Phase structural studies of the bi-tail type surfactant-water systems

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Hirohito Hirata
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Thesis

Nagoya Institute of Technology, Material Science and Engineering, Gokiso-cho, Showa-ku, Nagoya, Japan
List of papers

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1. Phase diagrams and phase structures of identical and mixed chain lithium di-n-alkyl phosphate-water binary systems. Asymmetric molecular shape effect
   H. Hirata, K. Maegawa, T. Kawamatsu, S. Kaneko, H. Okabayashi
   Colloid & Polymer Science, in press

2. Phase diagram and phase structure of the sodium di-n-pentyl phosphate-water system.
   $^1$H pulsed-gradient NMR self-diffusion, $^{31}$P NMR and x-ray diffraction studies
   H. Hirata, S. Aoki, K. Taga, H. Okabayashi, T. Yoshida, T. Kawakatsu
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3. Raman scattering spectra of sodium n-butyl(n-hexyl) phosphate aggregates and conformation about the phosphodiester P-O bonds in coagel phases
   H. Okabayashi, H. Hirata, Y. Suzuki, K. Taga, C. Mathew
   Vibrational Spectroscopy, in press

4. A small angle neutron scattering study of the ethyl(n-octyl) phosphate micelles in water
   H. Hirata, S. Katayama, H. Okabayashi, M. Furusaka, T. Kawakatsu
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5. A small angle neutron scattering study of the sodium di-n-pentyl phosphate micelles in water
   H. Hirata, H. Okabayashi, M. Furusaka, T. Kawakatsu
   Colloid & Polymer Science, in press

6. Small-angle neutron scattering study of bis(quaternary ammonium bromide) surfactant micelles in water. Effect of the spacer chain length on micellar structure
   H. Hirata, N. Hattori, M. Ishida, H. Okabayashi, M. Furusaka, R. Zana
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Chapter 1.

Introduction

A surfactant molecule generally comprises two distinct parts that are incompatible with each other: a polar head group and either one or two hydrocarbon chains. Typical examples of surfactants are soaps and phospholipids. When surfactant molecules are dissolved in water, the hydrophobic part tends to avoid contact with water, while the hydrophilic polar head group tends to be strongly hydrated. Such an amphiphilic nature of ionic surfactant molecules leads to formation of a variety of self-assembly structures (aggregate structures) in water and oil, as shown in Table 1-1. Aggregation of surfactant molecules formed in water or organic solvents can be seen as resulting from a compromise between the two different properties of the surfactant molecules. The main driving force for the formation of micelles in water is the hydrophobic interaction between the hydrophobic parts of the surfactant molecules [1-2], because considerable entropy is gained from the hydrophobic bonding by the hydrocarbon chains when micelles are formed.

The physico-chemical properties of biological cell membranes could be successfully mimicked by using bilayer vesicles formed from naturally occurring or synthetic phospholipids. In some works [3-7], it has been shown that simple, synthetic double-chain surfactant molecules also form vesicular assemblies with properties very similar to those of phospholipid vesicles. This made it possible to investigate the effect of structural variation of the surfactant molecule on the functional properties of vesicle-bilayers. Thus, vesicles formed by synthetic amphiphiles offer model systems for understanding in detail the characteristic properties of biological membranes [8-18].

Israelachivili et al. [19] have shown that the type and structure of an aggregate formed by different surfactant molecules depend on their geometrical packing properties, which can be represented by the characteristic packing parameters \( \nu/a_0l_c \) of a given
Table 1-1 Mean packing shapes of surfactants and the structures they form

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>$v/a_0 l_c$</th>
<th>Critical packing shape</th>
<th>Aggregate structure</th>
</tr>
</thead>
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<tr>
<td>Single chain surfactants with large head group area</td>
<td>$&lt; 1/3$</td>
<td>Cone</td>
<td>Spherical micelles</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$a_0$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$v$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$l_c$</td>
<td></td>
</tr>
<tr>
<td>Single chain surfactants with large head group area</td>
<td>$1/3 ~ 1/2$</td>
<td>Truncated cone</td>
<td>Cylindrical micelles</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Double chain surfactant with large head group area</td>
<td>$1/2 ~ 1$</td>
<td>Truncated cone</td>
<td>Flexible bilayers, Vesicles</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Double chain surfactant with small head group area</td>
<td>$~ 1$</td>
<td>Cylinder</td>
<td>Planar bilayers</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Double chain surfactant with small head group area</td>
<td>$&gt; 1$</td>
<td>Reversed truncated cone</td>
<td>Reversed micelles</td>
</tr>
</tbody>
</table>
amphiphilic molecule with optimal area $a_0$, hydrocarbon volume $v$ and critical hydrocarbon chain length $l_c$. Table 1-1 illustrates the representative structures formed by some common amphiphilic molecules, and how these structures can be modified by their ionic environment, temperature, chain unsaturation, etc.

For the surfactant molecules to assemble into spherical micelles, their optimal surface area $a_0$ must be sufficiently large, and, further, their hydrocarbon volume $v$ must be sufficiently small so that the radius of the micelle may not exceed the critical chain length $l_c$. Simple geometrical considerations show that only those amphiphilic molecules for which $v/a_0 < 1/3$ can form a spherical micelle, with their head group areas equal to $a_0$ and with the micelle radius not exceeding $l_c$. Some surfactants form spherical micelles near the critical micelle concentration [20, 21]. Most lipids that form spherical micelles have charged head groups, since this leads to large head group areas, $a_0$. An increase in surfactant concentration or addition of salts partially screens the electrostatic inter-head group repulsion and thereby reduces $a_0$. The lipid molecules that possess smaller head group areas, such that $1/3 < v/a_0 l_c < 1/2$, cannot form spherical micelles but can form prolate spherical micelles. At higher concentration of surfactants or salts, prolate spherical micelles grow into cylindrical (rod-like) micelles. Alkyl trimethylammonium halides in the presence of high salt concentrations come under this category, and large rod-like micelles are formed in these systems [22, 23].

Lipid molecules, that form oblate spheroid micelles, disk-like micelles (or fragments of bilayers) and bilayers, cannot form spherical micellar structures due to their small head group area, $a_0$, or because their hydrocarbon chains are too bulky to fit into such small aggregates, while maintaining the surface area at its optimal value. For bilayer-forming lipids, the value of $v/a_0 l_c$ must be close to 1, and this requires that for the same head group area $a_0$ and chain length $l_c$, their hydrocarbon volume $v$ must be about twice that of micellar-forming lipids. Therefore, lipid molecules with two hydrocarbon chains are likely to form bilayers, and indeed most of them do so. Bis(2-ethylhexyl) sulfosuccinate (Aerosol-OT, AOT), a double chain anionic surfactant, having a small
ionic head group and relatively short but bulky branched hydrocarbon tails, forms oblate micelles in water [21]. Single-chained lysolecithin molecules form small but non-spherical micelles, while lecithins with two long alkyl chains, such as ditetradecyl phosphatidylcholine and dihexadecyl phosphatidylcholine, form bilayers [24]. Similarly, alkyl trimethylammonium bromide (CₙTAB) forms micelles [25], while the double-chained analog forms bilayers [26].

Under certain considerations the formation of closed spherical bilayers (vesicles) is more favorable than planar bilayers. The energetically unfavorable edges, which exist in planar bilayers, diminish when the planar bilayers change into closed bilayers. Thus, so long as the lipids in a curved bilayer can maintain their areas at their optimal value, vesicles should take their preferred structures. When \( v/a_0l_c \) equals to 1, only planar bilayers will form. For a bilayer to curve, lipids in the outer monolayer must be able to pack, on average, into truncated cones. This requires that \( v/a_0l_c < 1 \).

For lipid molecules with very small optimal head group areas, with bulky polyunsaturated or branched chains (large \( v \) and small \( l_c \)), the \( v/a_0l_c \) value will exceed unity. Such lipids form reversed micellar structures in oil or precipitate out of aqueous solution. For example, AOT is poorly soluble in water but readily soluble in oil (benzene, decane, etc.) and forms reversed micelles [27].

In general, in a self-assembly system, the polar heads of surfactant molecules are located at the interface between the hydrocarbon and water regions, and the relative positions and distances between the polar heads, which are intimately associated with the packing state, are determined mainly by their electrostatic interaction and by the packing property of the alkyl chains [28-30]. For cesium or rubidium soaps in water, it has been found that the head groups form well developed hexagonal or rectangular crystalline arrays [31]. However, they are arranged randomly, and little is known of their packing geometry. In fact, a packing property is strongly dependent on many factors, such as the ionic environment, temperature, size of polar head group, length of alkyl chains, branching and unsaturation of hydrocarbon chains [32-36]. For ionic head groups, an
increase in surfactant concentration as well as increasing salt concentration, decreases the electrostatic inter-head group repulsion and thereby reduces $a_0$. Introduction of chain branching and unsaturation, particularly of cis double bonds, reduce $l_c$ and thus increases the $v/a_0 l_c$ value. Similar effects also occur when the effective volume ($v$) of the chains is increased due to penetration of organic molecules, such as low molecular weight alkanes, into the hydrocarbon chain regions. Variation in temperature can alter both $a_0$ and $l_c$, so that these effects are more subtle and generally less understood. For double-chained lipids in the fluid state ($T > T_c$), an increase in temperature $T$ increases the hydrocarbon chain motion involving trans-gauche isomerization and thereby reduces their limiting length $l_c$. If the head group area $a_0$ does not change significantly, as in the case of charged head groups, the net effect is an increase in $v/a_0 l_c$. However, temperature variation can also change the $a_0$ value. For example, the head group area of polyoxyethylenes decreases with an increase in temperature due to their increased hydrophobicity [37], and this results in an increase in $v/a_0 l_c$. Thus, with an increase in temperature, non-ionic spherical micelles grow in size and become more cylindrical [38, 39], while charged micelles shrink [40]. Zwitterionic micelles appear to behave somewhere in between, and their aggregation number hardly changes with temperature [41]. Therefore, it is very difficult to discuss quantitatively the relationship between the geometrical packing property of surfactant molecules and various factors. Under these circumstances, it is highly desirable to undertake further systematic studies on the molecular design and synthesis of a surfactant molecule and its aggregated structure.

