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INTERACTION OF CHLORIDE IONS WITH NONIONIC SURFACTANT AS MEDIATED BY INORGANIC CATIONS INCORPORATED IN SURFACTANT MICELLES

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The line width $\Delta\nu^{Cl}$ of ^{35}Cl NMR was measured for n-$C_{12}H_{25}O(CH_2CH_2O)_pH$ (p = 5, 6, 7, 8) / water / XCl (X = H, Na, Li) systems. The ^{17}O NMR line width $\Delta\nu^{O}$ due to water was also examined. The broadening of $\Delta\nu^{Cl}$ by introduction of the nonionic surfactant to aqueous XCl solutions was explained by the enhanced interaction of the chloride ions with surfactant micelles to which inorganic cations were incorporated.

The critical consolute temperature at which the nonionic surfactant phase segregates in aqueous solution on temperature rise is generally referred to as " Cloud Point ", and is well known for its sensitivities to the added inorganic electrolytes.1) Such an effect of added salts has been discussed in relation to the salting-in and salting-out phenomena, in which the emphasis has so far been made mostly on the interaction between water and inorganic salts,2) and very little on the interaction among solutes. Okahara, et al.,3) have reported that potassium ions are bound by the oxyethylene group of polyethyleneglycol mono n-dodecyl ether when potassium thiocyanates and iodides are added to the solution. We have studied the interaction between the chloride anion and nonionic surfactant by ^{35}Cl NMR line half-width measurements, and wish to report here that the counter cations have the mediating effect on the interaction.

Polyethyleneglycol mono n-dodecyl ether, $C_{12}E_p$ (p = 5, 6, 7, 8), were purchased from Nikko Chemicals, and inorganic electrolytes (NaCl, LiCl, HCl) used were reagent grade. All chemicals were used without further purifications. NMR spectra were measured on a Varian FT-80 A, operating at 7.794 and 10.782 MHz for ^{35}Cl and ^{17}O, respectively.4) Deionized water was used after distillation except for ^{17}O line width measurement in which about 1 atom % ^{17}O enriched water of The British Oxygen Co. Ltd. was used. In measuring ^{17}O line width, pH of the solution was adjusted at about 12 by adding KOH to avoid line width broadening by ^{1}H exchange.5) Cloud point (CP) of the solution was determined by visual observation.

The line widths of the ^{35}Cl and ^{17}O NMR signals are governed mainly by quadrupole relaxation. The well-known equation holds for line width $\Delta\nu$ under extreme narrowing condition:[6)]

$$\Delta\nu \propto (e^2Qq)^2 \ \tau_c \qquad (1)$$

where e^2Qq and τ_c are the quadrupole coupling constant and the rotational correlation time of the molecule or ion under consideration, respectively. For nonbonded ions such as Cl^- and Na^+, the quadrupole coupling constant is markedly affected by the change in the electrical environment of the ions considered. In particular ion-pair formation and ion-dipole interaction[7)] are important. On the contrary, the line width of water ^{17}O is almost independent of the electrical environment because the quadrupole coupling constant is principally determined by the O-H covalent bond.[8)] Thus, the only factor which affects the line width of water ^{17}O is τ_c or micro viscosity of the environment of the oxygen atoms. The viscosity-corrected line width of ^{35}Cl, $\Delta\nu_c^{Cl}$ as defined by Eq. 2, reflects mainly the change in the electrical environment of the chloride ions,

$$\Delta\nu_c^{Cl} \equiv \Delta\nu_a^{Cl} \left(\frac{\Delta\nu_0^O}{\Delta\nu_s^O} \right) \qquad (2)$$

where $\Delta\nu_s^O$ and $\Delta\nu_0^O$ express the line width of water ^{17}O in an aqueous solution and that in pure water, respectively, and $\Delta\nu_a^{Cl}$ indicates the apparent line width of ^{35}Cl. The validity of this assumption will be discussed further in forthcoming paper.[9)]

Figure 1 shows the effect of the added moles of oxyethylene units on $\Delta\nu_a^{Cl}$, $\Delta\nu_c^{Cl}$, and $\Delta\nu_s^O$, observed for the $C_{12}E_p$ (0.8 mol/kg) / water / NaCl (0.8 mol/kg) system at 31 °C. The line widths increase with increaseing the number of oxyethylene units, showing that the interaction between the polar group of surfactant and chloride ions is actually taking place. Table 1 shows the effect of cationic species X on the observed $\Delta\nu^{Cl}$ for aqueous solutions containing 0.5 mol/kg XCl and 1.2 mol/kg $C_{12}E_6$ at the temperature below CP (35 and 50 °C). The degree of broadening of $\Delta\nu^{Cl}$ due to interaction of the chloride ions with nonionic surfactants is compared for several chlorides with different cations X by taking the excess quantity as expressed in the following equation,

$$\Delta\nu_{excess}^{Cl} \equiv \Delta\nu_{sc}^{Cl} - \Delta\nu_{fc}^{Cl} \qquad (3)$$

