Micelle Formation of Sodium 1-Decanesulfonate and Change of Micellization Temperature by Excess Counterion

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Aqueous solution properties of sodium 1-decanesulfonate have been studied at 308.2 K by electroconductivity, membrane potential, and photochemistry in order to determine the micellization parameters for the mass-action model: the micellization constant K_n, the micellar aggregation number n, and the number of counterions binding to a micelle m. The numerical values are $\ln K_n = 133$, $n = 26$, and $m = 16.6$. These values account for the experimental concentrations of the surfactant ion and counterion to a concentration that is 3 times the critical micelle concentration (cmc). The micellization temperature (MT) or the Krafft temperature was determined to be 295.3 K from the temperature dependence of the cmc and of the aqueous solubility. The MT values shifted to higher temperature with increasing concentration of sodium chloride, and good agreement was found in the values evaluated from the difference between the aqueous solubility and the cmc in the presence of excess counterion.

Introduction

Sodium 1-alkanesulfonate is typical of a class of conventional anionic surfactants that are chemically more stable compared with sulfate analogues.[1−5] Nevertheless, reports on micelle formation of the sulfonates are fewer in number compared with those for the sodium 1-alkylsulfates. This is primarily due to their higher micellization temperature (Krafft point). On the other hand, micellization becomes evident for the sulfonate amphiphiles when the number of carbon atoms in the hydrophobic alkyl chain are eight or more. However, amphiphiles with a shorter alkyl chain would have a lower aggregation number for the micelle,[6] and consequently, micellization is found to occur over a rather wide concentration range. From this reason, as for shorter amphiphiles whose hydrophobic tail has 10 carbon atoms such as in the present case, micellization has not been well studied yet. The authors have employed the mass-action model to analyze micellization and related phenomena.[7] It seemed reasonable to examine the general applicability of the short-chain amphiphiles to the simple mass-action model of micellization. At the same time, the micellization temperature is another important parameter in defining the properties of ionic surfactants. From this point of view, sodium 1-alkanesulfonate is quite a suitable candidate for the examination of the mass-action model for micellization and change in the micellization temperature.

Experimental Section

Materials. Sodium 1-decanesulfonate of analytical reagent grade was from Tokyo Kasei Kogyo Co., Ltd. Purification was made by alternating batch extraction with diethyl ether of the dried sample and recrystallization from water. The purity was checked by elemental analysis, and the observed and calculated values are in satisfactory agreement: C 49.04 (49.16), H 8.62

(8.66)%, where the values in parentheses are the calculated ones. Sodium chloride was of guaranteed reagent grade from Wako Pure Chemical Industries, Ltd. and used without further purification as a source of counterion. Water used was distilled twice from alkaline permanganate solution.

Critical Micelle Concentration (cmc). The cmc was determined at 308.2 K by the usual conductivity method as the concentration at an intersection of two lines obtained by tracing specific conductance against concentration. The cmc was also determined in the presence of excess counterion by the same conductivity method, where the specific conductance of sodium chloride solution was subtracted from the observed conductance.

Aqueous Solubility. Aliquots of known concentration of stock surfactant solution were added stepwise to a measured volume of water, where the stock solution was kept at a temperature just above the MT so that the alkyl sulfonate does not precipitate out of the solution. The specific conductance of a solution at a specified temperature increased linearly with surfactant concentration up to a maximum value. It then remained constant with further increase in concentration after a small hump, accompanied by an apparent precipitate. The solubility was determined as the concentration at which the initial linearity intersected the back extrapolation of the limiting constant conductance. At temperatures above the micellization temperature (MT), a clear solution of known concentration above the cmc was cooled to below the MT. The solution coexisting with the sulfonate precipitate was heated very slowly from below the MT in steps of 0.2 K to above the MT. At each step, the temperature was maintained constant for more than 10 min under agitation. The conductances were plotted against temperature. Further increase after disappearance of the precipitate induced only a linear increase of the conductance. The original concentration is the solubility at the temperature where the linear increase starts.[8]

