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Electric Conductivity Analysis of Micellar Solution of Sodium Dodecyl Sulfate

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Electric conductivities at 298.2 K of sodium dodecyl sulfate solution above the cmc were analyzed from the concentrations of counterion, surfactant ion, and micelle based upon the mass action model of monodisperse micelle formation, where the three micellization parameters ($\log K_n=230$, $n=64$, and $m=46.7$) were employed. The ionic conductivity of micelle was found to be inconsistent not only with the micellar size of the identical charge but also with the conductivity of the dynamic radius of micelle of the identical charge. The inconsistencies could be solved by the hopping reaction of counterions between micelles through the overlapping of ionic diffuse double layers around micelle that takes place when two micelles come close together. The hopping reaction was found to start when the distance between micelles becomes less than 5 times the Debye length.

Sodium dodecyl sulfate (NaDS) is the ionic surfactant whose micelle formation has been investigated and examined most widely and most profoundly among a number of ionic surfactants.[1] However, an electric conductivity of the micelle itself in aqueous solution still remains unsolved, although the physical and electrostatic pictures[2—4] of the micelles have been presented in great detail.

In our previous paper,[5] the author has nicely analyzed the concentration changes of the counterion (Na^+) and the surfactant ion (DS^-) above the cmc with the total surfactant concentration from the mass action model of micelle formation, where they were obtained by improved electrochemical method.[6] It was also found that the concentration change of every chemical species could be evaluated by the three micellization parameters; the micellization constant K_n, the micelle aggregation number n, and the number of counterion per micelle m. The concentration changes of the counterion, the surfactant ion, and the micelle can give rise to an estimation of the contribution of these three chemical species to the total electric conductivity.

Up to the present, the NaDS solution has been analyzed from osmotic and activity coefficients[7] and from electric conductivity.[8] It was found from these studies that the micelle makes contribution to these properties to some extent, but the extent has not been made clear, yet. In addition, an equivalent conductivity of NaDS micelle has been evaluated,[9] but the validity of the obtained values has not been discussed.

In this study, then, the electric conductivity change of the NaDS solution was analyzed in order to present the picture of micellar solution from the view point of electric conductivity and to make clear the mechanism from which the conductivity of the micelle can be evaluated.

Experimental

Materials. Sodium dodecyl sulfate (NaDS) was specially prepared reagent grade from Nacalai Tesque, Inc. It was purified by alternating ether extraction and followed recrystallization from water two times. The purity was checked by the elemental analysis: C, 49.79 (49.98) and H, 8.66 (8.74)%, where the values in parentheses are the calculated ones. Water used was distilled twice from alkaline permanganate solution.

Electric Conductivity. Two concentrated mother solutions of NaDS were prepared; one of 79.87 mol m^{-3} for below the cmc and the other of 337.3 mol m^{-3} for above it. The conductivity was measured stepwise by introducing an aliquot volume of the mother solution into 15 mL of the water, where the cell was sealed in order for the solution not to contact open air. Temperature was controlled at 298.2 K within ±0.1 K. The measurement was started immediately after the preparation of the mother solutions in order to make the hydrolysis of NaDS minimized as much as possible..

Theoretical

The following equilibrium can be given for micelle formation of monodisperse ionic micelle:[10,11]

$$nS^- + mG^+ \xrightleftharpoons{K_n} M_n^{-(n-m)}, \tag{1}$$

where S^-, G^+, and M_n are surfactant ion, counterion, and micelle of aggregation number n, respectively. From Eq. 1 the micellization constant K_n is written as

$$K_n = [M_n]/([S]^n[G]^m), \tag{2}$$

where [S], [G], and $[M_n]$, are the corresponding concentrations, respectively, and the electroneutrality of solution holds,

$$[G] - [S] - (n-m)[M_n] = 0. \tag{3}$$

The mass balance for surfactant ion and counterion are respectively expressed as

$$C_t = [S] + n[M_n], \tag{4}$$

$$C_t = [G] + m[M_n], \tag{5}$$

where C_t is the total surfactant concentration. From Eqs. 3, 4, and 5, [S] and [G] are written as

$$[S] = (1 - n/m)C_t + (n/m)[G], \tag{6}$$

$$[G] = (1 - m/n)C_t + (m/n)[S]. \tag{6a}$$

From the logarithm of Eq. 2 and with Eqs. 4 and 6a one obtains

$$\ln [\mathrm{S}] = -(m/n)\ln [(1 - m/n)C_\mathrm{t} + (m/n)[\mathrm{S}]] - (1/n)\ln \mathrm{K}_n + (1/n)\ln [(C_\mathrm{t} - [\mathrm{S}])/n]. \quad (7)$$

This equation suggests that the concentrations of each chemical species can be evaluated at a certain surfactant concentration in combination with Eqs. 4 and 6a, once the three micellization parameters, K_n, n, and m, are obtained.

