The Dependence on Alkyl Chain Length of ^{1}H NMR Spectra of Surfactant Micelles with Aromatic Solubilizate

Takashi HOSHINO*,† and Yoshio IMAMURA
Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162
(Received April 5, 1989)

The splitting of methylene peaks in the ^{1}H NMR spectra of surfactants of various alkyl length was studied in aqueous solutions solubilized with aromatic compounds, as a function of the carbon numbers of alkyls. In these spectra the methylene signals of long alkyls split into doublets. The location of the solubilization site is discussed while comparing the results with previous ^{1}H NMR observations of long-alkyl-substituted molecules in aromatic solvents.

Among the spectroscopic studies on the microstructures and properties of the interiors of micellar aggregates in aqueous surfactant mixtures, there have recently been reported several studies involving NMR spectroscopy. Bunton et al.[1] and Grazel et al.[2] independently studied the ^{1}H NMR spectra of hexadecyltrimethylammonium bromide (CTAB). The signals of methylene protons of CTAB appeared as a singlet peak in the aqueous micelle, and split into a doublet upon the addition of aromatic solubilizate. Fendler et al.[3] reported a similar phenomena in the aromatic solubilizated micelles of sodium 1-dodecylsulfate (SDS). Miyagishi et al.[4] found that a doublet peak is observed for SDS micelles only for a solubilizate having a moderate hydrophobic-liophobic balance. For an interpretation of these experimental observations, it was suggested that an aromatic solubilizate was preferentially located parallel to the surfactant molecules in the palisade portion of the micelle; consequently, the splitting of the methylene signal in the ^{1}H NMR spectra could be ascribed to shielding by the large diamagnetic susceptibility of the aromatic ring of the solubilizate.

The present authors studied the splitting of methylene signals of the ^{1}H NMR spectra for a series of methyl alkanoates in aromatic solvents and determined the aromatic solvent-induced shift (ASIS) of the methylene protons for methyl alkanoates as a function of the chain length.[5] In this paper the authors describe the dependence of the methylene NMR spectra for the surfactant molecules with solubilized aromatic compounds on its alkyl chain length, and compare the results of previous studies concerning solutions; they also discuss the solubilization site in the interior of the micelles.

Experimental

As surfactant substances alkyltrimethylammonium bromides, sodium alkanesulfonates, and sodium alkanoates were applied in this study. These substances contain long alkyl groups with carbon number, n_c, from 6 to 18. All reagents used were commercial and of highest grade.

The samples for NMR measurements were prepared in D_2O solutions with a surfactant content of 0.5, 0.2 mol dm^{-3} or saturated. In every case the content of the surfactant was maintained much higher than the critical micellar concentration (cmc). Aromatics such as phenol, benzyl alcohol, and 1-chloronaphthalene were solubilized by surfactants. The contents of the aromatics in a D_2O solution were about 0.5 mol dm^{-3}, at which the chemical shift was almost constant and independent of the contents of the solubilizate.[6,7]

Measurements of the NMR spectra were performed using a JEOL JNM FX-100 FT NMR spectrometer operating at 100 MHz, at ambient temperature. Chemical shifts referred to the terminal methyl protons as the intramolecular standard, since the relative chemical shift between the split peaks was important in studying the surfactant systems. Although, the chemical shift of terminal methyl was slightly shifted relative to the external TMS or a trace DHO reference, upon the addition of aromatic solubilizates it was considered to be almost constant for any discussion of the relative shifts in the present study.

Results

In Fig. 1a, 100-MHz ^{1}H NMR spectra of a series of sodium n-alkanoates in D_2O with benzyl alcohol are shown as a typical example. Numeral letters in this figure indicate the total number of carbons, n_c, in long alkyl chains. Triplet peaks at higher fields were assigned to their terminal methyl protons and the rest to methylene protons. The small peaks at the lowest field were assigned to β-methylene protons. These peaks shifted to a higher field relative to the methyl peak with an increase in n_c and were concealed in a methylene envelope at $n_c \geq 14$. α-Methylene peaks, which appeared at lower field, are not shown in Fig. 1a. A singlet peak of the remaining methylenes (r-methylenes) was observed for sodium octanoate (n_c=8) and sodium decanoate (n_c=10). For sodium dodecanoate (n_c=12), a doublet peak was observed, although the lower-field split peak was much weaker than the higher-field peak. The intensity of the split peak at lower fields increased with the chain length relative to that of the higher field. Similar spectral changes were observed for sodium alkanoates in a phenol solubilizate system.

