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Anionic Surfactants with Divalent Counterions of Separate Electric Charge. III. Proton NMR Study

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The proton NMR spectra of 1-tetradecanesulfonates whose cationic counterion, the 1,1′-polymethylenedipyridinium ion (with even-numbered methylene groups up to 14), is divalent with separate electric charge, were measured. From the chemical shifts the pyridine rings were found to move about in quite hydrophilic environment of micellar surface region, leading to a downfield shift of methylene groups next to head group of surfactant ion. The chemical shifts of methylene groups of micellized counterions with more than eight methylene groups are different from those of corresponding counterions in aqueous environment and are similar to those of methylene group in hydrophobic micellar interior. These results strongly support the previous conclusion that the polymethylene group with more than eight methylene groups folds and penetrates micellar interior in their micellized state.

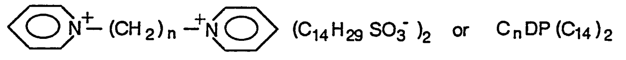
The properties of aggregates or micelles of ionic surfactants are strongly influenced by the kind of surfactant ion and counterion. Counterions of conventional anionic surfactants so far investigated have been alkali or alkaline earth metal ions, their electrical charge being localized within a very small volume. The electrical potential of such ions seems to be energetically stabilized by coulombic interaction. This leads to smaller aqueous solubility of surfactants, resulting in higher micelle temperature range[1] or higher Krafft point.[2–4] As for organic counterions, on the other hand, the counterion binding to micelles increases with its increasing hydrophobicity and promotes a micelle formation, where the size and shape of micelles are radically affected.[5–10] Surfactants with divalent counterions whose electric charge is diffuse[11] or separate,[12,13] in particular, have physicochemical properties much different from those of conventional surfactants.

In our preceding papers on anionic surfactants with divalent counterions of separate electric charge (1,1′-polymethylenedipyridinium ion, C_nDP^{2+}), the solubility and micelle formation[14] and the micellar size and surface activity[15] have been systematically studied. The conclusion was that the polymethylene chain with eight or more methylene groups folds and penetrates the hydrophobic micellar interior. However, the questions as to how deep the penetration is and where the location of pyridinium ion is still remain unsolved. One of the promising approaches to counterion binding is to employ the NMR technique.[16–18] This technique can also indicate the solubilization site of molecules in micelle in the case where they carry the π-electrons, like the couterions of ionic surfactants used in the present study.[19–24]

This paper, then, aims to solve the above two questions using the proton NMR technique and to confirm the conclusion from the preceding works by another experimental evidence.

Experimental

Materials. Anionic surfactants with divalent cationic counterions of separate electric charge, 1,1′-polymethylenedipyridinium tetradecane-1-sulfonate were the same as those used in the previous papers,[14,15] in which the surfactants were



$n = 2, 4, 6, 8, 10, 12, 14$

named as 1,1′-(1,ω-alkanediyl)bispyridinium tetradecane-1-sulfonate or $C_nBP(C_{14})_2$. C_nDPX_2 (X=Cl, Br) were kind gifts from Prof. Kuwamura's laboratory of Gunma University and were used without further purification except those which were purified by recrystallization from acetone–ethanol mixture. Water used as a solvent is D_2O from Merck Co., Ltd.

NMR Measurement. The concentration of $C_nDP(C_{14})_2$ is 0.01 mol dm^{-3} which is about 50 times cmc for three surfactants of n=2, 4, and 6, while that of C_nDPX_2 is 0.02 mol dm^{-3}. The sample solutions were sonicated for 30 min after apparent sample dissolution. As for solutions of $C_2DP(C_{14})_2$ and $C_{14}DP(C_{14})_2$ whose Krafft points are higher than the measurement temperature the recording was made before their precipitation. The chemical shift of residual HDO signal, δ=4.5, was used as the standard of the chemical shifts, because the molar ratio of water to the divalent ion of more than 2700 is so large that the effect of the divalent ion on bulk water structure can be negligible. The NMR spectra were recorded with a JEOL GX-400 p-FT NMR spectrometer at room temperature.