In order to discuss the perturbation effect of the local arrangement of polar heads on the micellar and mesomorphic properties of surfactant molecules in water, Zana et al. [42] investigated the effect of the spontaneous arrangement of the polar groups on the microstructure of the aggregates of a series of bis(quaternary ammonium bromide) surfactants, using cryogenic transmission electron microscopy. The results showed that the morphology of the aggregates depends on the molecular structure of the surfactants.
In the present study, two different types of surfactant molecule were used in order to understand the effect of molecular structure of both the hydrophobic and hydrophilic parts on the aggregate structure. One of them is a series of identical and mixed-chain di-\textit{n}-alkyl phosphates, which are bi-tailed anionic surfactants. Identical and mixed-chain di-\textit{n}-alkyl phosphates used in this study have an identical polar head group (identical \( \alpha_0 \)) and the same molecular weight (identical \( \nu \)), but with various combinations of hydrocarbon chains (different \( l_c \)). The other type is a series of bis(queatnary ammonium bromides). These molecules are bi-polar head group cationic surfactants in which two alkyl dimethylammonium bromide moieties are connected by a polymethylene chain, referred to as a spacer. Bis(queatnary ammonium bromide) surfactants, used in this study, have the same hydrocarbon chains (identical \( \nu \) and \( l_c \)) and different spacer lengths (different \( a_0 \)).

![Chemical Structures](attachment:chemical_structures.png)

Di-\textit{n}-alkyl phosphate anion
\( m = n \): identical-chain
\( m \neq n \): mixed-chain

Bis(queatnary ammonium) cation

Chapters 2 ~ 4 and chapter 6 of this thesis will describe the phase structure of identical and mixed-chain di-\textit{n}-alkyl phosphate-water systems in detail, using differential scanning calorimetry, \( ^1 \text{H} \)-pulsed-gradient NMR self-diffusion, \( ^{31} \text{P} \) NMR, x-ray low angle diffraction, Raman scattering spectra and small angle neutron scattering (SANS). In chapter 7, micellar structures of bis(queatnary ammonium bromide) in water will be reported using SANS analysis.
References


42. Zana, R.; Talmon, Y. Nature 1993, 362, 228.
Chapter 2.

Phase diagrams and phase structures of identical and mixed chain lithium di-n-alkyl phosphate-water binary systems. Asymmetric molecular shape effect

2-1. Introduction

It is well-known that amphiphilic molecules such as surfactants, lipids, proteins and synthetic copolymers can form a variety of self-assembly structures in water. In particular, the physico-chemical properties of biological cell membranes could be successfully mimicked by using bilayer vesicles formed from naturally occurring or synthetic phospholipids. Subsequent works [1-5] have shown that simple, synthetic double-chain surfactant molecules also form vesicular assemblies with properties very similar to those of phospholipid vesicles. This made it possible to investigate the effects of structural variations in the surfactant on the structural and functional properties of vesicle-bilayers. Thus, vesicles formed by synthetic amphiphiles offer model systems for understanding in detail the characteristic properties of biological membranes [6-16].

Israelachivili et al. [17] have shown that the type and structure of an aggregate formed by different surfactant molecules depend on their geometrical packing properties, which can be represented by the characteristic packing parameters \( \frac{\nu}{a_\theta l_c} \) of a given amphiphilic molecule with optimal area \( a_\theta \), hydrocarbon volume \( \nu \) and critical chain length \( l_c \). In general, in a self-assembly system, the polar heads of surfactants are located at the interface between the hydrocarbon and water regions, and the relative positions and distances between the polar heads which are intimately associated with the packing state, are determined mainly by their electrostatic interaction and by the packing property of the alkyl chains [17-19]. For cesium or rubidium soaps in water, it has been found that the head groups form well developed hexagonal or rectangular crystalline arrays [20].
However, they are arranged randomly, and little is known of their packing geometry. In fact, a packing property is strongly dependent on many factors, such as the ionic environment, temperature, polar-group size, and length and unsaturation of a hydrocarbon chain [21-26]. Therefore, it is very difficult to discuss quantitatively the relationship between the geometrical packing property of surfactant molecules and these many other factors. Under these circumstances it is highly desirable to undertake further systematic studies on the molecular design and synthesis of a surfactant molecule and its aggregate structure.

In order to discuss the perturbation effect of the local arrangement of polar heads on the micellar and mesomorphic properties of surfactant molecules in water, Zana et al. [27] investigated the effect of the spontaneous arrangement of the polar groups on the microstructure of the aggregates of a series of bis(quaternary ammonium bromide) surfactants, using cryogenic transmission electron microscopy. The results showed that the morphology of the aggregates depends on the molecular structures of the surfactants.

In this study, we sought to investigate the local arrangement effect of hydrocarbon moieties on the microstructures of bi-tailed surfactants. The lithium salts of di-\(n\)-pentyl (DPP), \(n\)-butyl(\(n\)-hexyl) (BHP), \(n\)-propyl(\(n\)-heptyl) (PHP) and ethyl(\(n\)-octyl) (EOP) phosphates, with characteristic packing parameters equal to 0.50, 0.43, 0.37 and 0.33, respectively, were synthesized, and the phase diagrams and phase structures of these double chain surfactant-water systems were determined. In particular, by using the thermotropic data of these phosphate-water binary systems we discuss the stability of the liquid crystalline structure formed by these phosphate anions in terms of their asymmetric molecular shape.
2-2. Experimental

2-2-1. Materials

Lithium salts of di-\textit{n}-pentyl (DPP), \textit{n}-butyl(\textit{n}-hexyl) (BHP), \textit{n}-propyl(\textit{n}-heptyl) (PHP) and ethyl(\textit{n}-octyl) (EOP) phosphates were prepared as follows. \textit{n}-Alkyl phosphorodichloridates (R-OP(O)Cl\textsubscript{2}) prepared using phosphoryl chloride and the corresponding alcohol (ROH, R: shorter chain) and vacuum-distilled several times. The R-OP(O)Cl\textsubscript{2} samples were converted to identical- and mixed-chain di-\textit{n}-alkyl phosphorochloridates, (R-O)(R'\textit{'}-O)P(O)Cl, by treatment with the corresponding alcohol (R'\textit{'}OH, R\textit{'}: longer chain) [28], and vacuum-distilled several times. The boiling points of R-OP(O)Cl\textsubscript{2} and (R-O)(R'\textit{'}-O)P(O)Cl are listed in Table 2-1. (R-O)(R'\textit{'}-O)P(O)Cl were treated with benzaldoxim (Furuka Chemie AG) by the method of Mukaiyama et al. [29], to yield phosphoric acid di-\textit{n}-alkyl esters, (RO)(R'\textit{'}O)P(O)OH. Phosphoric acid di-\textit{n}-alkyl esters were finally neutralized with lithium hydroxide aqueous solution, and the lithium salts were recrystallized in aqueous acetone. The series of di-\textit{n}-alkyl phosphate lithium salts thus obtained are termed Li(DAP). The sample identity was confirmed by \textsuperscript{1}H and \textsuperscript{13}C NMR and by elemental analyses. The agreement between the calculated and observed values of elemental analyses were within 0.2 %.

\[
\begin{align*}
\text{DPP anion} & : \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O} \xrightarrow{\text{P}} \text{O} \\
\text{BHP anion} & : \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O} \xrightarrow{\text{P}} \text{O} \\
\text{PHP anion} & : \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O} \xrightarrow{\text{P}} \text{O} \\
\text{EOP anion} & : \text{CH}_3\text{CH}_2\text{O} \xrightarrow{\text{P}} \text{O}
\end{align*}
\]
Table 2-1 The boiling points of R-OP(O)Cl₂ and (R-O)(R'-O)P(O)Cl

<table>
<thead>
<tr>
<th></th>
<th>R-OP(O)Cl₂</th>
<th>(R-O)(R'-O)P(O)Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPP</td>
<td>75 ~ 77 °C at 4 mmHg</td>
<td>108 ~ 110 °C at 4 mmHg</td>
</tr>
<tr>
<td>BHP</td>
<td>73 ~ 75 °C at 4 mmHg</td>
<td>110 ~ 113 °C at 4 mmHg</td>
</tr>
<tr>
<td>PHP</td>
<td>59 ~ 61 °C at 4 mmHg</td>
<td>111 ~ 113 °C at 4 mmHg</td>
</tr>
<tr>
<td>EOP</td>
<td>65 ~ 68 °C at 25 mmHg</td>
<td>117 ~ 119 °C at 4 mmHg</td>
</tr>
</tbody>
</table>

2-2-2. Phase diagram determinations and calorimetry

Sample solutions were prepared by weighing the Li(DAP) and water components into glass ampoules, which were then sealed and the contents homogenized by heating and shaking. The temperature dependence of the phase feature of the samples was determined by visual inspection as the ampoules were held in a temperature-controlled water-bath (rate of temperature elevation and cooling 0.1 °C/min). The temperature was measured with a digital thermometer (Sato Keiryoki).

The thermotropic transition temperatures of the Li(DAP)-water systems were determined with a differential scanning calorimeter (Rigaku DSC 8230), which was scanned at a rate of 2 °C/min by using a volatile pan with α-Al₂O₃ in the reference pan.

2-2-3. ³¹P and ²H NMR and x-ray diffraction measurements

³¹P NMR spectra were measured using high-power proton decoupling at 80.995 MHz on a Varian XL-200 spectrometer. The ³¹P chemical shifts (σ) of the DAP anions in D₂O solution were measured relative to the ³¹P signal of aqueous 85%-H₃PO₄ solution as an external reference.

²H NMR spectra were measured on a Varian XL-200 NMR spectrometer (30.71 MHz) with a spectral width of 15000 Hz, 16384 points in the time domain and an acquisition time of 0.5 ~ 2 s. All the ²H NMR measurements were made after thermal equilibrium of the samples had been confirmed.
The x-ray diffraction low-angle patterns were obtained using a RU-200 camera (Rigaku Denki Co.) with a three slits-system in the diffraction range of $1.2^\circ < 2\theta < 20^\circ$. Nickel-filtered CuKα radiation ($\lambda = 1.54 \text{ Å}$) was used. The temperature of the sample was controlled by air within $\pm 1^\circ \text{C}$ and was measured with a digital thermometer (Sato Keiryoki).
2-3. Results and discussion

2-3-1. Phase diagrams of the Li(DAP)-H\(_2\)O systems and phase structure

Figure 2-1[A] ~ [D] shows the phase diagram of the Li(DAP)-H\(_2\)O systems. For the Li(DPP)-, Li(BHP)- and Li(PHP)-H\(_2\)O binary systems, the phase diagrams consist of three regions (I, II and III). For region I, a homogeneous and transparent isotropic solution was obtained in common for the three systems. In region II, a lyotropic liquid crystalline state was obtained. The optically-isotropic property of region I and the lyotropic liquid crystalline state of region II were confirmed under a polarizing microscope. Region III was a coagel phase.