† Present address: Material Development Department, 2nd Group, Isuzu Motors Limited, Tutidana, Fujisawa, Kanagawa 252.

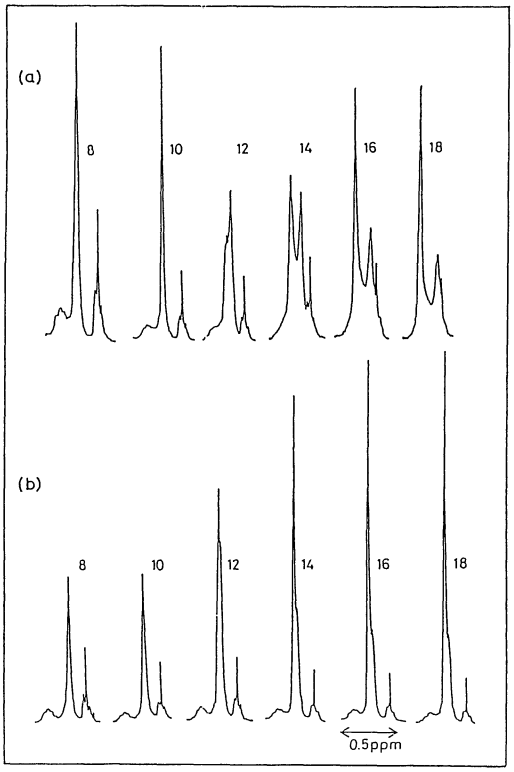

Fig. 1. 100 MHz ^{1}H NMR spectra of the series of sodium alkanoates in D_2O with benzyl alcohol as a solubilizate (a) and the series of methyl alkanoates in C_6D_6 (b).

The behavior of the ^{1}H NMR spectra for sodium alkylsulfonates with phenol or benzyl alcohol was quite similar to that for sodium alkanoates. A singlet peak of r-methylenes was observed for sodium 1-hexanesulfonate (n_c=6) and 1-octanesulfonate (n_c=8). A splitting of the methylene signal was observed for sodium 1-decanesulfonate (n_c=10). For compounds with longer alkyls, the intensity of the lower-field split peak increased relative to that of higher field with increasing chain length.

When alkyltrimethylammonium bromides (cationic surfactants) were used, no splitting of the methylene signal was observed upon the solubilization of phenol. However, splitting was observed upon the addition of 1-chloronaphthalene instead of phenol; thus, this solubilizate was used thereafter for this case. In the system of cationic surfactant/1-chloronaphthalene/D_2O, the splitting was similar to that for anionic surfactants, although the line broadening was greater than those observed in the case of the anionic surfactants mentioned above. In this series, a singlet peak of r-methylenes was observed for compounds with alkyl chains of 8 and 10 carbon atoms. For the compounds of $n_c \geq 12$, split methylene peaks were observed. The increase in the intensity of the lower field peak with the alkyl chain length relative to that of the higher-field peak was also observed. However, the width of these peaks increased to a greater extent with the chain length than that observed in the cases of anionic surfactants.

In Table 1 the smallest carbon numbers, $\langle n_c \rangle$ in alkyls, where the splitting of the methylene signal was observed, are listed for several compounds with long alkyl groups in micelle and together with the alkyl compounds in aromatic solvents.[5,8,9] Such splittings are commonly observed for compounds with an alkyl carbon number greater than 12. Exceptional examples are found in methyl alkanoates and normal alkanes in 1-chloronaphthalene solutions. In the former solution, the methylene signal splits into a doublet at $n_c \geq 12$ and into a triplet at $n_c \geq 20$.[5] In the latter case, no splitting was observed for n_c less than 18.[9]

Figure 2 shows the chemical shifts relative to the terminal methyl proton of sodium alkanoates and sodium alkanesulfonates with solubilized benzyl alcohol as a function of the total carbon numbers of alkyls, n_c. A similar result was obtained for a phenol solubilized system. For these two anionic surfactants, there are no differences in spectral appearance.