Activity of Counterion and Surfactant Ion. Sodium ion activity was measured at 308.2 K by an ion-selective electrode (Na-115B, TOA Electronics Ltd.) just as in the previous study,[9]

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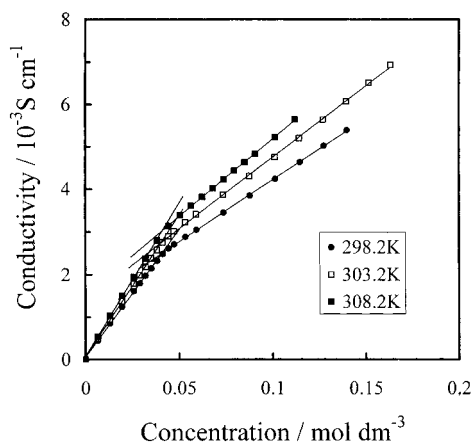
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Figure 1. Specific conductivity vs concentration at different temperatures.

Figure 2. Corrin–Harkins plot for determination of the degree of counterion binding to micelle at 308.2 K.

where the ion meter (IM-20E, TOA Electronics Ltd.) was standardized at two concentrations of sodium ion: 100 and 1950 ppm. The accuracy was confirmed by a solution of known counterion concentration between the two concentrations. The activity of the surfactant ion was determined at the same temperature by electromotive force (ΔE) measurement using a handmade anion-selective membrane.[10] The cell used was illustrated previously.[11] The sulfonate concentration in the reference solution was 1.0×10^{-3} mol dm^{-3}. The membrane potential was measured with a precision of ± 0.1 mV and was found to be quite reproducible. A linear relationship between ΔE and the logarithm of the surfactant ion below the cmc was used as a calibration line to determine the concentration of the surfactant ion above the cmc.

Aggregation Number. The aggregation number of the micelle was determined photochemically by the steady-state fluorescence quenching method,[12,13] where the probe and the quencher are tris(2,2′-bipyridine)ruthenium(II) chloride and 9-methylanthracene, respectively. The concentrations used were 3.0×10^{-4} and 6.0×10^{-4} mol dm^{-3} for the probe and the quencher, respectively. The steady-state experiments were carried out with a Hitachi 650-40 spectrofluorometer where excitation and emission wavelengths were 450 and 628 nm, respectively. The temperature was controlled at 308.2 K by a thermostated water jacket.

Results and Discussion

Changes of specific conductivity (κ) with concentration are shown in Figure 1, where the curves are clearly divided into two straight lines below and above a breakpoint corresponding to the cmc at three measured temperatures. Therefore, we did not need to plot the first derivatives of κ against concentration for a more precise determination of cmc, obeying the Phillips definition of cmc.[14]

In the previous papers on micellization of ionic surfactants, the mass-action model has been employed for physicochemical analysis, where the molar concentration was used instead of activity. The reason for the concentration is that the electroneutrality condition of the solution and the mass balance were necessary for the analysis. Such an analysis worked quite well for ionic surfactants whose cmc is relatively low, for example, sodium dodecyl sulfate.[15] However, the treatment is quite unreliable for surfactants that have higher cmc values (>40 mmol dm^{-3}); such is the case for the present surfactant. Hence, activity should be used instead of the concentration for thermodynamic analysis of the present surfactant. So for the
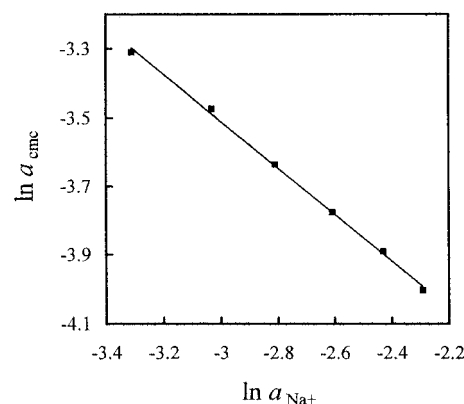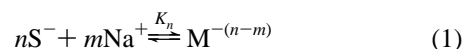
micellization of an ionic surfactant expressed by