Results and Discussion

The changes of specific and equivalent conductivities with total surfactant concentration are shown in Fig. 1. From the kink point the cmc was determined as 8.1 mol m^{-3}. The values of specific conductivities below and above the cmc are also given in Tables 1 and 2, respectively. The concentration changes of Na$^+$ and DS$^-$ ions above the cmc with total surfactant concentration were found to be perfectly elucidated by the three micellization parameters averaged over the concentration range from 20 to 80 mol m^{-3}; $\log K_n = 230$, $n = 64$, and $m = 46.7$.[5] They are given in Table 2 together with the micellar concentrations which are evaluated using Eq. 4.

NaDS perfectly dissociates itself in an aqueous solution below the cmc, and the ionic conductivity of Na$^+$ can be given by the following equation:[12]

$$\lambda_{\mathrm{Na}^+} = (50.10 - 1.141\sqrt{I})/10^4 \quad (\mathrm{S\,m^2\,mol^{-1}}), \quad (8)$$

where Eq. 8 is from the equation (7.29) and the coefficients are those evaluated from the values of the appendices 6.2 and 7.1 in Ref. 12. As $\Lambda = \lambda_{\mathrm{Na}^+} + \lambda_{\mathrm{DS}^-}$ below the cmc, λ_{DS^-} is easily evaluated. The values of λ_{DS^-} are shown in Fig. 2, and they can be expressed as

$$\lambda_{\mathrm{DS}^-} = (21.49 - 0.674\sqrt{I})/10^4 \quad (\mathrm{S\,m^2\,mol^{-1}}). \quad (9)$$

The value of 21.49 obtained by linear regression analysis is little less than the reference values (22—23×10^{-4} S m^2 mol^{-1}).[8,9]

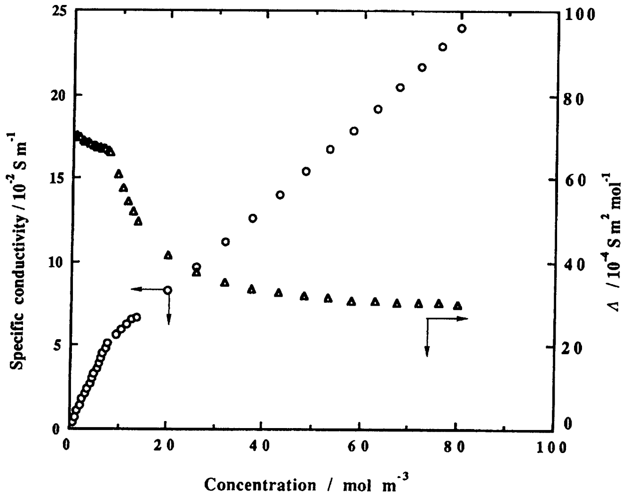

Fig. 1. Changes of specific (○) and equivalent (△) conductivities with surfactant concentration.

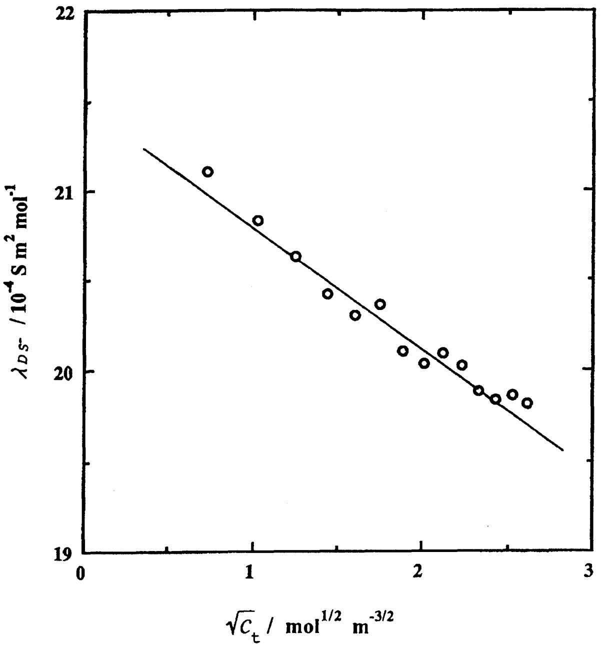

Fig. 2. Change of ionic conductivity λ_{DS^-} with surfactant concentration.