Results and Discussion

The proton NMR spectra of $C_nDP(C_{14})_2$ are shown in Fig 1. The NMR spectra of C_nDPX_2 are very helpful to analysing the spectra of $C_nDP(C_{14})_2$, because C_nDP are the counterions of the latter micelles and do not form micelles by themselves at the concentration of 0.02 mol dm^{-3}: The most hydrophobic counterion $C_{14}PPCl_2$ was found to form micelles around 0.02 mol dm^{-3}.[25] In other words, their chemical shifts of every ^1H bound to

Fig. 1. ^{1}H NMR spectra of $C_nDP(C_{14})_2$: **1** n=2, **2** n=4, **3** n=6, **4** n=8, **5** n=10, **6** n=12, **7** n=14.

carbon atom are those in a very hydrophilic or an aqueous environment. The chemical shifts of C_nDPX_2 are analyzed from their intensity and position, and assigned as shown in Table 1. The chemical shifts of the ^{1}H atoms in pyridine ring are spread in the lower field as expected from the effect of π-electrons, and those of the hydrogen atoms of methylenes near the pyridine ring are found also to be influenced by the electrons as is clear from the lower chemical shifts of $=N-CH_2-$ and adjacent $-CH_2-$. The chemical shifts of ^{1}H of methylene chain in aqueous environment are 0.88—0.99 ppm.

The chemical shifts of the surfactants are also analyzed on the same ground as those of C_nDPX_2. The results are given in Table 2. More than 90% of the couterions are supposed to be bound to micelles[15] and, therefore, the spectra can be said to represent their bound state. As far as ^{1}H atoms in pyridine ring are concerned, their chemical shifts are almost the same as those of C_nDPX_2, which suggests that the cationized rings remain in an aqueous environment in micellized state. These are quite different from the chemical shifts in hydrophobic environment, for example, 8.95, 8.58, and 8.13 ppm for the α-, γ-, and β-H atoms in cyclohexane.[26] The rings connected by the longer methylene chain have been expected to be drawn toward less hydrophilic region of inner micelle, but it has turned out from the results that this is not the case. In other words, the region of micellar surface where the rings are located is very hydrophilic aqueous environment. In Fig. 2 are illustrated the difference in the chemical shifts by deducting the chemical shifts in Table 1 from those in Table 2. It is worth to mention that the down-field shift in the pyridine ring increases in the order $\alpha > \gamma > \beta$. At the same time, the enhanced down-field shift of every methylene group in polymethylene chain clearly results from concentration of pyridine rings due to micelle formation. As for PM_1, its variation is quite similar to the variation of micelle aggregation number,[15] which indicates that methylene protons of PM_1 are very sensitive to a manner of packing of surfactant ions.

The proton chemical shifts of terminal methyl and other methylenes of surfactant ion, which are referred to M_1, M_2, M_3, M_4, and M_5, change quite gradually from ca. 0.5 to 2.5 ppm. The classification of methylene groups of the alkyl chain as M_1, M_2, M_3, M_4, and M_5 is made from the chemical shifts for sodium 1-dodecanesulfonate micelles. The proton chemical shift of ca. 0.5 ppm of M_1 in inner micelle region is much smaller than the chemical shift ca. 1 ppm in aqueous environment and those of outer micellar region. The ratio of the chemical shift of M_5 to that of M_1, 5.0 is

Table 1. ^{1}H NMR Chemical Shifts of C_nDP (δ/ppm)

Compound	Pyridinium			Polymethylene			
	α	γ	β	PM_1	PM_2	PM_3	PM_4
1	8.60	8.43	7.87	5.06	—	—	—
2	8.55	8.27	7.78	4.27	1.67	—	—
3	8.55	8.25	7.77	4.27	1.68	1.05	—
4	8.56	8.25	7.77	4.30	1.68	0.99	—
5	8.53	8.25	7.77	4.33	1.69	0.98	0.93
6	8.55	8.25	7.78	4.32	1.69	0.98	0.91
7	8.55	8.25	7.75	4.30	1.68	0.98	0.88

$>N-CH_2-CH_2-(CH_2)_n-(CH_2)_m-(CH_2)_n-CH_2-CH_2-N<$
PM_1 PM_2 PM_3 PM_4 PM_3 PM_2 PM_1
n=1,2 for PM_3 m=2,4,6 for PM_4