$$n\text{S}^- + m\text{Na}^+ \underset{}{\overset{K_n}{\rightleftharpoons}} \text{M}^{-(n-m)} \tag{1}$$

the activity of the surfactant ion (S$^-$) at the cmc obeys the following expression:[7]

$$\ln a_{\text{cmc}} = -(m/n) \ln a_{\text{Na}^+} + \text{constant} \tag{2}$$

This is an alternative expression of the Corrin–Harkins plot.[16] From a plot of the change in the cmc with counterion concentration, the degree of counterion binding per micelle (m/n) can be evaluated from the slope, where the activity coefficient $\gamma_{\pm}$ was evaluated from the following relation at 308.2 K,[17]

$$\gamma_{\pm} = -\frac{0.52\sqrt{I}}{1 + 1.66\sqrt{I}} + 0.161I \tag{3}$$

and I is the ionic strength. The observed cmc change obeyed the above linear relationship (Figure 2), and the m/n value was determined from the slope, 0.68.

The aggregation number of a micelle is a critical parameter and is usually evaluated from the molecular weight determined by the static light scattering method. This method was tried unsuccessfully for the determination in this case, but because of the extreme difficulty in removing dust from the solution, it was abandoned. An alternative photochemical method was employed for the determination, which uses the following relation:

$$\left[\ln \frac{I_0}{I}\right]^{-1} = \frac{C - \text{cmc}}{[\text{Q}]\bar{n}} \tag{4}$$

where I_0/I is the ratio of fluorescence intensity without and with the quencher, Q, C is the surfactant concentration, and $\bar{n}$ is the average aggregation number of micelles. The experimental results are shown in Figure 3, where a good linearity is observed and the intercept on the abscissa is just below the cmc, 40.6 mmol dm^{-3}. From the slope, the aggregation number was calculated to be 26, which is smaller than the literature value 40 at 303.2 K.[18]

The two micellization parameters have been determined from the above procedures to be $n = 26$ and $m = 17.7$. The micellization constant K_n can be calculated from following relation if two conditions are met, namely if the aggregation number is large and the cmc value is small:[7]

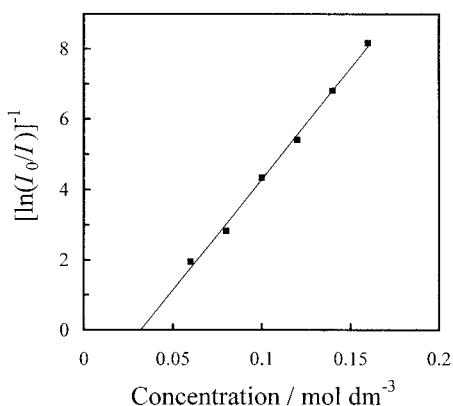$$1/K_n = 2n(n + m)(\text{cmc})^{n+m} \tag{5}$$

Figure 3. Dependence of fluorescence intensity on surfactant concentration. [probe] $= 3.0 \times 10^{-4}$ and $[Q] = 6.0 \times 10^{-4}$ mol dm^{-3}.
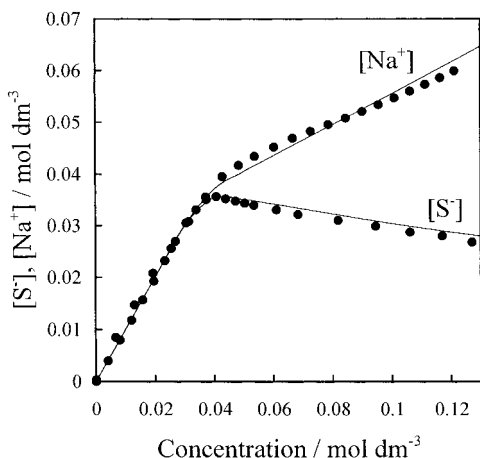

Figure 4. Change of bulk concentrations [Na$^+$] and [S$^-$] with total surfactant concentration above the cmc. Solid lines are the evaluated values for the three parameters $\ln K_n = 133$, $n = 26$, $m = 16.6$.