Now that the concentration changes of Na$^+$, DS$^-$, and micelle with surfactant concentration have been obtained, it is possible to divide the equivalent conductivity (Λ) above the cmc into that of each chemical species,

$$\Lambda = \lambda_{\mathrm{Na}^+}[\mathrm{Na}^+] + \lambda_{\mathrm{DS}^-}[\mathrm{DS}^-] + \lambda_\mathrm{M}[\mathrm{M}_n], \quad (10)$$

where Eqs. 8 and 9 were applied to the solutions above the cmc and the contribution of charged micelle was taken into account to calculate the ionic strength. The λ_M values thus obtained are given in Table 2 and Fig. 3. From Fig. 3 the shielding factor (0.5) of ionic micelle to the ionic strength[8] was found to have an influence of less than 10% to the ionic conductivities.

When a moving particle is lager in size compared with the surrounding solvent molecule, the Einstein–Stokes equation can be applied to the relation between the ionic conductivity of micelle with the charge z of -17.3 and its radius r:

$$\lambda_\mathrm{M} = |\, z \,|\, F^2/6\pi N\eta r, \quad (11)$$

where F is the Faraday's constant, N is the Avogadro's number, η is the viscosity coefficient of solvent. The radius of the micelle was evaluated to be 0.11—0.13 nm from the values of ionic conductivities of micelles in Table 2, which is too short to accept. On the other hand, the radius of micelle was evaluated to be 2.53 nm from its diffusion coefficient.[13] This radius is longer than the full length of DS$^-$ ion, 2.07 nm evaluated by the Tanford method[14] and from the CPK atomic model. This means that micelles move about with many solvent molecules and with counterions around them in

Table 1. Electric Conductivity Changes of Sodium Dodecyl Sulfate below the cmc at 298.2 K with Total Surfactant Concentration (C_t : Total Surfactant Concentration, I: Ionic Strength, κ : Specific Conductivity, λ : Ionic Conductivity)

C_t	$\sqrt{I}$	κ	λ_{Na^+} [a)]	λ_{DS^-}
$\mathrm{mol\,m^{-3}}$	$\mathrm{mol^{1/2}\,m^{-3/2}}$	$\mathrm{10^{-2}S\,m^{-1}}$	$\mathrm{10^{-4}\,S\,m^2\,mol^{-1}}$	$\mathrm{10^{-4}\,S\,m^2\,mol^{-1}}$
0.529	0.727	0.3723	49.27	21.11
1.051	1.025	0.7333	48.93	20.84
1.566	1.251	1.085	48.67	20.63
2.075	1.440	1.429	48.46	20.42
2.576	1.605	1.766	48.27	20.30
3.072	1.753	2.103	48.10	20.37
3.561	1.887	2.423	47.95	20.10
4.044	2.011	2.743	47.81	20.03
4.521	2.126	3.063	47.67	20.09
4.992	2.234	3.373	47.55	20.02
5.457	2.336	3.676	47.43	19.88
5.916	2.432	3.973	47.32	19.84
6.370	2.524	4.273	47.22	19.86
6.818	2.611	4.563	47.12	19.81

a) From Eq. 8.

Table 2. Concentration Changes of Counterion [Na^+], Surfactant Ion [DS^-], and Micelle [M_n] and of Specific Conductivity (κ) with Total Surfactant Concentration above the cmc, and Corresponding Electric Conductivity Changes