Table 2. ^{1}H NMR Chemical Shifts of $C_nDP(C_{14})_2$ (δ/ppm)

Compound	Pyridinium			Polymethylene				M_5	M_4	M_3	M_2	M_1
	α	γ	β	PM_1	PM_2	PM_3	PM_4					
0′	—	—	—	—	—	—	—	2.66	1.57	1.13	1.07	0.67
1′	8.63	8.29	7.82	5.09	—	—	—	2.50	1.44	0.97	0.91	0.51
2′	8.63	8.23	7.78	4.54	1.87	—	—	2.47	1.43	1.03	0.90	0.50
3′	8.64	8.28	7.81	4.38	1.72	1.12	—	2.50	1.43	1.06	0.89	0.50
4′	8.65	8.26	7.82	4.38	1.69	1.08	—	2.50	1.43	0.93	0.92	0.52
5′	8.63	8.27	7.81	4.43	1.73	1.06	1.00	2.50	1.46	0.91	0.91	0.51
6′	8.65	8.26	7.82	4.43	1.74	1.04	0.96	2.38	1.49	0.91	0.91	0.51
7′	8.67	8.25	7.79	4.48	1.74	1.04	0.96	2.38	1.47	0.91	0.91	0.52

0′: $\underset{M_1}{CH_3}\text{–}\underset{M_2}{(CH_2)_8}\text{–}\underset{M_3}{CH_2}\text{–}\underset{M_4}{CH_2}\text{–}\underset{M_5}{CH_2}\text{–}SO_3^-Na^+$

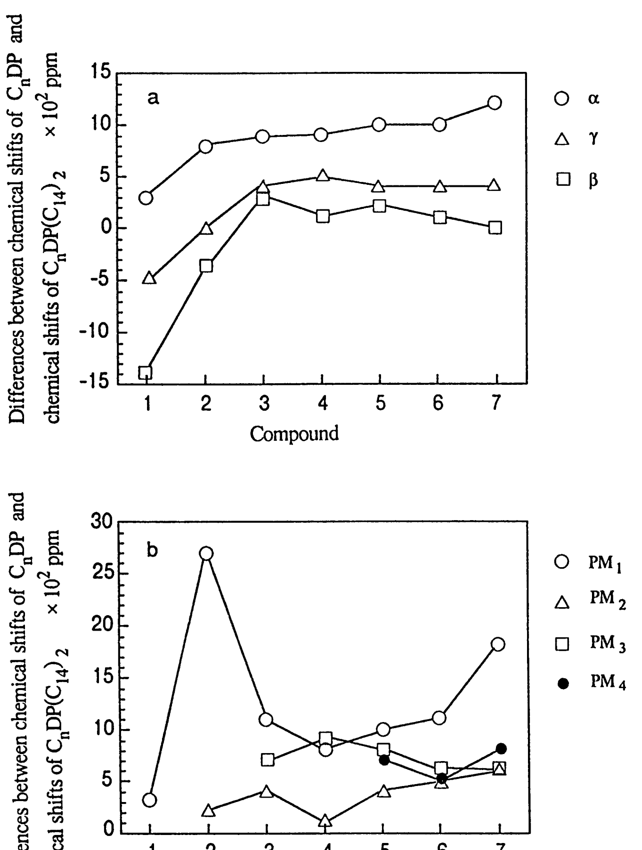


Fig. 2. The difference in the chemical shifts of counterions (a) pyridine protons, (b) polymethylene protons.

larger than that of sodium 1-dodecanesulfonate micelles, 4.0.[27] The higher ratio is due to the effect of the π-electrons of the counterions. These findings indicate the moving about of pyridine rings around the miceller surface region. The chemical shift (δ=0.96—1.08) of methylene groups (PM_3 and PM_4) of the counterions ($n \geqslant 8$) in micellized state are similar to those of methylene groups (M_2 and M_3) of surfactant ion. This suggests that PM_3 and PM_4 methylenes of counterions and M_2 and M_3 methylenes of surfactant ion are located in a similar hydrophobic environment.

The present results by ^{1}H NMR study strongly support the previous result that the polymethylene group with more than eight methylene groups folds and penetrates the hydrophobic micellar interior.

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