

Examination of Surface Adsorption of Sodium Chloride and Sodium Dodecyl Sulfate by Surface Potential Measurement at the Air/Solution Interface

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The surface potential (ΔV) of the air/sodium chloride solution interface was measured by using an ionizing ^{241}Am electrode method at 298.2 K. The surface potential steeply increased from 0 up to 15 mV with increasing concentration, then gradually increased up to 20 mV between 1 and 10 mmol dm^{-3} , and finally stayed almost constant at 20 mV up to the concentration of 20 mmol dm^{-3} . This result means that sodium ions concentrate more just near the air/solution interface, whereas chloride ions concentrate more far below the interface above the bulk region of electroneutrality. The dipole moment was derived from the surface potential value, from which the width of the interfacial layer was estimated as a function of the magnitude of electric charge. As for the sodium dodecyl sulfate solution, on the other hand, the surface potential steeply decreased from 0 down to -80 mV with increasing concentration from 0 to 0.01 mmol dm^{-3} , then rapidly increased up to -50 mV between 0.1 and 3 mmol dm^{-3} , then linearly increased up to 0 mV with increasing concentration from 3 mmol dm^{-3} up to the CMC, 8 mmol dm^{-3} , then quite rapidly decreased again down to -82 mV from the CMC to 10 mmol dm^{-3} , and finally stayed almost constant at -82 mV up to the concentration of 20 mmol dm^{-3} . The above variations of the surface potential cannot be elucidated by the conventional surface excess, and therefore, the new concept of surface adsorption was presented for a simple salt and a typical anionic surfactant.

Introduction

The surface tension of an aqueous solution of a simple salt like NaCl increases with increasing the salt concentration due to the negative adsorption according to the Gibbs adsorption equation.¹ On the other hand, the surface tension of a surfactant solution like sodium dodecyl sulfate (SDS) decreases with an increase in concentration due to the positive adsorption and then stays almost constant above the critical micelle concentration (CMC). The point there is that the surface excess remains almost constant over the concentration range from ca. half CMC to the CMC for almost all surfactants which are able to form micelles above the CMC, although the surface tension steeply decreases with increasing concentration up to the CMC. This is called “the Gibbs paradox”.²

The recent study on evaporation of water from surfactant solutions has made it clear that the surfactant molecules are not concentrated just at the air/solution interface.^{3–6} In addition, some surfactant molecules were found to form a bimolecular layer just like cell-membranes below the air/solution interface,^{7,8} judging from the surface excess by the dependence of surface tension on the concentration, where the headgroups stay at the membrane surface and the hydrophobic tails intrude inward.

The surface potential results from the deviation of electric charges from the electroneutrality in a bulk phase

and is therefore able to indicate the position of the electric charge just around the air/solution interface. In other words, the potential values have a high possibility to make us to determine the position of ions just near the air/solution interface.^{9,10} No paper has appeared on a surface potential study of soluble surfactant solutions, as far as the authors know.

In this paper, the authors determined and analyzed the surface potential of solutions for a simple salt, NaCl, and a typical anionic surfactant, SDS, as a function of their concentration. Then, the new concept of the surface excess is presented, which is quite different from the conventional surface excess by the Gibbs isotherm.

Experimental Section

The surface potential was measured using an ionizing ^{241}Am electrode positioned at a certain level above the air/solution interface, while a reference electrode was immersed in the identical solution of 100 mL. The standard deviation for the potential values was ca. 5 mV. The surface potential was standardized to be zero for just the air/water interface. An aliquot of the concentrated solution of NaCl and sodium dodecyl sulfate (SDS) was added stepwise into 100 mL of water in order to increase their concentration, where each addition of the mother solution was made after the potential became stable. The surface potential value depends on the distance between the ionizing electrode surface and the air/liquid interface, and therefore, the calibration for the potential was made first for the distance by changing the total volume of water after fixing the electrode position.

NaCl from Nacalai tesque was used after heating at 1023 K for 24 h to remove any organic impurity. Sodium dodecyl sulfate of specially prepared reagent grade from Nacalai tesque was purified by ether extraction, first, and from recrystallization from water, second. Water used here was triply distilled (surface

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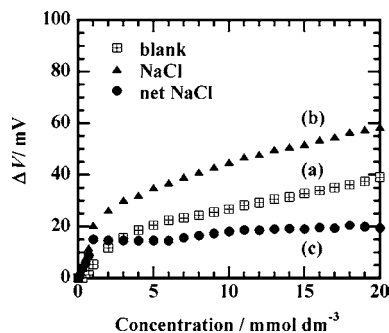


Figure 1. Change of the surface potential (ΔV) with NaCl concentration at 298.2 K, where curve a indicates the change of the potential with volume of purified water, curve b is the potential change with NaCl concentration with the same volume of curve a, and curve c is the net potential change with NaCl concentration.

tension of 71.9 mN m^{-1} and the resistivity of $18 \text{ M}\Omega \text{ cm}$). All measurements were performed at 298.2 K.