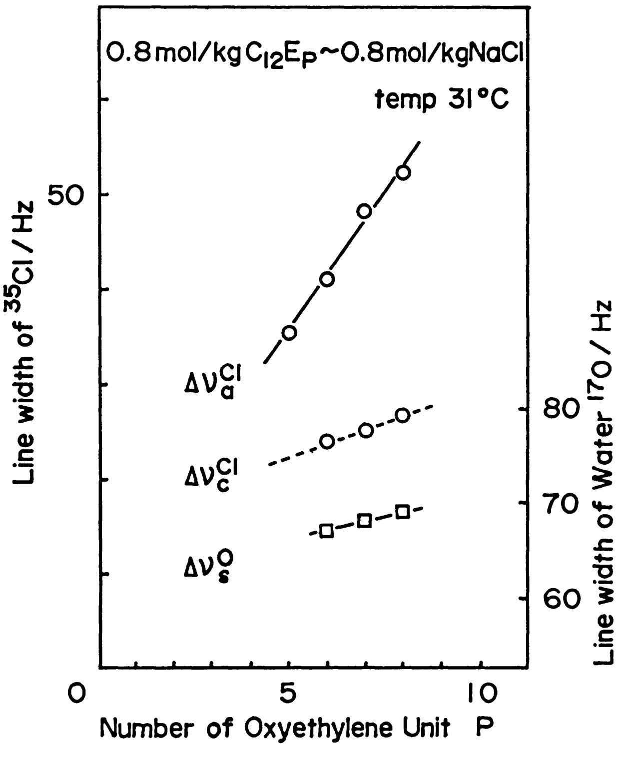

Fig.1. Interaction between (CH_2CH_2O) and Cl^-.

where $\Delta\nu^{Cl}_{sc}$ and $\Delta\nu^{Cl}_{fc}$ indicate the viscosity-corrected line width of ^{35}Cl for the aqueous solution of XCl with and without $C_{12}E_6$, respectively. As the value of $\Delta\nu^{Cl}_{sc}$ should reflect the degree of ion-surfactant interaction and may be expressed by the usual two state model, Eq. 3 is rewritten to give Eq. 4.

$$\begin{aligned}\Delta\nu^{Cl}_{excess} &\approx [\; x_b\,\Delta\nu^{Cl}_{bc} + (\,1 - x_b\,)\,\Delta\nu^{Cl}_{fc}\;] - \Delta\nu^{Cl}_{fc}\\ &= x_b\,(\,\Delta\nu^{Cl}_{bc} - \Delta\nu^{Cl}_{fc}\,) \qquad (\,4\,)\end{aligned}$$

The terms x_b and $\Delta\nu^{Cl}_{bc}$ in Eq. 4 denote the fraction and the intrinsic line width of the chloride ions bound to nonionic surfactant molecules, respectively. The $\Delta\nu^{Cl}_{excess}$ value, that is, the magnitude of interaction between the chloride ion and the nonionic surfactant, is found to vary in the order: HCl > LiCl > NaCl. Since the chloride ions are common to all XCl, the difference in $\Delta\nu^{Cl}_{excess}$ is ascribed to the effect of cations which mediates the interaction between chloride ions and surfactant molecules. The observed change in CP data (Table 1) indicates that NaCl added to the solution has the tendency of salting the surfactant out whereas HCl salts it in. LiCl seems to have the effect intermediate of the two, since LiCl gives almost no change in the CP value. (The temperature dependence of $\Delta\nu^{Cl}_{excess}$ is not discussed here, and will be argued elsewhere for wide temperature range measured.[13)])

All the results may reasonably be explained by proposing the following model (Eq. 5) in which the cations X^+ are bound to polyoxyethylene moiety of surfactant micelles ($(C_{12}E_p)_m$,[14)] as in cyclic polyoxyethylene known as crown ether.[15)] The resultant positively charged polyvalent micelles would attract chloride anions Cl^- on their surfaces and effect broadening of the NMR line width.[16)]

$$\begin{aligned}&(\,C_{12}E_p\,)_m + n\,X^+ \rightleftharpoons (\,C_{12}E_p\,)_m\,X_n^{n+}\\ &(\,C_{12}E_p\,)_m\,X_n^{n+} + q\,Cl^- \rightleftharpoons (\,C_{12}E_p\,)_m\,X_n^{n+}\,Cl_q^{q-} \qquad (\,5\,)\end{aligned}$$

The protons are considered from $\Delta\nu^{Cl}_{excess}$ values to interact with the oxyethylene unit more strongly than other cations. The salting-in phenomena caused by the addition of HCl should at least be partially rendered to the enhanced hydration

Table 1. Effect of cations on the binding of chloride ions to nonionic surfactant[10-12)]

XCl	35 °C					50 °C				
	$\Delta\nu^{Cl}_{a}$	$(\Delta\nu^{0}_{0}/\Delta\nu^{0}_{s})$	$\Delta\nu^{Cl}_{sc}$	$\Delta\nu^{Cl}_{fc}$	$\Delta\nu^{Cl}_{excess}$	$\Delta\nu^{Cl}_{a}$	$(\Delta\nu^{0}_{0}/\Delta\nu^{0}_{s})$	$\Delta\nu^{Cl}_{sc}$	$\Delta\nu^{Cl}_{fc}$	$\Delta\nu^{Cl}_{excess}$
NaCl CP ≈ 53 °C	56.3	0.551	31.0	8.5	22.5	33.0	0.650	21.5	6.5	15.0
LiCl CP ≈ 58 °C	64.6	0.563	36.4	13.2	23.2	41.6	0.650	27.0	10.5	16.5
HCl CP ≈ 63 °C	66.5	0.554	36.8	11.5	25.3	43.2	0.650	28.1	8.8	19.3

of surfactant molecules which acquired positive charge. While NaCl seems to weaken the surfactant-water interaction since the concentration of the free sodium cation, which is strongly hydrated, is higher than that of the free proton. In conclusion, it may safely be said that the binding of cations to nonionic surfactant is partly responsible for the salting-in or salting-out phenomena as well as the effect of added electrolyte on the activity of water.

References

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10) The line width $\Delta\nu$ is expressed by Hz.
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