Table 1. The Smallest Carbon Numbers in Alkyl Chain, $\langle n_c \rangle$, where the Splitting of Methylene Proton Signal was Observed

Surfactant	Solubilizate	$\langle n_c \rangle$	Ref.
Sodium alkanoate	Benzyl alcohol	12	a)
	Phenol	12	a)
Sodium alkanosulfonate	Benzyl alcohol	10	a)
	Phenol	10	a)
Alkyltrimethylammonium bromide	1-ClNap[b]	12	a)
	Phenol	None	a)
Solute	**Solvent**		
Methyl alkanoate	1-ClNap[b]	12, 20[c]	5
	Benzene	12	5
Normal alkane	1-ClNap[b]	18	8
	Benzene	None	9

a) Present investigation. b) In 1-chloronaphthalene. c) The methylene signal of the compound with longer side chain than n_c=20 was split into triplet.

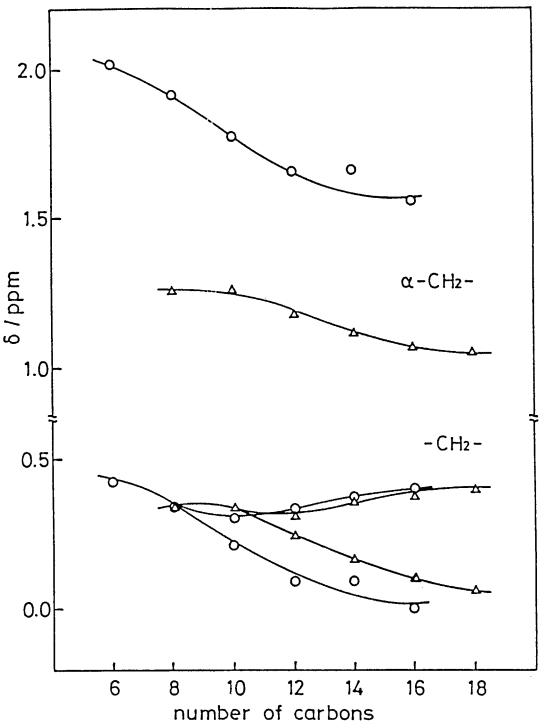

Fig. 2. Plots of the ^1H chemical shifts vs. carbon numbers, n_c, in alkyls of sodium alkanoates (△) and sodium alkylsulfonates (○) in D_2O with benzyl alcohol.

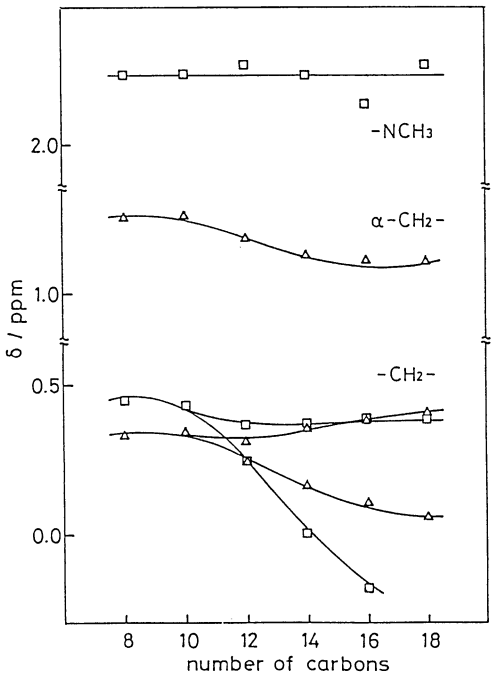

Fig. 3. Plots of the ^1H chemical shifts vs. n_c for sodium alkanoates in D_2O with benzyl alcohol (△) and for alkyltrimethylammonium bromides in D_2O with 1-chloronaphthalene (□).

Figure 3 shows a comparison between a cationic surfactant, alkyltrimethylammonium bromides and an anionic surfactant, sodium alkanoates. Since the

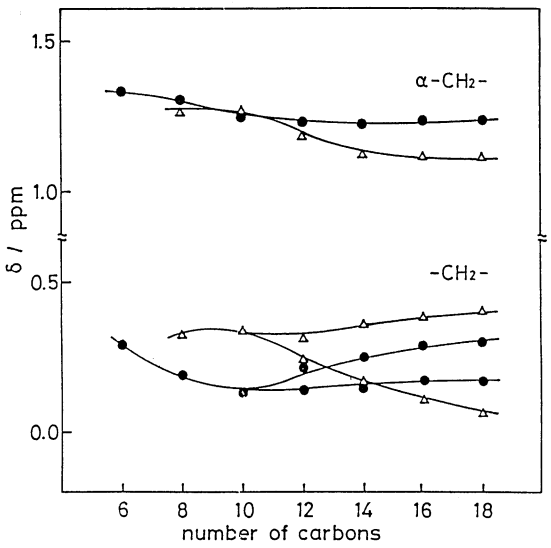

Fig. 4. Plots of the ^1H chemical shifts vs. n_c for sodium alkanoates in D_2O with solubilized benzyl alcohol (△) and methyl alkanoates in 1-chloronaphthalene (●).