Results and Discussion

Figure 1 shows the surface potential of just purified water depending on the total volume (a), that of NaCl solution (b), and that due to net NaCl concentration (c), where the abscissa for curve a is the volume necessary for the corresponding NaCl concentration. In other words, curve c is obtained by subtracting curve a from curve b. The surface potential is always positive, although it steeply increases at very low concentrations with the concentration. At the concentrations above 1 mmol dm^{-3} , the surface potential gradually increases and then remains almost constant above 10 mmol dm^{-3} , which means that the distribution of ions is determined at very low concentrations. This is quite an interesting new finding. In addition, the cationic sodium ions concentrate more just near the air/solution interface, whereas chloride ions concentrate more far below the interface in the interfacial region above the bulk region of electroneutrality. From the surface potential, the dipole moment was derived using the following equation for the three layers model of the insoluble monolayer:¹¹

$$\Delta V = \frac{1}{A\epsilon_0} \left(\frac{\mu_1}{\epsilon_1} + \frac{\mu_2}{\epsilon_2} + \frac{\mu_3}{\epsilon_3} \right) \quad (1)$$

where A represents the mean molecular area. μ_n and ϵ_n denote the dipole moment normal to the surface and the permittivity, respectively, where subscripts 0, 1, 2, and 3 are contributions of vacuum, subphase, headgroup for surfactant, and its tail group, respectively. In the present case, only the subphase can contribute to the surface potential. The width (r) of the interfacial layer at the air/solution interface is quite an important factor to characterize the interface. Namely, the width of the layer is the distance from just the air/solution interface to the place beneath the interface from which the electroneutrality of solution starts to be satisfied. The dipole moment can be related to electric charge (e)

$$\mu_1 = er \quad (2)$$

The result for the surface potential of 20 mV at 15 mmol dm^{-3} is shown in Figure 2, where the interfacial layer was estimated as a function of the magnitude of the electric charge of the dipole moment calculated by using the

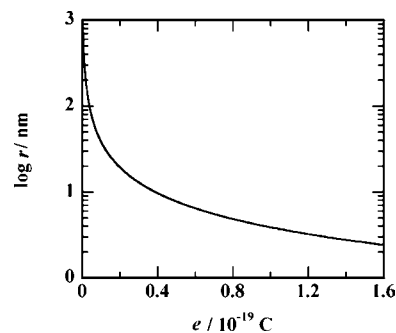


Figure 2. Change of the interfacial distance from the bulk of electroneutrality to the air/solution interface with the magnitude of cationic charge.

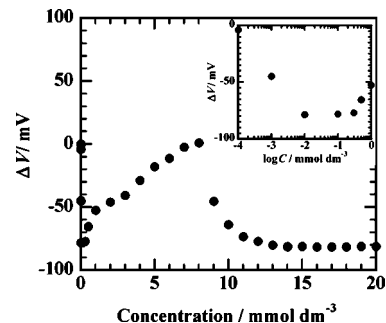


Figure 3. Change in the surface potential with SDS concentration, where the insert is the potential change for quite dilute SDS solutions.

numerical values of 28 nm^2 for A , $8.85 \times 10^{-21} \text{ C}^2 \text{ J}^{-1} \text{ nm}^{-1}$ for ϵ_0 , and 78.3 for ϵ_1 . The A value is obtained by surface charge density derived from the surface potential at the NaCl concentration as given above. When the sodium ion is fully charged, the length of the dipole becomes 2.4 nm. In reality, however, the cation is partially neutralized by the chloride ion present in the upper interfacial region. In other words, the interfacial region should be longer than 2.4 nm in depth just from the interface to the place in the bulk where the electroneutrality starts to hold.