The K_n value based on eq 5 becomes $\ln K_n = 132$. However, the two conditions above are not satisfied for the present surfactant. An additional experiment was carried out to determine the micellization constant from the change of counterion concentration [Na$^+$] with surfactant concentration above the cmc (Figure 4). From eq 1 the micellization constant can be expressed by

$$K_n = \frac{[M]}{[S^-]^n[Na^+]^m} \quad (6)$$

where the activity coefficients of three chemical species are included in the micellization constant. The mass balance for the counterion and surfactant ion can be expressed as

$$[M] = \frac{C - [Na^+]}{m} = \frac{C - [S^-]}{n} \quad (7)$$

where C is the total surfactant concentration. Equations 6 and 7 lead to the following relationship between C and the counterion concentration [Na$^+$]:

$$\ln K_n = \ln \frac{C - [Na^+]}{m} - n \ln\left[C - \frac{n(C - [Na^+])}{m}\right] - $$
$$m \ln[Na^+] \quad (8)$$

When both values of n and m are known and the relation between C and [Na$^+$] has been obtained, the K_n value can be evaluated at any surfactant concentration above the cmc.
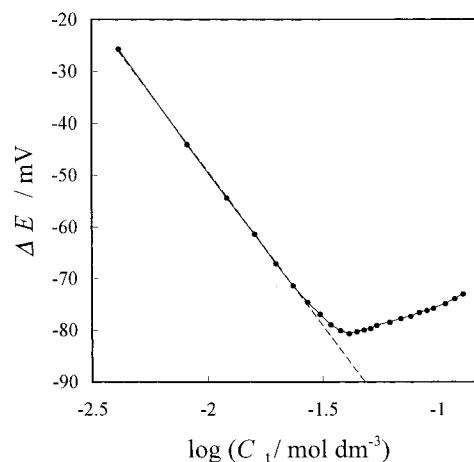

Figure 5. Relationship between membrane potential (ΔE) and surfactant concentration at 308.2 K.

Furthermore, if only the value of either n or m is known, the other two parameters can be evaluated from eq 8 by measuring at additional surfactant concentrations above the cmc. The same evaluation can be made if the variation of surfactant ion concentration with surfactant concentration above the cmc is known. For values of $n = 26$ and $m = 17.7$ this approach yields $\ln K_n = 133.1 \pm 0.2$, while K_n and m/n values, when $n = 26$, became $\ln K_n = 132.4-133.4$ and $m/n = 0.67-0.71$. The two different analyses lead to very good agreement in the reported parameters.

The mass-action approach has been shown to be applicable for the analysis of micelle formation. In addition, it is important to examine whether the micellization parameters obtained above are experimentally realistic. The surfactant ion concentrations were experimentally determined as a function of surfactant concentration above the cmc (Figure 5). As for any anion-selective membrane, the selectivity was examined to see whether it obeys the Nernst relation. The slope of the relation was found to be -60.9 mV, which is very close to the ideal value (-61.2 mV). After the quality of the anion-selective electrode is verified, it is possible to obtain the degree of counterion binding to micelle (m/n) using the following equation derived from eq 7:

$$\frac{m}{n} = \frac{C - [Na^+]}{C - [S^-]} \quad (9)$$

The m/n value increased with increasing concentration: 0.55 at 0.06 mol dm^{-3} and 0.66 at 0.12 mol dm^{-3}. This increase is quite normal because the aggregation number should increase with increasing concentration according to the mass-action law. By use of the above set of parameters, the derived curves can be superposed onto the experimental data. The set thus obtained are $(K_n, n, m) = (133, 26, 16.6)$, giving the solid calculated lines for the counterion and surfactant ion in Figure 4. The calculated values are in good agreement with the experimentally determined values in the concentration range from cmc to 3 times the cmc, although one set of the parameter values cannot perfectly cover such a large concentration range, as mentioned above.