For the Li(EOP)-H\(_2\)O system, the phase diagram consists of four regions (I, II, III and IV). The regions I, II and III are an isotropic solution, and lyotropic liquid crystalline and coagel phases, respectively. In region IV, a homogeneous and transparent hard gel phase was obtained.

For the Li(DAP) sample solutions in region I, only narrow and symmetrical \(^{31}\)P NMR signals were observed in common. The \(^{31}\)P chemical shifts (\(\sigma\)), which are sensitive to the formation of aggregates [30-33], were measured at various concentrations. The \(^{31}\)P chemical shift (\(\sigma\)) vs. inverse concentration (1/C) plot for Li(EOP)-D\(_2\)O system is shown in Fig.2-2. The inflection point is observed at concentration 2.3 wt%.

Such a concentration dependence of the \(^{31}\)P \(\sigma\) values can also be explained by a pseudophase and two-site model [34, 35]. The observed chemical shift (\(\sigma\)) is a weighted average of the chemical shifts in the monomeric and in the micellar state, since the exchange rate of the EOP anions between the bulk solution and the micelles is generally fast on the NMR time scale. Thus, the observed \(\sigma\) value is expressed [36] by equation (2-1),

\[
\sigma = \frac{C}{C} \sigma_{\text{mono}} + \frac{(C - C\text{MC})}{C} \sigma_{\text{mic}} \tag{2-1}
\]
Fig. 2-1[A]. Phase diagram of the Li(DPP)-H₂O binary system. The solid lines show the phase boundary assumed by visual inspection and the filled circles denote the phase transition temperatures obtained from the DSC temperature elevation curves. Region I: homogeneous aqueous solution; region II: lyotropic liquid crystalline phase; region III: coagel phase (below the line abdef).
Fig. 2-1[B]. Phase diagram of the Li(BHP)-H₂O binary system. The solid lines show the phase boundary assumed by visual inspection and the filled circles denote the phase transition temperatures obtained from the DSC temperature elevation curves. Region I: homogeneous aqueous solution; region II: lyotropic liquid crystalline phase; region III: coagel phase (below the line abdef).
Fig. 2-1[C]. Phase diagram of the Li(PHP)-H$_2$O binary system. The solid lines show the phase boundary assumed by visual inspection and the filled circles denote the phase transition temperatures obtained from the DSC temperature elevation curves. Region I: homogeneous aqueous solution; region II: lyotropic liquid crystalline phase; region III: coagel phase (below the line abdef).
Fig. 2-1[D]. Phase diagram of the Li(EOP)-H$_2$O binary system. The solid lines show the phase boundary assumed by visual inspection and the filled circles denote the phase transition temperatures obtained from the DSC temperature elevation curves. Region I: homogeneous aqueous solution; region II: lyotropic liquid crystalline phase; region III: coagel phase (below the line abc'fgi); region IV: hard gel phase.
$^{31}$P chemical shift ($\sigma$) vs. $1/C$ plots for Li(EOP)-D$_2$O system region I.

**Fig. 2.**
where $C$ is the total concentration of Li(EOP), and $\sigma_{\text{mono}}$ and $\sigma_{\text{mic}}$ are the $^{31}\text{P}$ chemical shifts for the monomers and micelles, respectively. Plots of $\sigma$ vs. $1/C$ are well described by equation (2-1). The $CMC$ values derived from the same procedure are 5.0 wt\% for Li(DPP), 4.3 wt\% for Li(BHP), 3.7 wt\% for Li(PHP) and 2.3 wt\% for Li(EOP).

As shown in Fig.2-3, low-field shoulders were found in the $^{31}\text{P}$ NMR spectra of the Li(DAP) samples in region II and the spectral features are similar to that of the bilayer-type sodium di-$n$-butyl phosphate [37]. Such characteristic asymmetry is due to the chemical shift anisotropy ($\Delta\sigma$) of a $^{31}\text{P}$ nucleus in the polar group, arising from the restricted anisotropic motion of the DAP anions [38]. It can be seen that the $\Delta\sigma$ value becomes small in the order Li(EOP) $<$ Li(PHP) $<$ Li(BHP) $<$ Li(DPP), showing that the asymmetric molecular shape of these dialkylphosphates affects the $^{31}\text{P}$ chemical shifts anisotropy of a $^{31}\text{P}$ nucleus. In order to discuss the differences in $\Delta\sigma$ among these dialkyl phosphates in detail, it is highly desirable to make some molecular conformational studies by x-ray crystallographic methods, and also some theoretical calculations of the chemical shift shielding tensors of the dialkyl phosphate moiety. In any case, however, we may assume that region II is more structurally organized than region I and that a lamellar-like structure probably exists in this region.

The x-ray low angle diffraction patterns of the Li(DAP) samples in region II and of the Li(EOP) samples in region IV were measured at various concentrations. Wide and diffuse reflections were observed. It was found that the interplaner spacing ($d$) strongly depends on both the water-content and the species of Li(DAP) and a decrease in water-content results in a decrease in the $d$ value (Fig.2-4). Moreover, the $d$ value was found to increase in the order of Li(DPP) $<$ Li(BHP) $<$ Li(PHP) $<$ Li(EOP). In particular, the increase in $d$ was most clearly seen between Li(PHP) and Li(EOP). Since the radial electron density distributions calculated by Fourier transformation of the x-ray diffraction intensities become a measure of the distance between two polar layers sandwiched by
Fig. 2-3. $^{31}$P NMR spectra of the samples in region II at 25 °C (a: Li(DPP) 70 wt%, b: Li(BHP) 70 wt%, c: Li(PHP) 70 wt% and d: Li(EOP) 50 wt%) and the chemical shift anisotropies ($\Delta\sigma$).
Fig. 2-4. Concentration-dependence of the $d$ values for the Li(DAP)-H$_2$O systems
(DPP (○); BHP (□); PHP (△); EOP (×)) at 25°C.
hydrocarbon layers, the observed $d$ values provide information on the structure of the bilayer-type aggregates [39]. Therefore, this observation indicates that the thickness of the bilayer in a lamellar-type structure and $d$ increase in the same order. The differences in $d$ during Li(DPP), Li(BHP) and Li(PHP) are not so marked. However, there exists a marked difference in $d$ between Li(PHP) and Li(EOP). The result may be explained as follows.

In the case of Li(DPP), a structural model similar to the bilayer formed by lipid molecules can be presented (Fig. 2-5). When mixed chain di-$n$-alkyl phosphates form the bilayer-type structure, we may assume that the two di-$n$-alkyl chains are closely packed in a manner which alternatively combines short and long $n$-alkyl chains (Fig. 2-5[A]). In such a closely packed bilayer, the thickness of the bilayer formed by mixed chain dialkyl phosphates should be equal to that for Li(DPP). The observed data are not in accord with the results assumed by this model. Probably, this inconsistency arises from differences in the segmental mobility of the shorter $n$-alkyl chains. In general, it has been found for surfactant molecules in aqueous solutions that as the length of the $n$-alkyl chain decreases, the segmental mobility progressively increases. This is also the case for Li(DAP) in aqueous solutions. Therefore, we may assume that the segmental mobility of shorter $n$-alkyl chains increases in the order Li(BHP) < Li(PHP) < Li(EOP), preventing the formation of a closely packed structure. Thus, the contribution of a loosely packed structure to the thickness of a bilayer increases, resulting in progressive increase in the thickness (Fig. 2-5[B]). For Li(EOP), in particular, a loosely packed model, rather than a closely packed model, may be applied, since the orientation of the ethyl group at the interface of a bilayer may be disturbed, owing to the small hydrophobicity and high segmental mobility.

For the Li(EOP)-H$_2$O binary system, region IV is a hard gel phase. The samples in region IV provide a very sharp $^{31}$P NMR signal which corresponds well to that of cubic phase [40]. The x-ray low angle diffraction patterns of Li(EOP) samples in region IV
were also measured at various concentrations. The SAXS data from the cubic phase revealed two strong peaks. The corresponding lattice parameters for the two samples were found to be, 28.30 Å and 24.66 Å for 60 wt% and 27.08 Å and 23.48 Å for 65 wt%. Although the number of reflections is not sufficient for an unambiguous indexing, we have found that the data fit reasonably well to a face-centered-cubic structure [41].
Fig. 2-5. Schematic model of DAP bilayers. [A]: closely packed structure, [B]: loosely packed structure.
2-3-2. Thermotropic properties of the Li(DAP)-H₂O systems

Figure 2-6[A] ~ [D] shows DSC curves for the Li(DAP)-H₂O solutions and describes the variation of the phase transition with water content. The phase transition temperatures for representative samples are listed in Table 2-2 together with the ΔH values calculated from the peak area. For these DSC curves, endothermic peaks were found in the temperature range -20 ~ 10 °C. In order to investigate the nature of the thermal transitions, DSC measurements were also made for the Li(DAP)-D₂O systems. The corresponding endothermic peaks shifted to a higher temperature by 4 °C with respect to those of the Li(DAP)-H₂O systems. If one considers that the melting point of pure D₂O is about 4 °C higher than that of pure H₂O [42], the result suggests that the thermal transitions are ascribed to melting of bulk-like water in the aggregates formed by DAP anions. Thus, for the Li(DAP) sample solutions (10 wt%), the thermal transitions starting at -2.1 °C (Li(DPP)), -1.3 °C (Li(BHP)), -1.9 °C (Li(PHP)) and -1.6 °C (Li(EOP)) are ascribed to melting of bulk-like water.

Figure 2-7 shows variation of the ΔH value due to melting of the ice which corresponds to the bulk-like water in the Li(DAP) samples. The ΔH values obtained from the DSC curves of the DAP-H₂O systems are colinear. By extrapolation of the linear ΔH vs. concentration (wt%) plots to ΔH = 0, we may assume a number for water molecules bound with the polar ion pair (Li⁺PO₄⁻) of a surfactant molecule at a Li(DAP) concentration of 44.4 wt%. The result suggests that there are 17 molecules of H₂O per molecule of surfactant at this concentration. It is evident that these water molecules are strongly bound to the DAP polar groups. For the AOT-H₂O system, Casillas et al. [43] have already obtained the number of waters bound strongly to the AOT polar group using this treatment. Since the aggregate structure of the Li(DAP) molecules depends upon the water content, the hydration number thus obtained is useful for discussion of the aggregate structure [44, 45].