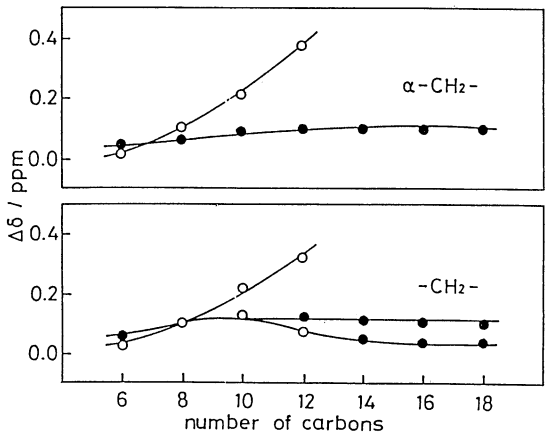

Fig. 5. Plots of differences of ^1H chemical shifts for sodium alkanoates in D_2O with and without benzyl alcohol (○), and for methyl alkanoates in $CDCl_3$ and 1-chloronaphthalene (●).

α-methylene peak in alkyltrimethylammonium bromide could not be observed distinctly, ^1H chemical shifts for methyl protons in the polar head group are shown.

Figure 4 shows the variation in the chemical shift of sodium alkanoates in D_2O with solubilized benzyl alcohol and those of methyl alkanoates in 1-chloronaphthalene solutions as a function of the alkyl carbon numbers. In both casees, splitting of the methylene signals was observed for long alkyl chains, and the doublet peak at higher fields behaved similarly to the α-methylene signal with respect to the chain length. The separation width of the doublet peaks of methyl alkanoates in an aromatic solvent was much smaller than that observed in the micelle system.

Figure 5 shows the induced shifts for surfactants

by aromatic solubilizate and aromatic solvent-induced shifts. The induced shifts for surfactants denote the difference of the chemical shift for a surfactant molecule, with and without the aromatic solubilizate. ($\Delta\delta_m$=δ(without solubilizate)$-\delta$(with it)) ASIS (aromatic solvent induced shift) denotes the differences in the chemical shifts of a solute molecule in an aromatic solvent and in $CDCl_3$ ($\Delta\delta_s$=$\delta(CDCl_3)-\delta$(aromatic solvent)); these chemical shifts referred to the terminal methyl protons as the intramolecular standard.

Discussion

The peak-splitting phenomena of the methylene signals of the ^{1}H NMR pectra were also reported for normal alkanes[8] and methyl alkanoates[5] in aromatic solvents. There was no appreciable difference in the smallest alkyl carbon numbers, $<n_c>$, where the splitting was observed in surfactants and alkyl chain derivatives. Other similarities between aromatic solubilized micelles and the long alkyl derivatives in aromatic solvents were observed for both the concentration dependence[3,4] and the temperature dependence of the NMR spectra.[4,5,10-13] The marked difference in the spectra of the alkyl compounds in an aromatic solvent and surfactant molecules with an aromatic solubilizate is twofold. In micelles, the spectral shape of the methylene peaks is broader than in the case of an aromatic solvent and the separation of the split peaks is much larger in the former case than in the latter. The ^{1}H NMR spectra of a series of methyl alkanoates in benzene solutions are shown in Fig. 1b.

The sepparation of split peaks was much greater in micelles than in solutions. For example, at n_c=12, the separation for the micelle was about 4-times larger than that for the solution. In solutions, a solute molecule is surrounded by several solvent molecules. However, the content of aromatics solubilized in the micelle is much smaller. It was reported that eight molecules of 5-chlorobenzoxazolidone were solubilized in one hexadecyltrimethylammonium bromide micelle, e.g. one 5-chlorobenzoxazolidone is solubilized by 7.63 surfactant moleccules.[14] Thus, for the surfactant systems the larger effect was indicated, in spite of smaller numbers of surrounding aromatics. The differences in the spectral appearance in the two systems may be attributed to an inhomogeneity in the distribution of aromatic solubilizate in the micelles, rather than to a difference in the microdynamic mobility of alkyl groups between the solutions and micelles.