C_t	[Na^+]	[DS^-]	[M_n]	I	κ	λ_{Na^+}	λ_{DS^-}	λ_M
$\mathrm{mol\,m^{-3}}$	$\mathrm{mol\,m^{-3}}$	$\mathrm{mol\,m^{-3}}$	$\mathrm{mol\,m^{-3}}$	$\mathrm{mol\,m^{-3}}$	$\mathrm{10^{-2}S\,m^{-1}}$	$\mathrm{10^{-4}S\,m^2\,mol^{-1}}$	$\mathrm{10^{-4}S\,m^2\,mol^{-1}}$	$\mathrm{S\,m^2\,mol^{-1}}$
13.49	8.859	7.174	0.0987	22.75	6.701	44.66	18.27	0.145
19.84	10.12	6.547	0.208	39.41	8.221	42.93	17.26	0.132
25.95	11.37	6.001	0.312	55.27	9.711	41.62	16.48	0.128
31.82	12.61	5.529	0.411	70.43	11.17	40.52	15.83	0.126
37.48	13.85	5.123	0.506	85.03	12.59	39.58	15.27	0.125
42.93	15.08	4.778	0.596	98.91	14.00	38.75	14.78	0.125
48.19	16.29	4.488	0.683	112.4	15.36	38.00	14.34	0.125
53.26	17.49	4.248	0.766	125.2	16.67	37.33	13.95	0.125
58.16	18.68	4.052	0.845	137.5	17.95	36.72	13.58	0.125
62.89	19.86	3.898	0.922	149.5	19.20	36.16	13.25	0.125
67.46	21.01	3.781	0.995	161.0	20.48	35.62	12.94	0.126
71.88	22.16	3.698	1.065	171.9	21.68	35.14	12.65	0.126
76.17	23.29	3.645	1.133	182.6	22.88	34.68	12.38	0.127
80.03	24.32	3.622	1.194	192.2	23.98	34.28	12.14	0.127

the form of ionic atmosphere. The above experimental dynamic radius and the micellar charge can also make us estimate the ionic micellar conductivity of micelle, $62.9\times10^{-4}\ \mathrm{S\,m^2\,mol^{-1}}$, which is only about 5% of the experimentally evaluated values in Table 2. This value is also unacceptable.

Next problem is to solve the above two inconsistencies or how to establish a reasonable concept to accept on the ionic conductivity of ionic micelles. High specific conductivity of metal is due to free electrons moving about metal atoms, which suggests some hint on higher conductivity of ionic micelles. In other words, some counterions can move freely from one micelle to the other micelle through the overlapping of diffuse double layers around micelle when two micelles come close together. This phenomenon has been termed the hopping reaction of counterion in order to establish the mechanizm of electron transfer reactions in ionic micellar system.[15)] The rate constant k_h of the following reaction was found to be $2.6\times10^9\ \mathrm{M^{-1}\,S^{-1}}$ at ambient temperature.

$$Eu^{2+}M_1 + M_2 \xrightarrow{k_h} M_1 + Eu^{2+}M_2, \qquad (12)$$

where $Eu^{2+}M$ is the micelle associated with an Eu^{2+} ion and M_1 and M_2 are different NaDS micelles. The rate constant k_h for Na^+ ion should be larger than the above value, because the monovalent counterion is easier to escape from the micelle than the divalent counterion due to less electrostatic interaction with the micelle. In this discussion, then, the rate constant was assumed to be $3.0\times10^9\ \mathrm{M^{-1}\,S^{-1}}$. If the rate constant was simply

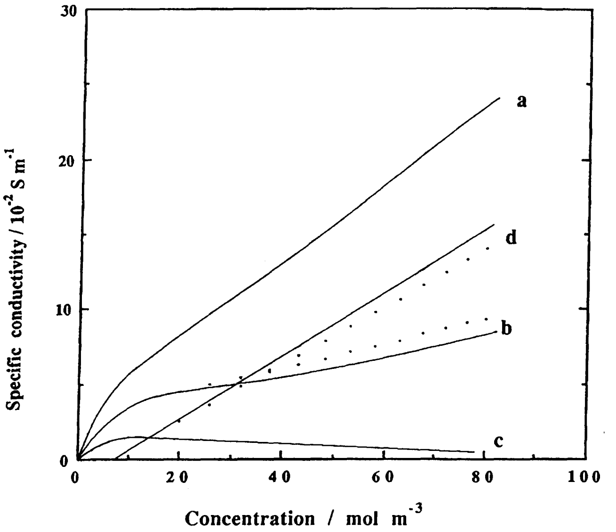

Fig. 3. Changes of specific conductivity (a) and of ionic conductivities of counterion (b), surfactant ion (c), and micelle (d) with surfactant concentration, where dots are in the case of shielding factor 0.5 of ionic micelles to ionic strength.[8]