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Fig. 2-6[A]. Representative DSC curves of the Li(DPP)-H₂O system (a: 10 wt%, b: 30 wt%, c: 50 wt% and d: 70 wt%).
Fig. 2-6[B]. Representative DSC curves of the Li(BHP)-H$_2$O system (a: 10 wt%, b: 30 wt%, c: 50 wt% and d: 70 wt%).
Fig. 2-6[C]. Representative DSC curves of the Li(PHP)-H$_2$O system (a : 10 wt%, b : 30 wt%, c : 50 wt% and d : 70 wt% ).
Fig. 2-6[D]. Representative DSC curves of the Li(EOP)-H₂O system (a: 30 wt%, b: 50 wt%, c: 60 wt% and d: 70 wt%).
Table 2-2 Phase transition temperature \( (T_t, ^\circ C) \) and \( \Delta H \) (J g\(^{-1}\) of sample) for the DAP-water systems

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<th>( \Delta H )</th>
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<th>( \Delta H )</th>
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<th>( \Delta H )</th>
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Fig. 2-7. Variation of the $\Delta H$ value due to the melting of ice corresponding to bulk-like water (water 1) for the Li(DAP)-H$_2$O coagel phase (DPP (○); BHP (□); PHP (△); EOP (×)).
In order to investigate the cause of peaks 2 and 3 in Fig. 2-6[A] ~ [D], the temperature dependence of the $^2\text{H}$-NMR spectrum for the DAP-D$_2$O systems was measured. The results are briefly described below [46].

It was found that the spectral features of the $^2\text{H}$-NMR and $^{31}\text{P}$-NMR strongly depend on temperature. Below the transition temperature of peak 3, only symmetrical and broad $^2\text{H}$ and $^{31}\text{P}$ resonance signals were observed, while, above that of peak 3, $^2\text{H}$-NMR powder patterns [37, 47] and $^{31}\text{P}$-NMR spectral patterns characteristic of a lamellar structure [37-39] were observed. This observation indicates that peak 3 derives from the disorder to lamellar transitions. Above the transition temperature of peak 2, only symmetrical and sharp $^2\text{H}$ and $^{31}\text{P}$ resonances were observed, showing that peak 2 comes from the lamellar to disorder transition.

For the concentrated samples, it was found that the areas of the two endothermic peaks deriving from peak 1 and peak 2 tend to become very small or disappear as peak 3 becomes predominant. Furthermore, we found that the thermal transition peaks 5 and 6 appear for the DSC curve of the concentrated Li(PHP) sample (70 wt%) and of the Li(EOP) samples (70 wt%). The endothermic peak 5 for Li(PHP) and Li(EOP) should be due to the coagel to liquid crystal transition. For concentrated samples of the Li(DPP)- and Li(BHP)-water systems, similar observations were made.

Recently, we have reported that the conformational preference about the P-O bonds depends upon the extent of hydration and occurs for both identical and mixed chain di\textit{n}-alkyl phosphate sodium salt-water systems in the coagel state [44, 45]. This fact implies that the aggregate structure of these systems in the coagels depends upon the hydrated environment of the phosphate group. Thus, for the coagel samples of Li(PHP) and Li(EOP), we may also assume that the conformational preference about the P-O bond occurs at the transition temperature. The endothermic peak 6 may be related to the conformational preference about the P-O bonds. Further investigation is highly desirable, in order to elucidate the cause of this transition. For the Li(DAP) samples in the lyotropic
liquid crystalline state, endothermic peaks (peak 4) are observed in common in the temperature range 40 ~ 80 °C (Fig. 2-6), and may be caused by variation of the molecular ordering of the aggregates upon the lyotropic to the isotropic transition (II → I transition), since none of these peaks shifted to a higher temperature when D₂O was used as solvent. Figure 2-8 shows the concentration dependence of the ΔH value for the endothermic peaks derived from the II → I thermal transition. The ΔH values tend to increase with an increase in concentration, showing that the aggregate structure of DAP anions in the liquid crystalline state is stabilized with increasing concentration. Furthermore, it should be emphasized that the extent of variation in the ΔH value depends upon the species of DAP. That is, the extent of ΔH variation increases in the order Li(EOP) < Li(PHP) < Li(BHP) < Li(DPP), suggesting that the stability of the aggregate structure in the liquid crystalline state also increases in this order.

For the DSC curves of the Li(EOP)-H₂O samples in region IV, in which the samples are in a hard gel state, the endothermic peak (peak 4) is also observed in the temperature range 45 ~ 50 °C, and may be ascribed to variation in the structural ordering of the aggregates upon the hard gel to isotropic transition, since in no case did this peak shift to a higher temperature when D₂O was used as solvent.
Fig. 2-8. Concentration dependence of the $\Delta H$ value due to the II $\rightarrow$ I transition in the Li(DAP)-H$_2$O systems (DPP (○); BHP (□); PHP (△); EOP (×)).
2-4. Conclusion

Lithium salts of di-n-pentyl (DPP), n-butyl(n-hexyl) (BHP), n-propyl(n-hexyl) (PHP) and ethyl(n-octyl) (EOP) phosphates were synthesized and the phase diagrams of the lithium phosphate-water binary systems were determined. The phase diagrams of the \(\text{Li(DPP)-, Li(BHP)- and Li(PHP)-water systems contain three regions (I, II and III) in common, which correspond to a homogeneous transparent one-phase solution, and lyotropic liquid crystalline and coagel phases, respectively. However, the Li(EOP)-H}_2\text{O system contains an additional hard gel phase (region IV).}

\(\text{^31P NMR spectra suggest that region I is a monomer } \leftrightarrow \text{micelle equilibrium phase and region II is a lamellar phase. X-ray diffraction results show that for the Li(DPP)-, Li(BHP)- and Li(PHP)-water systems the two n-alkyl chains are closely packed in the lamellar phase in a manner which alternatively combines short and long chains, while in EOP-water system the two long chains are loosely packed. Furthermore, it may be assumed from } \text{^31P NMR spectra and x-ray diffraction results that region IV in the Li(EOP)-water system is a cubic phase.}

Thermotropic properties for these \(\text{Li(DAP)-water systems were also investigated by DSC temperature profile curves. From the } \Delta\text{H variation upon the II } \rightarrow \text{I thermal transition, we assumed that stability of the aggregate structure in the liquid crystalline state increases in the order Li(EOP) } < \text{ Li(PHP) } < \text{ Li(BHP) } < \text{ Li(DPP). Thus, we have found that thermotropic properties for a series of Li(DAP)-water binary systems are closely correlated with the extent of asymmetric molecular shape in DAP.}
References

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Chapter 3.

Phase diagram and phase structure of the sodium di-\textit{n}-pentyl phosphate-water system. $^1$H pulsed-gradient NMR self-diffusion, $^{31}$P NMR and x-ray diffraction studies

3-1. Introduction

In many thermoanalytical studies [1-8] on the binary systems of water and phosphatidylcholine, it has been pointed out that water molecules incorporated into the polar layer of the aggregate systems play an essential role for the mechanism of the phase transition. Kodama et al. [9, 10] have demonstrated the predominant role of so-called "newly incorporated water" for phase change in the dipalmitoyl phosphatidylcholine-water system in a detailed thermoanalytical study. For the same binary system, conformational studies by the use of x-ray diffraction and infrared spectroscopic methods have also indicated that the water content plays an important role in the thermodynamic stable phase [11-13]. However, a phosphatidylcholine molecule is large in the size, and, moreover, has three kinds of polar groups (ester groups, the phosphate anion and trimethylammonium cation moieties). Therefore, it is very difficult to discuss the interactions between each polar group and water molecules from the thermoanalytical data. It was thought that further understanding of the interactions between a phospholipid and water molecules would be obtained by using a simple surfactant molecule as a model of the phospholipid.

Dialkyl phosphates with simple \textit{n}-alkyl chains are well suited for further investigation of a phospholipid. Thus far, the conformations of simple dialkyl phosphate anions in aqueous solution have been studied mainly by infrared and Raman spectroscopic methods [14]. The x-ray crystallographic analysis of barium diethyl
phosphate [15] showed that the two C-O bonds occupy gauche positions with respect to the P-O bonds, confirming the conclusion of the spectroscopic studies.

In our previous paper [16], detailed Raman studies of the barium di-n-pentyl phosphate-water system indicated that two types of aggregation structure with different Ba$^{2+}$...PO$_4^{-}$ interaction modes coexist in the liquid crystal. Furthermore, it was found that the all-trans form of the alkyl group was favored in the micellar state. Recently, for the dipentyl phosphate-water system [17], we demonstrated that the phase transition from the lyotrophic state to the coagel phase leads to a marked variation in the conformation about the phosphodiester P-O bonds, and that this is strongly dependent upon the water content in the system. Although studies on simple dialkyl phosphates have increased understanding of the physico-chemical properties of phospholipid aggregates, investigations of phase diagrams and phase structures of the simple dialkyl phosphate-water binary systems are few in number.

We report the phase diagram of the sodium di-n-pentyl phosphate-water system and discuss the phase structure in detail, using $^1$H-pulsed-gradient NMR self-diffusion, $^{31}$P NMR and x-ray diffraction studies.
3-2. Experimental

3-2-1. Materials

Sodium di-\textit{n-}pentyl phosphate Na(DPP) was prepared by neutralization of phosphoric acid di-\textit{n-}pentyl ester with a solution of NaOH. The preparation of phosphoric acid di-\textit{n-}pentyl ester was described in chapter 2-2-1. Products were identified by $^1$H, $^{13}$C NMR spectral and elemental analyses. Since the sodium salt was hygroscopic, the barium salt was used for the elemental analysis. Anal. C$_{20}$H$_{44}$O$_8$P$_2$Ba : Calc: C, 39.26; H, 7.25. Found: C, 39.06; H, 7.47.

3-2-2. Phase diagram determinations and calorimetry

Sample solutions were prepared by weighing the Na(DPP) and H$_2$O components into glass ampoules, which were then sealed and the contents homogenized by annealing. The thermotropic transition temperature of the Na(DPP)-water system was determined with a differential scanning calorimeter (Rigaku DSC 8230) which was scanned at a rate of 2 °C/min by using a volatile pan with $\alpha$-Al$_2$O$_3$ in the reference pan. The temperature dependence of the phase feature of the samples was determined by visual inspection as the ampoules were held in a temperature-controlled water-bath (rate of temperature elevation and cooling 0.1 °C/min). The temperature was measured with a digital thermometer (Sato Keiryoki).