From the results and discussion above, it is clear that the mass-action model is quite suitable for predicting the micellization properties. This is because such a simple mass-action approach is applicable to micelle formation over a concentration range up to several times the cmc, even when the aggregation number is low($<$30) and the cmc value is relatively high, as demonstrated by the present surfactant.
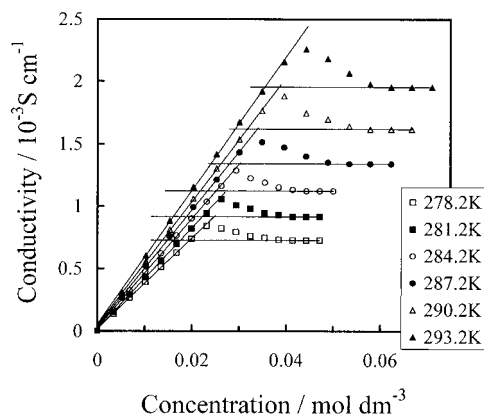
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Figure 6. Changes of conductivity with surfactant concentration at different temperatures below the MT.
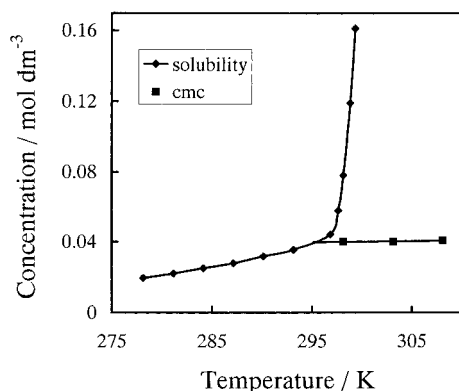

Figure 7. Changes of aqueous solubility and cmc with temperature.

Now that the micellization equilibria have been clarified, we can shift our attention to the change in micellization temperature with excess counterion. Figure 6 shows the conductivity change with surfactant concentration at several temperatures below the MT. The aqueous solubility was determined according to the method mentioned in the Experimental Section. In Figure 7 the changes in cmc value and aqueous solubility with temperature are shown. The temperature at which the two curves intersect each other is 295.3 K, which is the micellization temperature (MT) or the Krafft temperature for sodium 1-decanesulfonate, but never the Krafft point.[19] The micellization temperature is a rather practical parameter from which the enthalpy change of dissolution was calculated to be 54.1 kJ mol^{-1} from the change in solubility with temperature from the van't Hoff relation. The value is very close to the reported values of 50 and 49 kJ mol^{-1}.[20,21] At the MT and under atmospheric pressure, the following relation must hold from a consideration of the constant chemical potential of the surfactant due to divariant solid phase.[22]

$$[Na^+][S^-]\gamma_\pm^2 = K_s \qquad (10)$$

where K_s is the solubility product and the ionic strength I for $\gamma_\pm$ is equal to the aqueous solubility $[S^-]$. Furthermore, the aqueous solubility is equal to the cmc so that the aqueous solubility $[S^-]$ without any additive satisfies the following expression.

$$[Na^+] = [S^-] = cmc \qquad (11)$$

When excess counterion is added to the system, ln(cmc) decreases, obeying the Corrin–Harkins relation (eq 2), while the aqueous solubility decreases, following eq 10 at constant
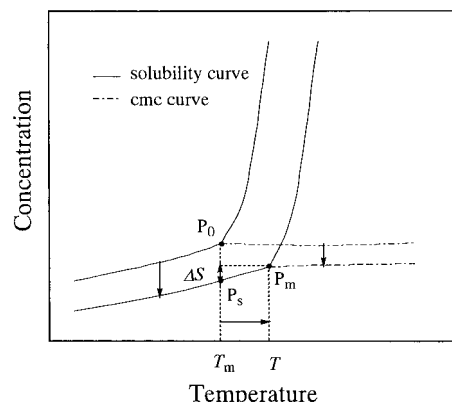
temperature.[7]