It has been said that the simple salt is negatively adsorbed, because the surface tension increases with an increase in the concentration. However, this explanation seems quite strange, because the surface potential stays almost constant regardless of the concentration over the concentrations from 1 up to 20 mmol dm^{-3} . The interfacial tension or the surface tension is a thermodynamical parameter, which is a macroscopic property determined by a number of molecules around the interface or the surface. When the concentration of ionic species increases, hydrated water molecules around the ions also increase in number. This brings about a more organized structure of molecules in the bulk region of electroneutrality below the air/solution interface, which results in a stronger force to break the structure below the interface or in more energy to increase the interfacial area. This elucidation for the increase in the interfacial tension with the salt concentration is quite reasonable to accept. In addition, there is nothing to do with a negative adsorption.

Figure 3 illustrates the change of the surface potential with the SDS concentration, where the potential is the average value of seven measurements to make the complicated change more reliable and the correction is made for the volume change of the solution as mentioned above. The surface potential steeply decreased from 0 down to -80 mV within a small concentration range from 0 to $0.01 \text{ mmol dm}^{-3}$, then steeply increased up to -50 mV between 0.1 and 3 mmol dm^{-3} , then linearly increased up

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to 0 mV from 3 mmol dm⁻³ to the CMC, 8 mmol dm⁻³, then steeply decreased down to -82 mV from the CMC to 10 mmol dm⁻³, and finally stayed almost constant at -82 mV up to the concentration of 20 mmol dm⁻³. It took ca. 10 h for one run, 5 h below the CMC and another 5 h above the CMC. An important thing was the fact that the potential change could be traced irrespective of beginning concentration, which means that the potential is the equilibrium one and that the decomposition of SDS and the adsorption of dodecanol that followed are unnecessary to consider. The initial sharp decrease in the surface potential is due to the adsorption of DS⁻ at the interface, where the Na⁺ ion is completely dissociated from DS⁻ and stays far away from the adsorbed DS⁻ due to the extremely dilute solution. However, with an increase in the concentration, Na⁺ ions tend to concentrate very near the interface, as is the case of NaCl, and then, the potential starts to increase with the concentration. In the previous study,^{7,8} it was found to be highly possible for ionic surfactants to form a bimolecular layer just like a cell-membrane below the air/solution interface, judging from the surface excess by the dependence of surface tension on the concentration, where the headgroups stay at the bilayer surface with the tail groups intruding inward.⁷ Then, the condensed negative charges at the bilayer surface attract the positive Na⁺ ions, which results in a further increase in the surface potential up to the CMC. Above the CMC, however, micelle formation starts in the bulk far below the interface, where the conventional micellar aggregates in the bulk are more stable energetically than the bilayer aggregates. Then, the bilayer aggregates near the interface degrade with increasing micellar concentration above the CMC. In other words, the degradation starts from the CMC and ends at 10 mmol dm⁻³, above which only adsorbed DS⁻ ions and concentrated Na⁺ ions near the interface determine the surface potential. A further increase in the SDS concentration only makes the number of micelles in the bulk increase and does not change the distribution of the ions in the interfacial region. This is the reason why the surface potential remains constant above the concentration. This change in the surface potential with the SDS concentration can be supported by the evaporation rate of water from the SDS solution and the activation energy.⁸ That is, the evaporation rate has no relation with the conventional surface excess⁸ and the evaporation rate is truly proportional to the mole fraction at the air/solution interface.⁶ A quite reasonable change in the surface potential was

also observed for a cationic surfactant, which supports the present SDS potential change. A detailed analysis of these surface potentials will be reported in a subsequent report including cationic and nonionic surfactant.¹² Further study using an ionic surfactant with a polyvalent counterion and a phototechnique would be required for the present purpose.

To establish a new scientific concept, many experimental evidences are necessary to support it. In other words, when any experimental evidence and the accepted concept contradict each other, the conventional concept cannot be accepted as true. In this sense, the following two conventional concepts, the negative adsorption for NaCl and the excess adsorption of surfactant molecules just at the air/solution interface, are quite doubtful.

Summary

The surface potential of the air/sodium chloride solution interface was measured by using an ionizing ²⁴¹Am electrode method. The surface potential steeply and then gradually increased and then stayed almost constant at 20 mV at concentrations above 10 mmol dm⁻³. This result shows that sodium ions concentrate more than chloride ions near the air/solution interface above the bulk region of electroneutrality. As for sodium dodecyl sulfate, the surface potential steeply decreased first, then increased up to 0 mV with increasing concentration up to the CMC, then rapidly decreased again down to -82 mV, and then stayed at the same value up to the concentration of 20 mmol dm⁻³. The variations of the surface potential cannot be elucidated by the conventional surface excess, and therefore, the new concept of surface adsorption was presented for a simple salt and a typical anionic surfactant.

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