3-2-3. $^{31}$P NMR measurements

$^{31}$P NMR spectra were measured using high-power proton decoupling at 80.995 MHz on a Varian XL-200 spectrometer. The $^{31}$P chemical shift ($\sigma$) of the DPP anions in D$_2$O solution were measured relative to the $^{31}$P signal of aqueous 85 %-H$_3$PO$_4$ solution.
3-2-4. Self-diffusion coefficient measurements

The Fourier-transform $^1$H pulsed gradient ($^1$H FT-PG) NMR self-diffusion was measured on a JEOL FX-100 NMR Fourier Transform spectrometer, equipped with a gradient unit at 99.60 ($^1$H) MHz using an internal D$_2$O lock [18-21]. The absolute magnitude of the field gradient $G$ was calibrated against the self-diffusion coefficient value ($2.30 \times 10^{-9}$ m$^2$ s$^{-1}$) of pure water (H$_2$O) at 25 °C [22]. The temperature of the sample in the tube was measured with a thermocouple and was controlled to ± 0.5 °C. The self-diffusion coefficients of Na(DPP) in D$_2$O were obtained from the (CH$_2$)$_4$-proton NMR signal of the pentyl-chain. For the two-phase solution in region II, measurements were made at the same controlled temperature immediately after separation of the upper and lower layers.

3-2-5. X-ray diffraction measurements

X-ray diffraction low-angle patterns were obtained using a RU-200 camera (Rigaku Denki Co.) with a three slits-system in the diffraction range of $1.2° < 2θ < 20°$. Nickel-filtered CuKα radiation ($\lambda = 1.54$ Å) was used. The temperature of the sample was controlled by air within ± 1 °C and was measured with a digital thermometer (Sato Keiryoki).
3-3. Results and discussion

3-3-1. Phase diagram of the Na(DPP)-water system

Figure 3-1 shows the phase diagram of the Na(DPP)-water system, which consists of five regions. For the representative sample solutions of the concentrated Na(DPP)-water system, the phase-transition temperatures and the $\Delta H$ values obtained from DSC curves are listed in Table 3-1. A homogeneous and transparent one-phase solution was obtained in region I, while region II is a two-phase solution system, having transparent upper and lower layers. For region II, it was found that the volume percentage of the upper layer decreased linearly and conversely, that of the lower layer increased with an increase in weight-percentage of Na(DPP). This observation is a consequence of the lever rule and proves that the two-phase system is in equilibrium in region II. In region III, hydrated crystals and an aqueous solution of Na(DPP) were found to coexist. For region IV, a homogeneous, transparent and viscous one-phase solution was obtained at higher temperatures, and could be regarded as a gel phase at room temperature. In region V, a homogeneous, transparent and fluid phase was obtained. The optically-isotropic properties of samples in the lower layer of region II and in region IV were confirmed under a polarizing microscope.

Table 3-1 The phase transition temperatures ($T_t$, °C) and the $\Delta H$ (J g$^{-1}$) values

<table>
<thead>
<tr>
<th>wt%</th>
<th>$T_t$</th>
<th>$\Delta H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60.00</td>
<td>81.8</td>
<td>6.74</td>
</tr>
<tr>
<td>70.04</td>
<td>3.9</td>
<td>8.49</td>
</tr>
<tr>
<td></td>
<td>95.5</td>
<td>11.17</td>
</tr>
<tr>
<td>79.86</td>
<td>24.7</td>
<td>73.68</td>
</tr>
<tr>
<td></td>
<td>74.8</td>
<td>2.93</td>
</tr>
</tbody>
</table>
Fig. 3-1. Phase diagram of Na(DPP)-water system: A (100 °C, 68.5 wt%), B (85.0 °C, 72.5 wt%) and C (23.2 °C, 77.3 wt%). Region I: homogeneous aqueous solution; region II: two-phase solution; region III: solid Na(DPP) and its solution; region IV: homogeneous and transparent gel; region V: transparent and liquid solution. Solid lines show the phase boundary lines assumed by visual inspection, and solid circles indicate the phase transition points determined by the DSC curves.
3-3-2. Self-diffusion coefficients and aggregate structure

Self-diffusion coefficients provide important information on aggregate structure and association behavior, because molecular association in solution greatly affects the translational motion of a molecule. It has been suggested that measurement of self-diffusion coefficients is a direct approach for elucidating the structural organization of aggregated systems [22].

The self-diffusion coefficients \((D)\) of the Na(DPP) anions in water were measured for regions I, IV and V. Figure 3-2 shows the \(\ln D\) vs. inverse concentration \((1/C)\) plots for region I at 25 \(^\circ\)C. In the plots, two inflection points are found at concentrations of 4.7 and 10.7 wt\%. Below a concentration of 4.7 wt\%, the \(D\) values are almost constant \(\left(4.09 \sim 4.14 \times 10^{-10} \text{ m}^2 \text{s}^{-1}\right)\), but above this concentration they tend to decrease with an increase in concentration. This observation can be explained by a simple two-site model [23], which is in a single monomer \(\leftrightarrow\) micelle equilibrium state. In this model, the Na(DPP)-water system contains a finite concentration of the DPP anion monomer, contributing to the observed self-diffusion coefficient. The observed self-diffusion coefficients are population-weighted averages of the \(D\) value of the monomer and that of the micelles, and are given by equation (3-1),

\[
D = PD_{\text{mic}} + (1 - P)D_{\text{mono}} \quad (3-1)
\]

where \(P = (C - CMC)/C\), \(C\) is the total concentration of Na(DPP), and \(D_{\text{mono}}\) and \(D_{\text{mic}}\) are the self-diffusion coefficients of the DPP anions in the monomer and micellar states, respectively. Thus, the first inflection point should be due to formation of micelles.

The variation of \(\ln D\) at the first \(CMC\) (4.7 wt\%) is not so marked. However, as discussed later, the existence of the first \(CMC\) (4.6 wt\%) was confirmed by the concentration dependence of the \(^{31}\)P NMR chemical shift.
Fig. 3-2. The lnD vs. 1/C plots for the Na(DPP)-D₂O system in region I. a: 4.7 wt% and b: 10.7 wt%. Filled circle (●) and open circle (○) correspond to the results of water and DPP anions, respectively.
As the concentration increases beyond the first CMC, the $D$ value tends to decrease. However, the slope in the plots changes markedly at concentrations greater than 10.7 wt%, which can be regarded as a second CMC. It has already been reported for surfactant solutions that the micellar structure changes above the second CMC [23]. Therefore, we may assume for simple dialkyl phosphate anions that such a variation in the aggregate state occurs above the second CMC.

For the two-phase solution in region II, self-diffusion measurements at the same controlled temperature were made immediately after separation of the upper and lower layers. We have confirmed that there is a marked difference in the $D$ values of the upper and lower layers and that the $D$ values of the upper layer are very close to those of region I while those of the lower one are similar to those of region IV. Thus, in region II we may assume that regions I and IV coexist and that the two phases are in equilibrium. This conclusion is also supported by $^{31}$P NMR results.

The $D$ values of water molecules are constant below the first CMC, while beyond this concentration the values tend to decrease slightly until they rapidly decrease above the second CMC. Such a behavior for the $D$ value of water molecules at concentrations above the first CMC comes from the increased contribution of the slow motion of hydrated water molecules, and the obstruction effect of micellar formation.

The activation energy ($E_a$) for the self-diffusion of the DPP anions has been measured for regions I, IV and V, as listed in Table 3-2. The size of the micelle and the viscosity of the solvent which depends exponentially on the temperature, contribute to the $D$ value. Therefore, the observed $E_a$ value reflects the macroscopic behavior of a phase. The $E_a$ value (20.3 kJ mol$^{-1}$) obtained at a concentration of 3.8 wt% obviously reflects self-diffusion of the mono-dispersed DPP anions. The activation energy ($E_a = 26.7$ kJ mol$^{-1}$), which has been determined for the 15 wt% Na(DPP) solution, should be regarded as a superposition of contributions from the fast diffusion of mono-dispersed DPP anions and the slow diffusion of the micelles. The $E_a$ values of $32.0 \sim 35.4$ kJ
mol⁻¹, obtained for the samples at concentrations above the second CMC, imply a restricted state for DPP anion diffusion in this region.

**Table 3-2** Self-diffusion coefficients (\(D, 10^{-10} \text{[m}^2\text{s}^{-1}\text{]}\)) and activation energies (\(E_a, \text{kJ mol}^{-1}\))

<table>
<thead>
<tr>
<th>wt%</th>
<th>25 °C</th>
<th>50 °C</th>
<th>70 °C</th>
<th>80 °C</th>
<th>(E_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase I</td>
<td>3.8</td>
<td>4.08 ± 0.27</td>
<td>6.65 ± 0.22</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>15.0</td>
<td>1.17 ± 0.02</td>
<td>2.40 ± 0.33</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>0.49 ± 0.01</td>
<td>1.43 ± 0.05</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>34.9</td>
<td>0.51 ± 0.01</td>
<td>1.15 ± 0.09</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Phase IV</td>
<td>75.0</td>
<td>–</td>
<td>–</td>
<td>0.53 ± 0.02</td>
<td>0.91 ± 0.26</td>
</tr>
<tr>
<td>Phase V</td>
<td>75.0</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Figure 3-3 shows the temperature dependence of the self-diffusion coefficient for the 75 wt% DPP solution. The \(\ln D\) vs. \(1/T\) plot consists of two straight lines, the temperature (348 K) at the inflection point corresponds to the transition temperature from region IV to region V in the Na(DPP)-D₂O system. Activation energies obtained for the two regions are listed in Table 3-2. The high activation energy (67.3 ± 3.58 kJ mol⁻¹) for region IV indicates that the DPP anions are in an extremely restricted state. In region V, the \(D\) value at higher temperatures is very close to that of the DPP anions in the concentrated samples in region I, thereby indicating a similarity in their aggregated structure.
Fig. 3-3. Temperature dependence of the $D$ value for the 75 wt%-Na(DPP) solution.
3-3-3. $^{31}$P NMR chemical shifts and $^{31}$P signal shapes

Only narrow and symmetrical $^{31}$P resonance signals were observed for region I, reflecting an isotropic motional averaging of monomers and Brownian tumbling of the Na(DPP) micelles. The $^{31}$P chemical shift ($\sigma$) vs. log(1/C) plot is shown in Fig. 3-4. Two inflection points are observed, at concentrations of 4.6 and 17.0 wt%. Such a concentration dependence of the $^{31}$P $\sigma$ values can also be explained by a pseudo-phase and two-site model. The observed chemical shift ($\sigma$) is a weighted average of the chemical shifts in the monomeric and micellar states, since the exchange rate of the DPP anions between the bulk solution and the micelles is very fast. Thus, the observed $\sigma$ value is expressed [23] by equation (3-2),

$$\sigma = \left( \frac{CMC}{C} \right) \sigma_{\text{mono}} + \left[ \frac{(C - CMC)}{C} \right] \sigma_{\text{mic}}$$  \hspace{1cm} (3-2)

(assuming that the concentration in the monomeric state is constant above the CMC), where $C$ is the total concentration of DPP, and $\sigma_{\text{mono}}$ and $\sigma_{\text{mic}}$ are the $^{31}$P chemical shifts for the monomers and micelles, respectively. Plots of $\sigma$ vs. log(1/C) are well described by equation (3-2). The first inflection point (4.6 wt%), therefore, implies the presence of a CMC and gives a value in good agreement with that (4.7 wt%) obtained from the plot of lnD vs. 1/C.

