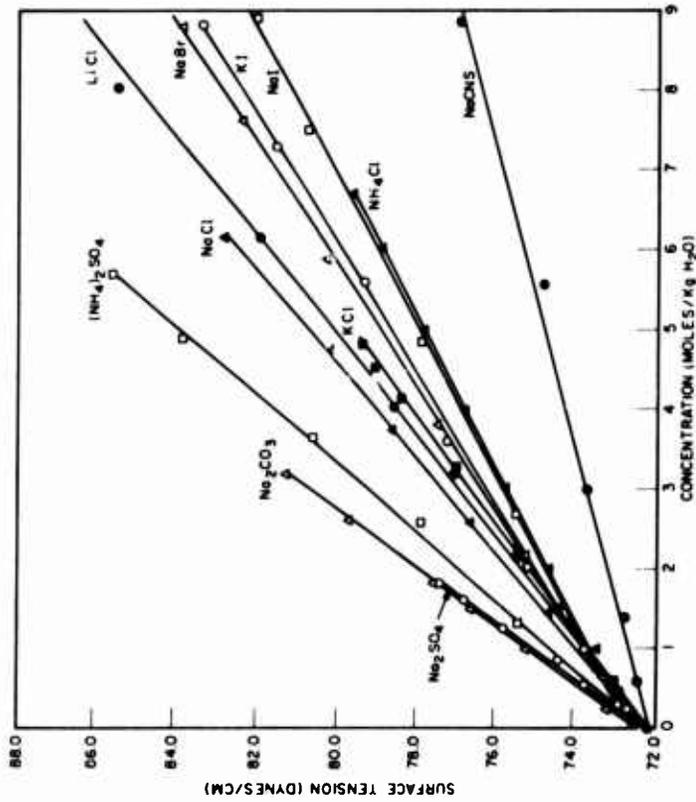
CONCLUSIONS

The results of this investigation, in conjunction with the work of Frumkin (3) and Randles (5), demonstrate that various ions in solution can greatly alter the surface potential of water. In many cases it appeared as though the anion was the most influential, for with the electrolytes studied it seemed to determine the sign of the potential change and to a great extent its relative magnitude. This suggests that the anions may be preferentially associated with the water molecules near the surface, being attracted by the electrical double layer at the water surface with the positive side of the double layer oriented toward the solution. From this picture of a water surface, a negative change in surface potential seems to follow logically from the addition of an electrolyte to the solution. It is difficult to explain the occurrence of a positive ΔV if one assumes that the potential changes arise solely from the electrostatic potential at the interface, for this would mean that the cations are approaching closer to the interface, and thus closer to the positive side of the double layer, than are the anions. It is difficult to understand why Na^+ and Mg^{++} would approach the interface in the presence of a SO_4^{--} ion and not in the presence of a Cl^- or an NO_3^- .

In addition to the electrostatic effect, it is possible the ions may influence ΔV by changing the orientation of the polar water molecules in the surface. A relatively small



(b) Electrolytes with divalent cations



(a) Electrolytes with monovalent cations

Fig. 4 - Surface tension vs concentration for aqueous electrolyte solutions

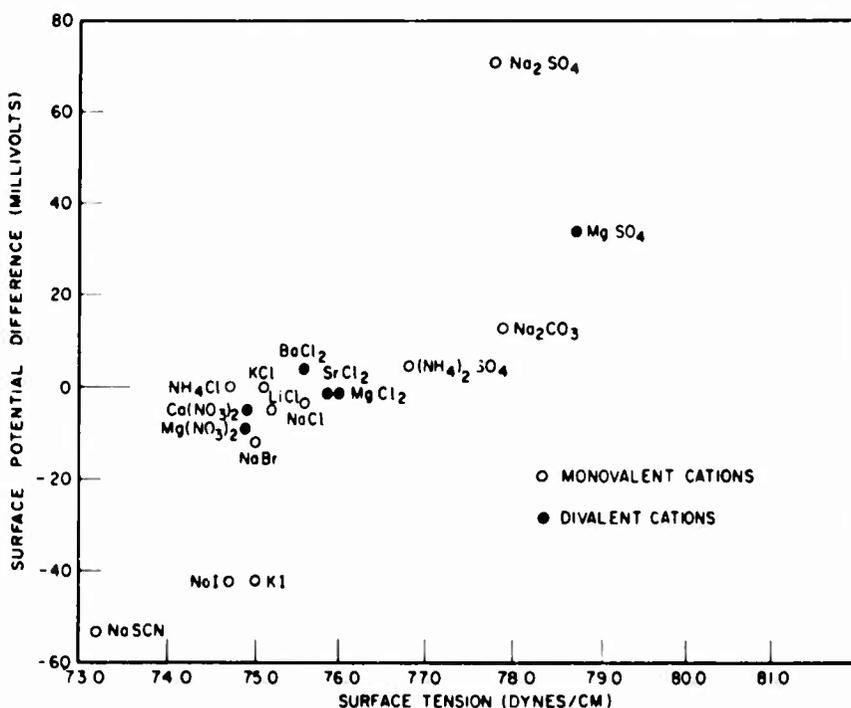


Fig. 5 - Surface potential differences vs surface tension for electrolyte solutions at a concentration of 2m

change in the average orientation of the surface water molecules should be sufficient to give ΔV changes of the magnitude shown in Fig. 1. If it is true that in each case the anions are less strongly repelled from the surface than the cations, then it must be assumed that the anions SO_4^- , CO_3^- , and $\text{C}_2\text{H}_3\text{O}_2^-$ are reorienting the water in such a way as to overcome the negative electrostatic contribution to surface potential and give a resulting positive ΔV . Hydrolysis of the ions may also have an important effect. It is interesting that those anions giving a positive potential change are all so-called "structure-making" anions, as opposed to Cl^- , NO_3^- , I^- , Br^- , and CNS^- which are classed as "structure-breaking." Thus the groups of anions giving rise to surface potentials of different signs are known to interact differently with the water structure. Several orientations for water molecules in the vicinity of an anion have been postulated (23-25); however, the problem of constructing a model and a theory for surface potential that will be in good agreement with experimental data seems extremely difficult. The theory proposed by Randles took into account only the electrostatic potentials of the ions and their adsorption, or repulsion, by the surface double layer. As he pointed out, the poor agreement between his theory and his experimental results showed that the molecular structure of the water in association with the ions cannot be ignored.

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Surface potential Surface tension Inorganic salts Ionizing electrode Aqueous electrolyte solutions Electrolytic solutions						