Figure 3 shows a comparison between cationic and anionic surfactants. It was reported that the peak splitting of methylenes was observed for SDS micelles, only when the solubilizate had a moderate hydrophobic-liophobic balance.[4] In addition, 1-chloronaphthalene is least soluble in the system. Thus, measurements for an SDS/1-chloronaphthalene/D_2O system were not performed. A detailed comparison between anionic and cationic surfactant systems is impossible, since the components are different from one other in these systems. However, it is important to show that the peak-splitting mechanism in both anionic and cationic surfactant systems would be identical. In the case of ASIS phenomena in solution, the difference between 1-chloronaphthalene and other aromatic solvents could almost be completely ascribed to a difference in the magnitude of the magnetic anisotropy.[15] The difference in cationic and anionic surfactants is that the separation between the split peaks in the former is larger than that in the latter. The origin of this difference may be attributed to the larger magnetic anisotropy of the naphthalene ring and to the larger interaction between the aromatic solubilizate and the polar head group of the surfactants. This interaction is larger for cationic than for anionic surfactants.[16] In anionic surfactants, the chemical shifts of α-methylene peaks varied depending on the alkyl carbon numbers. In alkyltrimethylammonium bromide, the chemical shifts of the methyl peaks of the polar head group do not depend on the chain length; this fact was attributed to the solubilization of the aromatics in the inner hydrophobic part of the micelle.

Ulmius et al.[17] and Miyagishi and Nishida[18] reported the assignment of the split methylene signals of the NMR spectra in CTAB and SDS, respectively. In the present study, assignments were performed for the r-methylene peaks of the surfactants of various chain length, based on the intensities of the split peaks. The results are shown in Table 2. There are some small differences in the numbers of the methylenes assigned to the high-field peaks. The numbers were approximately constant within the range of 3 to 5, while the total methylene length varied from 10 to 18. The number of the methylene assigned to the higher-field peak corresponds to the shielded part of the alkyl chain more strongly than other protons as a results of the magnetic anisotropy produced by the aromatic solubilizate. The length of these affected methylenes measured from the micelle surface is approximately 10 Å (about 6 methylene units near the polar head group, which includes α and β methylenes and 4 methylene units assigned to higher peak); this roughly agreed with the size of phenol or benzyl alcohol molecules, which presumably accessed to the polar end of the surfactant.

For the split r-methylene peaks of methyl alkanoates in solution, the aromatic solvent-induced shifts were almost independent of the chain length. These solute molecules are almost equally affected by the ASIS effect, regardless of any change in the chain length. Regarding the induced shifts for surfactant molecules, a stronger dependence on the chain length than the ASIS for methyl alkanoates was observed, especially for the α-methylene peaks and higher-field split peaks. Figure 5 shows that the ASIS contributes

Table 2. The Number of the Methylene Unites Assigned to Higher- and Lower-Field Split Peaks

Surfactant Solubilizate	Sodium alkanoate				Sodium alkanosulfonat				C_nTA Br[a] ClNAP[d]		Me $C_n$ate[b] Benzene	
	BZAL[c]		Phenol		BZAL[c]		Phenol					
n_c	High	Low	High	Low	High	Low	High	Low	High	Low	High	Low
10	—	—	—	—	4.1	2.9	4.5	2.5	—	—	—	—
12	4.6	3.4	5.1	2.9	4.5	4.5	5.2	3.8	4.8	4.2	3.9	4.1
14	4.7	5.3	5.2	4.8	3.4	7.6	4.6	6.4	5.4	5.6	2.9	7.1
16	3.7	8.3	3.9	8.1	4.9	8.1	—	—	3.7	7.3	2.7	9.3
18	3.4	10.9	4.0	10.0	—	—	—	—	5.2	9.8	2.9	11.1

a) Alkyltrimethylammonium bromide. b) Methyl alkanoate in benzene solution. c) Benzyl alcohol. d) 1-Chloronaphthalene.

more effectively for the surfactant with a longer chain length. This suggests that the difference in the shielding effects at the inner core and neighbor of the surface of the micelle varies with the chain length. The solubilized content of aromatics, association number of micelle, and so on changed with the chain length, though the solubilization site is not considered to change with the chain length since the numbers of the methylene units in the shielded part were almost independent of the total chain length, as indicated in Table 2. In general, the solubilized content increases with the chain length and more aromatics are considered to be solubilized near the polar head groups. Thus, for longer chain lengths the methylenes close to the polar head group are more shielded than are the inner methylenes.