For region I, in the concentrated region, there is another inflection point at a concentration of 17.1 wt%, which may then be regarded as the second CMC, although this value is greater than that (10.7 wt%) obtained from the plot of lnD vs. 1/C.

Variation of the $D$ value at the CMC is a direct reflection of the association behavior of the hydrocarbon part of a DPP anion, since the resonance signals of methylene-protons were used for measurements of the $D$ value. However, variation of $^{31}$P $\sigma$ may be caused by shielding effect of Na$^+$ counter ion to PO$_4^{3-}$ anion. The extent of screening of the counter ion is strongly dependent on the aggregate structure, as discussed later. In fact,
Fig. 3-4. $^{31}$P chemical shift ($\sigma$) vs. log($1/C$) plots for region I: a: 4.6 wt%, b: 17.2 wt%.
the degree of ionization ($\alpha$), obtained by small angle neutron scattering analysis (chapter 6), is 0.3 at a concentration of 10 wt%. Therefore, for highly concentrated solutions in region I, it may be assumed that the degree of ionization at the interface of aggregates becomes very small. Thus, the second CMC, obtained from the concentration dependence of the $^{31}$P $\sigma$ value, may reflect variation of the polar electrical-double layer structure, due to the structural change in the Na(DPP) micellar aggregate. Furthermore, the x-ray diffraction patterns provide evidence that a lamellar-like structure may be present in concentrated solutions in region I, as discussed below. We may assume that polar groups are more densely packed in a lamellar-like structure than in a micelle, since the increased screening action of counter ions results in a decrease in the repulsive force between the anions.

Thus, at the second CMC, variation of the aggregate structure may cause an environmental change to the polar layer, resulting in a difference between the second CMC values determined by measurements of the $^{31}$P $\sigma$ and $D$ values.

It has already been found for dihexanoyl phosphatidylcholine [24] that micellization brings about a shift of the $^{31}$P NMR signal and that the $^{31}$P $\sigma$ vs. log(1/C) plots could be explained by equation (3-2). Matsushita et al. [25] and Yoshida et al. [26] have also reported that, for the simple mono- and di-alkyl phosphate-water systems, an upfield shift of the $^{31}$P signal (caused by micellization) is caused by complex formation between the phosphate anions and the counter ions [27, 28]. Therefore, the upfield shift of the $^{31}$P signal seen for DPP anions may be explained by formation of such a complex.

For the samples in region I, it has been found that the half-height width ($\Delta V^{1/2}$) of the $^{31}$P signal depends upon the concentration of Na(DPP) (data not shown). The $\Delta V^{1/2}$ results may be summarized as follows. The $\Delta V^{1/2}$ values (0.023 ppm) are almost constant below the first CMC, and are almost equal to that (0.025 ppm) of diethylphosphate anions in the monomeric state, reflecting an isotropic motion of the whole molecule. The $\Delta V^{1/2}$ value observed at concentrations between the first and second
CMCs is also a weighted average of the $\Delta \nu^{1/2}$ values for the monomers and micelles in the two-site model [22]. The $\Delta \nu^{1/2}$ value increases with an increase in concentration above the first CMC, and a further increase of the half-height width occurs at concentrations above the second CMC.

For region II, the $^{31}$P NMR spectra of the upper and lower layers were also measured. For the upper layer, only a symmetrical $^{31}$P signal having a narrow half-height width was observed, and the $\sigma$ and $\Delta \nu^{1/2}$ values are very similar to those for the micellar solutions in region I. Therefore, for the upper layer, the $^{31}$P signal comes from the micelles which are in equilibrium with the monomers. Conversely, for the lower layer in region II, an asymmetric $^{31}$P signal having a low-field shoulder similar to that for the sample in region IV appears (Fig.3-5), showing that the $^{31}$P signal for the lower layer arises from the ordered aggregate system. The characteristic asymmetry for the $^{31}$P signal should be due to the chemical shift anisotropy ($\Delta \sigma = \sigma_\parallel - \sigma_\perp$) of a $^{31}$P nucleus in the phosphate group, arising from restricted anisotropic motion of the DPP anions. Thus, the results of the $^{31}$P NMR spectra support the coexistence of regions I and IV in region II.

For region IV, we have confirmed that the $^{31}$P NMR spectra also provide the asymmetric $^{31}$P signal in which the $\Delta \sigma$ value strongly depends upon the temperature, as shown in Fig.3-5. An increase in temperature brings about a marked chemical shift anisotropy for the $^{31}$P signals, indicating that a highly-organized structure of phosphate anions is formed. The $^{31}$P line shape suggests that formation of a lamellar-like structure occurs in this region, as confirmed by x-ray diffraction. In particular, for the sample solution in region IV, the $^{31}$P chemical shift anisotropy ($\Delta \sigma$) tends to increase with an increase in temperature. This observation is typical of an alignment of $^{31}$P chemical shift tensors perpendicular to the magnetic field with a narrow angular distribution about the direction of the magnetic field. In fact, for the dibutyl phosphate-water system [29], this orientation effect has been found to be characteristic of DM II type-discotic lyomesophase [30], formed by aggregation of large disklike micelles in the magnetic field.
Fig. 3-5. $^{31}$P NMR spectra of the samples in region IV at various temperatures (a: 25 °C, b: 50 °C, c: 70 °C and d: 90 °C) and the chemical shift anisotropies ($\Delta \sigma = \sigma_\perp - \sigma_\parallel$).
Thus, we can assume that the lower layer in region II and region IV are more structurally organized compared with region I and the upper layer in region II.

For region V, symmetric and narrow $^{31}$P NMR signals have been observed, indicating that this region is the isotropic phase.
3-3-4. X-ray diffraction pattern

The x-ray low-angle diffraction patterns of the samples were measured at different temperatures, to aid further understanding of the phase structure for the Na(DPP) water system. Figure 3-6 shows the x-ray diffraction patterns of the Na(DPP)-H$_2$O systems. For the lower layer samples in region II and the samples in region IV, the lattice spacings at 18.8 and 26.9 Å are observed within the temperature range 25 ~ 90 °C. The strong reflection at 3 ~ 5° corresponds to the first-order reflection and the very weak reflection at 8.3° to the second-order reflection. This observation indicates that an ordered structure of DPP aggregates is formed in these phases.

The corresponding interplanar spacings (d) for the Na(DPP)-H$_2$O systems are listed in Table 3-3 and show that the d values are strongly dependent upon concentration. However, the effect of temperature is very small, implying that the ordered structure of the Na(DPP) aggregates is very stable in the temperature range 25 ~ 90 °C.

Since the $^{31}$P NMR spectra for the lower layer samples in region II and those in region IV show asymmetric characteristics of a bilayer-type structure with respect to their line shapes, the observed d values possibly reflect the concentration-dependence of the thickness of a bilayer.

The radial electron density distributions were calculated by Fourier transformation of the x-ray diffraction intensities. The separation (r, Å) between two high electron density peaks may be useful as a measure of the distance between two polar-layers sandwiched between the hydrocarbon layers. The dependence of the r value on concentration is shown in Fig.3-7. The r values are 27 Å at high water-content and 24.5 Å at low-water content. In particular, the r values (24 ~ 25 Å) obtained from the concentrated samples correspond closely to the thickness of a bilayer whose formation can be assumed from the geometrical structural parameters of the Na(DPP) molecule. Thus, the x-ray diffraction data provide further evidence for the ordered structure of the aggregate system which was assumed from the self-diffusion and $^{31}$P NMR behavior.
Fig. 3-6. X-ray diffraction patterns of the Na(DPP)-water system at 25 °C (a) and 90 °C (b): (A) lower-layer sample (50 wt%, region II), (B) 72 wt% (region IV).
Fig. 3-7. Concentration dependence of the $r$ values for the Na(DPP)-water system at different temperatures: $\diamond$ : 50 °C, $\Box$ : 70 °C and $\bigcirc$ : 90 °C.
Table 3-3 The interplanar spacings $d$ Å and the $r$ Å values *

<table>
<thead>
<tr>
<th>wt%</th>
<th>25 °C</th>
<th>50 °C</th>
<th>70 °C</th>
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<td>23.0</td>
<td>28.1</td>
<td>22.5</td>
<td>26.9</td>
<td>22.6</td>
</tr>
</tbody>
</table>

* The separation between two high electron density peaks in the radial distribution function calculated by Fourier transformation.
3-4. Conclusion

The phase diagram and phase structure of the Na(DPP)-water system have been investigated by \textsuperscript{1}H pulsed-gradient NMR self-diffusion, \textsuperscript{31}P NMR, and x-ray diffraction methods. The results can be summarized as follows.

1. The phase diagram of the Na(DPP)-water system consists of five regions (I, II, III, IV and V). Region I is a homogeneous and transparent one-phase solution and region II a two-phase solution having transparent upper and lower layers. In region III, hydrated crystals and a solution of Na(DPP) coexist. Region IV is a transparent gel phase at room temperature and a homogeneous, transparent and viscous one-phase solution at higher temperatures. Region V is a homogeneous, transparent and fluid phase.

2. For region I, the presence of first and second values of the CMCs can be assumed from the results of the self-diffusion coefficient and \textsuperscript{31}P NMR spectra. The first CMC values (4.6 and 4.7 wt\%) obtained by the two methods are in good agreement each other. However, for the second CMC, the value (17.1 wt\%) obtained by \textsuperscript{31}P NMR is greater than that (10.7 wt\%) determined by a plot of \(\ln D\) vs. 1/C. The marked difference between these second CMC values arises from the different methods of determination: the \textsuperscript{31}P NMR method reflects environmental variation of the polar layer and, in particular, the binding process of the counter ions, while the \(D\) value method depends upon the translational motion of a hydrocarbon tail. Region II is a two-phase area in which regions I and IV coexist. However, for region IV the DPP anions are in an extremely restricted state and the highly-organized structure of the phosphate anions is formed. Moreover, the \(D\) value and \textsuperscript{31}P NMR spectra show that region V is isotropic and its phase structure is very similar to that for the concentrated sample in region I.