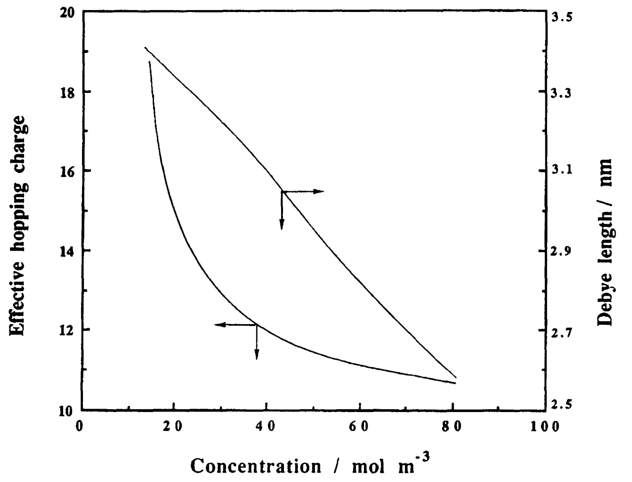

Fig. 4. Changes of effective hopping charge of micelle and of the Debye length around micelle with surfactant concentration.

interpreted from molecular point of view, the constant turns to be 5.0×10^{-15} molecule^{-1} S^{-1}. Now it becomes possible to calculate the number f of the hoppings per second which take place when each micelle comes near to other micelles above the cmc, because the micellar concentration is known. On the other hand, the average distance l over which Na$^+$ moves at each hopping can be assumed to be an average distance between micelles. The l value is also possible to evaluate from the micellar concentrations. Then, the average displacement per second or the average velocity of Na$^+$ ion, u, in one direction can be evaluated from the following equation based upon the displacement by diffusion:

$$u=\sqrt{fl^2/3} \tag{13}$$

At the same time, the ionic conductivity of an ion with charge z' is expressed in combination with the velocity of ion as follows:

$$\lambda_{\mathrm{M}}=z'Fu. \tag{14}$$

Now, from the values of λ_{M}, the effective charge of the micelles for the hopping reaction can be estimated. They are shown in Fig. 4 together with the Debye length ($1/\kappa$, thickness of ionic atmosphere) around the micelles, where the monomeric surfactant ion and counterion are taken into account for the ionic strength. As the number of bound counterion per micelle is 46.7 as mentioned above, the effective hopping charge per micelle between 10 and 20 is quite reasonable. In addition, the fact that it decreases with surfactant concentration can be elucidated from the corresponding decrease in the Debye length, or decreasing overlapping between ion atmospheres around micelles. This means that outer counterions only can participate in the hopping reaction. On the other hand, the ionic conductivity of micelle decreases with micellar concentration as is usual cases (see Eqs. 8 and 9) when the distance between micelles is long, and it stays almost constant at higher micellar concentrations (Table 2). The upward deviation from the decrease means that the hopping reaction of counterions starts and remains almost constant due to nearly constant ratio of l to $1/\kappa$ (Fig. 5), when the ratio becomes less than 5, or 2.5 per micelle.

The hopping rate constant employed in the above discussion may not be strictly correct, but the results obtained are quite reasonable. This fact truly indicates that the hopping reaction of the counterions among micelles is indispensable to elucidate not only electrical conductivity but also any reaction relating to counterion in ionic micellar solutions.

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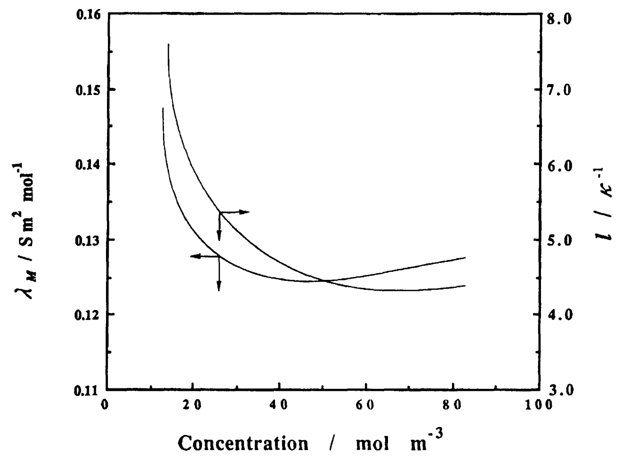

Fig. 5. Changes of ionic conductivity of micelle (λ_{M}) and of ratio of distance between micelles (l) to the Debye length ($1/\kappa$) with surfactant concentration.

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