$$([Na_{ex}^+] + [S^-])[S^-]\gamma_\pm^2 = K_s \qquad (12)$$

or

$$\ln a_{S^-} = -\ln a_{Na^+} + \ln K_s \qquad (12')$$

where $[Na_{ex}^+]$ is the excess concentration of sodium ion, $[S^-]$ is the solubility of surfactant in the presence of excess counterion, and the ionic strength I for $\gamma_\pm$ of eq 12 becomes $[Na_{ex}^+] + [S^-]$. From eq 12' the slope is -1, while that of eq 2 is $-(m/n)$ whose value is larger than -1. It is clear that eqs 2 and 12' start to decrease from the same point P_0 with increasing excess counterion at the MT (T_m in Figure 8). Therefore, the difference (ΔS) between the cmc value and the aqueous solubility is proportional to the presence of excess sodium ion (Figure 8). Although the cmc value shows a slight variation with temperature, the aqueous solubility changes directly with temperature according to the van't Hoff relationship.

As is clear from Figure 8, the magnitude of the difference, or the distance between points P_s and P_m, corresponds to the solubility increase due to increasing temperature or to an increase in the micellization temperature. The solubility $[S^-]$ at P_s can be obtained by solving eqs 3, 10, and 12 for the excess counterion concentration ($[Na_{ex}^+]$). The cmc or $[S^-]$ at P_m can be estimated from the Corrin–Harkins plot at this concentration, assuming that the value of m/n remains constant over a small temperature increase.[23] The MT increase ($T - T_m$) is easily calculated from the difference between the two concentrations of $[S^-]$ using ΔH in

$$\Delta \ln[S^-] = \frac{\Delta H}{2R}\left(\frac{1}{T_m} - \frac{1}{T}\right) \qquad (13)$$

However, the micellization temperature in the presence of excess counterion was experimentally obtained as follows. The change in conductance of the sodium chloride solution at the specified concentration ($[Na_{ex}^+]$) with temperature was determined in the presence of a coexisting surfactant solid phase. This experiment directly determines the solubility change with temperature in the presence of excess sodium chloride. The micellization temperature is roughly measured from a steep increase in the conductance with temperature. Next, the cmc was determined under the above-measured conditions for MT and $[Na_{ex}^+]$ but just above the rough MT. The temperature at which the conductivity for the former solubility is equal to the conductivity

Figure 8. Schematic illustration for change of micellization temperature in the presence of excess counterion.
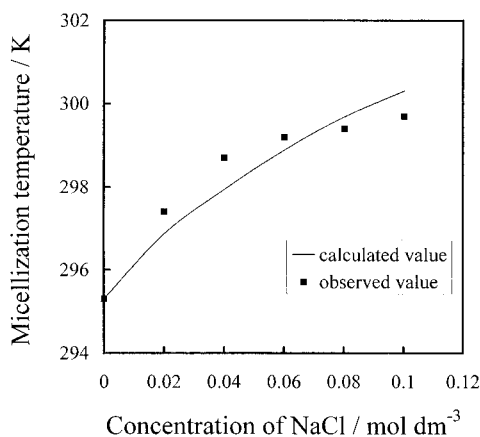
Figure 9. Changes of observed and calculated micellization temperatures with excess sodium chloride concentration.

at the cmc should be the correct micellization temperature in the presence of excess counterion or excess sodium chloride. Figure 9 illustrates the observed and the calculated MT values. Both values agree very well with each other within ±0.8 K. This strongly suggests that the above analysis for the micellization temperature is quite reasonable and acceptable. In addition, it strongly indicates that the micellization temperature is determined both by the relationship between cmc and solubility and by the dependence of both parameters on temperature. Clearly, the micellization temperature is absolutely not the phase transition temperature of the hydrated surfactant solid.[19]

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