As described in the previous sections, the appearance of the methylene peak splitting in the NMR spectra in both surfactant and aromatic solubilizate systems does not necessarily indicate a concentrated distribution of the solubilizate around surfactant molecules, since the splittings are observed in homogeneous aromatic solutions, such as methyl alkanoates in benzene. In these homogeneous phases, small differences in the preference of the orientation of the aromatic molecules for polar groups and the methylene part of the solute molecules, induces peak splitting in the r-methylene spectra, as has already been reported. The phenomena of the splitting of the r-methylene peaks are common to aromatic solutions and surfactant systems. However, surfactant systems yield much larger separations and broadening of the split peaks compared to aromatic solutions. This larger separation of the split peaks can be explained in the context of an inhomogeneous distribution of the aromatics in micelles. The inhomogeneity in micelles must be promoted by an increase in the alkyl chain length of surfactants. This interpretation would be supported by the fact that the induced shifts for the surfactants depends on the chain length, while the induced shifts for the aromatic solutions exhibit no dependence on the chain length.

Conclusion

It was found that the splitting of the methylene peaks of the NMR spectra observed in micelles with aromatic solubilizates is induced by a magnetic anisotropy produced by aromatic molecules, similar to that found in a homogeneous solution. However, the larger separation of the split peaks and marked dependence of the induced shifts for α- and higher-split methylene peaks on the chain length of the surfactant molecules indicate a condensed distribution of aromatic solubilizates at the polar end of the alkyl chains within the micelles.

References

1) C. A. Bunton, M. J. Minch, J. Hidalgo, and L. Sepulveda, *J. Am. Chem. Soc.*, **95**, 3262 (1973).
2) M. Grazel, K. Kalyanasundam, and J. K. Thomas, *J. Am. Chem. Soc.*, **96**, 7869 (1974).
3) J. H. Fendler, E. J. Fendler, G. A. Infante, P. -S. Shih, and L. K. Patterson, *J. Am. Chem. Soc.*, **97**, 89 (1975).
4) S. Miyagishi and M. Nishida, *J. Colloid Interface Sci.*, **73**, 270 (1980).
5) T. Hoshino and Y. Imamura, *Bull. Chem. Soc. Jpn.*, **61**, 2957 (1988).
6) E. Kolehain, *J. Colloid Interface Sci.*, **105**, 273 (1985).
7) E. Kolehain and R. Laatikainen, *J. Colloid Interface Sci.*, **121**, 148 (1988).
8) K. J. Liu, *J. Polym. Sci., Part A-2*, **5**, (1967).
9) K. J. Liu, *Polymer*, **10**, 951 (1969).
10) K. J. Liu, *J. Polym. Sci., Part A-2*, **6**, 947 (1968).
11) I. Ando and A. Nishioka, *Kobunshi Kagaku*, **29**, 306 (1970).
12) J. Matumoto, I. Ando, A. Nishioka, and H. Tanaka, *Report Prog. Polym. Phys. Jpn.*, **21**, 429 (1978).
13) M. A. Winnik, A. Mar, W. F. Reynolds, Ph. Dais, B. Clin, and B. Caussade, *Macromolecules*, **12**, 257 (1979).
14) C. J. Chen and S. G. Frank, *J. Colloid Interface Sci.*, **92**, 396 (1983).
15) J. Fernandez Bertran and M. Rodriguez, *Org. Magn. Reson.*, **21**, 6 (1983).
16) P. Mukerjee and J. R. Cardinal, *J. Phys. Chem.*, **82**, 1620 (1978).
17) J. Ulmius, B. Lindman, G. Lindblom, and T. Drakenberg, *J. Colloid Interface Sci.*, **65**, 88 (1978).
18) S. Miyagishi and M. Nishida, *J. Colloid Interface Sci.*, **78**, 195 (1980).