3. The radial electron density distributions indicate that a highly-organized structure is formed for the concentrated samples in region I, for the lower layer sample in region II, and in region IV, and that the structure is similar to that of a bilayer having a thickness which depends on the concentration. The results of the low-angle x-ray diffraction
patterns for the highly-organized structure agree well with those qualitatively predicted by $^{31}P$ NMR spectra.
References


Chapter 4.

Raman scattering spectra of sodium \( n \)-butyl(\( n \)-hexyl) phosphate aggregates and conformation about the phosphodiester P-O bonds in coagel phases

4-1. Introduction

Conformational studies on dialkyl phosphates involved in an aggregated structure are important for understanding the physico-chemical properties of phospholipid bilayers. For the conformation of simple dialkyl phosphates in the solid state, x-ray crystallographic analysis has been performed for barium diethylphosphate [1], for which the two C-O bonds were found to take the gauche positions with regard to the phosphodiester P-O bonds. The conformation of dialkyl phosphate anions in aqueous solution has been studied mainly by vibrational [2] and \( ^1\)H and \( ^{13}\)C NMR [3] spectroscopic methods.

The vibrational spectroscopic studies of dimethyl phosphate (DMP) [2] have suggested that the GG form is predominantly stabilized for the conformation about the P-O bonds in aqueous solution. Conversely, depolarized Rayleigh scattering and vibrational spectra of DMP [4] have showed that the GT and TT forms are highly populated. In an identical-chain di-\( n \)-alkyl phosphate anion, nine rotational isomers about the phosphodiester P-O bonds can be considered. However, only three molecular forms (GG, GT and TT) are possible, since the four mirror images can be omitted and two-molecular forms are also omitted because of their instability resulting from the steric hindrance.

Jayaram et al. [5] have assumed the relative conformational free energies of hydration for DMP, indicating that the differences in the hydration free energies for the various conformations are small. The small conformational differences for the hydration free energies of DMP may be ascribed to dialkyl phosphates having longer \( n \)-alkyl chains,
which give preference to the $TT$ and $GT$ forms in the phosphate anion owing to the hydration environment in the solid state.

The vibrational bands, which arise from the skeletal deformation modes, appear in the low frequency region below 600 cm$^{-1}$ and provide direct information on the steric structure of molecules [6-14]. In particular, the accordion-like vibrational mode characteristic of the all-trans hydrocarbon chain is a powerful indicator of conformational change upon alteration of the aggregate structures [9, 10].

In our previous paper [14], for sodium di-$n$-pentyl phosphate in the crystalline state, it has been assumed from the experimental and calculated results of the accordion vibrational mode that preferential stabilization of a specific rotational isomer about the P-O bonds occurs and the species of stabilized molecular form strongly depends on the degree of hydration.

In the present study, we report the Raman scattering spectra of a mixed-chain di-$n$-alkyl phosphate, sodium $n$-butyl($n$-hexyl) phosphate. In particular, the sensitivity of the accordion-like vibrational mode to the conformational preference about the P-O bonds in this molecule is discussed in detail.
4-2. Experimental

4-2-1. Materials

The sample of sodium $n$-butyl($n$-hexyl) phosphate Na(BHP) was prepared by neutralization of phosphoric acid $n$-butyl($n$-hexyl) ester with sodium hydroxide aqueous solution. Phosphoric acid $n$-butyl($n$-hexyl) ester was synthesized by the same method reported in chapter 2-2-1. Identification of the BHP sample was made by $^{13}$C NMR spectral and elemental analysis. Anal. $C_{10}H_{22}O_{4}PNa$: Calcd: C, 49.19; H, 9.08; Found: C, 48.79; H, 9.51. Na(BHP) was dehydrated by vacuum drying in an oil bath at 150°C (sample I). In the dehydrated Na(BHP), water was undetectable by infrared spectroscopy. The liquid crystalline samples of Na(BHP) were prepared by heating of the 8:2 and 7:3 Na(BHP)-H$_2$O (wt%) mixtures, which were termed sample II and sample III, respectively.

4-2-2. Phase diagram determinations

Sample solutions were prepared by weighing the Na(BHP) and water components into glass ampoules, which were then sealed and the contents homogenized by shaking. The temperature dependence of the phase feature of the samples was determined by visual inspection as the ampoules were held in a temperature-controlled water-bath (rate of temperature elevation and cooling 0.1 °C/min). The temperature was measured with a digital thermometer (Sato Keiryoki).

4-2-3. Calorimetry

The thermotropic transition temperature of the Na(BHP)-water system was determined with a differential scanning calorimeter (Rigaku DSC 8230), which was scanned at a rate of 2 °C/min by using a volatile pan with $\alpha$-Al$_2$O$_3$ in the reference pan.
4-2-4. Raman scattering measurements

The Raman scattering spectra were excited by the 514.5 nm line of an Ar ion laser (NEC GLG-3200) and were recorded on a JEOL JRS-400D Raman spectrometer. For measurements in the temperature range -170 to 25 °C, BHP in a capillary was placed in a variable-temperature capillary cell system (JEOL RS-VTC41).

4-2-5. Normal coordinate calculation

The normal vibrations of a Na(BHP) molecule were calculated by the use of the modified Urey-Bradley force field. A HITAC M-260K system in the Center of Information Processing Education of the Nagoya Institute of Technology was used for the calculations, using the program NCTB prepared by Shimanouch et al. [15]. Structural parameters of barium di-ethyl phosphate determined by x-ray analysis [1] were used for BHP; \( r(P=O) = 1.51 \, \text{Å} \), \( r(P-O) = 1.605 \, \text{Å} \), \( r(C-O) = 1.51 \, \text{Å} \), \( r(C-H) = 1.09 \, \text{Å} \), and \( \angle \text{COP} = 120^\circ \). It was assumed that the other valence angles were tetrahedral and that the internal rotation angle were 60° for the gauche (G) form and 180° for the trans (T) form.

Force constants were taken from those of sodium di-n-pentyl phosphate [14]. The force constants were modified by the least-squares method to obtain the best fit between the calculated and the observed frequencies of dehydrated sample (sample I) cooled at -170 °C, which was assumed to take up the GG form in the solid state. These corrected force constants were then used for normal coordinate calculations of the other possible rotational isomers of a Na(BHP) molecule. The force constants used are listed in Table 4-1. Assignments were based on the potential energy distributions.
<table>
<thead>
<tr>
<th>Force Constant</th>
<th>Value</th>
<th>Force Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>K(C-H), CH₃</td>
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<td>F(H·C·H)</td>
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<tr>
<td>K(C-H), CH₂</td>
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<td>F(C·C·H)</td>
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<td>K(C-C)</td>
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<td>F(C·C·C)</td>
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<tr>
<td>K(C-O)</td>
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<td>F(C·C·O)</td>
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<tr>
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<td>F(C·O·P)</td>
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<td>K(P=O)</td>
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<tr>
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<td></td>
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<tr>
<td>H(H-C-H), CH₂</td>
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<td>Y(C-C)</td>
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<tr>
<td>H(C-C-H), CH₃</td>
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<td>Y(C-O)</td>
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<tr>
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<td>Y(P-O)</td>
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<tr>
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<tr>
<td>H(C-C-O)</td>
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<td>κ(CH₃)</td>
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</tr>
<tr>
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<td>κ(CH₂)</td>
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<tr>
<td>H(C-O-P)</td>
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<td>p(P-O)</td>
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<tr>
<td>H(O=P=O)</td>
<td>0.150</td>
<td>n(CH₃)</td>
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</tr>
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</table>
4-3 Results and discussion

4-3.1. Thermotropic properties of the Na(BHP)-H₂O system

The phase diagram of the Na(BHP)-H₂O system consists of two regions (A and B) in the concentration range 60.0 ~ 90.0 wt% as shown in Fig. 4-1. Region A is in a homogeneous transparent liquid crystalline state and region B in a coagel phase.

Figure 4-2 shows the differential scanning calorimetric results of samples II and III. The temperatures of the thermotropic phase transition are listed in Table 4-2 with the ΔH values calculated from the peak area. Sample II (8:2 Na(BHP)-H₂O mixture) is in the lyotropic liquid crystalline state above the phase transition temperature of 13.5 °C, while in the range 2.3 ~ 13.5 °C and below 2.3 °C it is in the coagel state. Sample III (7:3 Na(BHP)-H₂O mixture) is in the lyotropic liquid crystalline state above 3.2 °C and in the coagel state in the temperature range -7.8 ~ 3.2 °C and below -7.8 °C. For the lithium n-butyl(n-hexyl) phosphate-H₂O system in the lyotropic liquid crystalline state, the existence of a phase structure similar to a lamellar was suggested by the observation that the ³¹P NMR line shape had a low-field shoulder (chapter 2-3-1). For the Na(BHP) samples used in the present study, a lamellar structure was also confirmed by x-ray diffraction (d = 20.9 Å: sample II, d = 22.1 Å: sample III, at 25 °C).

<table>
<thead>
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<th>Sample</th>
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</thead>
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<td>72.2</td>
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</tr>
<tr>
<td></td>
<td>3.2</td>
<td>52.1</td>
</tr>
</tbody>
</table>

71
Fig. 4-1. Phase diagram of the Na(BHP)-H₂O system. A: lyotropic liquid crystalline phase, B: coagel phase.
Fig. 4-2. Differential scanning calorimetry of (a) sample II and (b) sample III.
4-3-2. Vibrational spectra of samples I, II and III

For the samples I, II and III, Raman spectra were investigated in the region 100 ~ 3000 cm⁻¹. It was found that the lyotropic liquid crystal to coagel transition results in a marked variation in the Raman spectra with the spectral features being strongly dependent upon the water content. For the surfactant-water binary system, it has already been considered that crystals of hydrated surfactant molecules are formed in the coagel phases [16]. Taking into account the results of previous investigations for di-n-alkyl phosphates [14], for the Na(BHP) molecules in the solid state and coagel phase we may assume that the n-butyl and n-hexyl chains take up the all-trans conformations and that conformers about the two CH₂-O bonds are in the trans form.

Normal coordinate analysis was carried out to interpret the Raman spectra of the three samples. In the present calculations, it was assumed that the conformations about every CH₂-CH₂ bond and about the two CH₂-O bonds are trans. Three conformations of trans (T), gauche (G) and gauche' (G') about the phosphodiester P-O bonds are possible. However, only four rotational isomers (GG, GT, TG and TT) were used for the calculations of the normal modes (Fig.4-3). The mirror images (G'G', G'T and TG') were omitted, and the GG' and G'G isomers were also omitted because of their instability due to steric hindrance.
Fig. 4-3. Schematic representation of four rotational isomers (GG, GT, TG and GG) about the P-O bonds. The conformations about every CH$_2$-CH$_2$ bond and two CH$_2$-O bonds were assumed to be in the trans conformation.
4.3.3. The 200 ~ 600 cm\(^{-1}\) region

Figure 4-4 shows the Raman spectra of the samples I, II and III in the region 200 ~ 600 cm\(^{-1}\) at different temperatures. Table 4-3 lists the calculated skeletal deformational frequencies for the four possible conformers of Na(BHP) in the 200 ~ 600 cm\(^{-1}\) region, together with the assignments and the observed frequencies. Results indicate reasonable agreement between the calculated values and the observed frequencies.

In particular, for the TT form about the P-O bonds, it is expected that the accordion-like vibrational frequencies arising from the all-\textit{trans} \(n\)-butyl and \(n\)-hexyl chains appear at higher frequency, compared with the calculated results for the other three conformers. The result is consistent with that for sodium di-\(n\)-pentyl phosphate, which has been demonstrated in our previous paper [14]. From the calculated results of the \(GT\) form, the two accordion vibrational modes are expected to appear at 298 and 254 cm\(^{-1}\). The former band frequency arises from the accordion modes of the all-\textit{trans} \(n\)-butyl chain, which is in the \textit{gauche} position with respect to the P-O bond, and the latter band frequency comes from the accordion mode of the extended \(n\)-hexyl chain in the \textit{trans} configuration about the P-O bond.

For sample I (dehydrated BHP), the Raman bands measured at -170 °C are successfully assigned to the \(GG\) form. The bands at 222 and 306 cm\(^{-1}\) can be assigned to the accordion vibrational modes of the \(n\)-hexyl and \(n\)-butyl chains, respectively. When we compare the Raman spectra measured at 25 °C and -170 °C with each other, it is found that there exists a marked difference between the relative intensity \((I_{253}/I_{223})\) at 25 °C and that \((I_{255}/I_{222})\) at -170 °C: \(I_{253}/I_{223} = 2.2\) and \(I_{255}/I_{222} = 1.1\). That is, a rise in temperature brings about an increase in the relative intensity. This observation can be explained in the following way.

From the results of normal mode calculation, we can expect that the accordion frequency coming from \(n\)-hexyl chain for the \(GT\) form appears at 254 cm\(^{-1}\). Even in the hydrated sample, probably, the \(GT\) form in addition to the \(GG\) form also exists and its
Fig. 4-4. Raman spectra of samples (a) I, (b) II and (c) III in the 100 ~ 600 cm\(^{-1}\) region.
Table 4-3 Observed and calculated frequencies (cm\(^{-1}\)) of Na(BHP) in the 200–600

<table>
<thead>
<tr>
<th></th>
<th>Sample I</th>
<th></th>
<th>Sample II</th>
<th></th>
<th>Sample III</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solid</td>
<td>Solid</td>
<td>Lyotropic</td>
<td>Coagel</td>
<td>Lyotropic</td>
<td>Coagel</td>
</tr>
<tr>
<td>obsd a)</td>
<td>25 °C</td>
<td>-170 °C</td>
<td>25 °C</td>
<td>-170 °C</td>
<td>25 °C</td>
<td>-170 °C</td>
</tr>
<tr>
<td>572vw</td>
<td>573vw</td>
<td></td>
<td>574vw</td>
<td>571vw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>547vw</td>
<td>553vw</td>
<td></td>
<td>550vw</td>
<td>546vw</td>
<td></td>
<td>549vw</td>
</tr>
<tr>
<td>517vw</td>
<td>518vw</td>
<td></td>
<td>519vw, b</td>
<td>515vw</td>
<td></td>
<td>519vw, b</td>
</tr>
<tr>
<td></td>
<td>480sh</td>
<td>473vw</td>
<td>470vw</td>
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<td>471vw</td>
</tr>
<tr>
<td>450vw, b</td>
<td></td>
<td></td>
<td>441vw</td>
<td>410vw, sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>392vw</td>
<td>398vw</td>
<td>395vw</td>
<td>393w</td>
<td>385vw, b</td>
<td>385vw</td>
<td></td>
</tr>
<tr>
<td>371vw</td>
<td>373vw</td>
<td>375vw</td>
<td>374vw, sh</td>
<td>341vw</td>
<td>343vw</td>
<td></td>
</tr>
<tr>
<td>298vw</td>
<td>306vw</td>
<td>298w</td>
<td>299w</td>
<td>298w</td>
<td>298w</td>
<td></td>
</tr>
<tr>
<td>253vw</td>
<td>255vw</td>
<td>260vw, b</td>
<td>258vw</td>
<td>261vw, b</td>
<td>255vw</td>
<td></td>
</tr>
<tr>
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<td>222vw</td>
<td>221vw, b</td>
<td>220vw, b</td>
<td></td>
<td>218vw</td>
<td></td>
</tr>
</tbody>
</table>

a) s, strong; m, medium; w, weak; v, very weak; sh, shoulder; b, broad.

b) δ, deformation; a, antisymmetric; s, symmetric; r, rocking; w, wagging; s, scissoring;
| cm⁻¹ region |
|---|---|---|---|
| calc d | assignment b) |
| GG | GT | TG | TT |
| 579 | 570 | 578 | 574 | δₙSkel (GG, TG, TT) | δOPO(GT, TT), wPO₂⁻ (GT) |
| 557 | 545 | 534 | 531 | δOPO(GG), δₙSkel(GT) |
| 511 | 519 | 510 | 511 | tPO₂⁻ |
| 485 | 489 | 491 | δₙSkel |
| 474 | 462 | 468 | δₙSkel, wPO₂⁻ (TG) | δₙSkel, δOPO |
| 453 | | | | tPO₂⁻ (GT) |
| 410 | | | | tPO₂⁻ (GG, TT), sPO₂⁻ (TT) |
| 370 | 382 | 383 | 384 | sPO₂⁻ (GG), sPO₂⁻ (GT, TG), tPO₂⁻ (TT) |
| 340 | 332 | 345 | 360 | δₙSkel(GG, GT, TT), sPO₂⁻ (GT), tPO₂⁻ (TG) |
| 294 | 298 | 294 | 303 | δₙSkel(butyl), tPO₂⁻ (GG, GT), δOPO(TG), δₙSkel(hexyl) (TT) |
| 259 | 260 | 259 | 259 | τC-C |
| 259 | 259 | 259 | 259 | τC-C |
| 254 | | | | δₙSkel(hexyl), τC-C |
| 233 | 234 | 237 | | δₙSkel |
| 228 | 226 | | | δₙSkel(hexyl) |

<sup>t</sup>, twisting; <sup>τ</sup>, torsion
population must increase with increasing temperature, resulting in such an increase in relative intensity. Furthermore, the vibrational mode characteristic of the $GT$ form, deriving from the coupling between asymmetric skeletal deformation mode of hydrocarbons and deformational mode of the OPO segment, is expected to appear at 453 cm$^{-1}$. In the Raman spectrum at 25 °C, a very broad band at 450 cm$^{-1}$ appears and corresponds well to the calculated frequency (453 cm$^{-1}$), implying that the relative amount of the $GT$ form increases with increasing temperature.

Thus, for dehydrated Na(BHP) sample in the solid state, we may assume that the $GG$ and $GT$ forms coexist and lowering in temperature brings about the stabilization of the $GG$ form.

In the Raman spectrum of sample II in the coagel state, the Raman bands at 258 and 299 cm$^{-1}$ appear and are assigned to the accordion modes of the $n$-hexyl and $n$-butyl chains, respectively. The two bands are greater than that at 220 cm$^{-1}$, indicating that the $GT$ form is stabilized in the coagel sample. Furthermore, it should be emphasized that the Raman band observed at 441 cm$^{-1}$ corresponds to the calculated frequency 453 cm$^{-1}$ of the $GT$ form and can be regarded as a band characteristic of the $GT$ form.

For sample III in the coagel state, the Raman spectral feature in the low frequency region is very similar to that for sample II in the coagel state, both in frequency and intensity. However, it should be noted that the Raman band corresponding to the 441 cm$^{-1}$ band for sample II disappears for this sample in coagel state, implying that the relative amount of the $GT$ form is very small and the $TT$ form may be stabilized in the coagel phase.

These observations in the low-frequency region reveal that the extent of hydration of the phosphate groups affects the conformational preferences about the phosphodiester P-O bonds for Na(BHP) in the solid and coagel states.
4.3-4. The 700 ~ 1250 cm\(^{-1}\) region

The calculated frequencies of symmetric and antisymmetric O-P-O stretching \([\nu_s(OPO)\text{ and }\nu_a(OPO)]\), symmetric and antisymmetric PO\(_2^+\) \([\nu_s(PO_2^+)\text{ and }\nu_a(PO_2^+)]\) stretching, C-C stretching \([\nu(CC)]\), and the vibrational modes characteristic of the CH\(_2\) and CH\(_3\) groups in the 700 ~ 1250 cm\(^{-1}\) region are listed in Table 4-4, together with the observed frequencies and assignments. Figure 4-5 shows the Raman spectra of sample I in the solid state, samples II and III in the lyotropic liquid crystalline and coagel phase in the 700 ~ 1000 cm\(^{-1}\) region.

For samples II and III in the lyotropic liquid crystalline state, the Raman spectral features in this region are very similar to each other. However, for the samples in the coagel state, the Raman spectral feature seems to be strongly dependent on the water content. For sample III in the coagel state, the Raman band at 803 cm\(^{-1}\) appears, while for the coagel sample II the band corresponding to this band is not found. As is seen in Table 4-4, the results of normal mode calculations indicate that the 803 cm\(^{-1}\) band is characteristic of the TT form about the P-O bonds. Thus, we may assume that the Raman spectra in this region reflect the preferential stabilization of the TT form for samples III in the coagel state.

The stabilization of a specific rotational isomer about the P-O bonds is reflected in the Raman spectra in the CH\(_2\) rocking region. In the Raman spectra for sample I, the Raman bands at 906 ~ 907 cm\(^{-1}\) appear at 25 and -170 °C, while the Raman band corresponding to these bands disappears for samples II and III in the coagel state. Therefore, the Raman bands at 906 ~ 907 cm\(^{-1}\) are characteristic of the GG form about the P-O bonds, although it is difficult to expect the presence of the bands from the present calculated results.

As expected from the normal mode calculations (Table 4-4), there exists a possibility for overlapping of the \(\nu(CO), \nu(CC), \nu(CH_2)\) and \(\nu_s(PO_2^+)\) modes in the 1000 ~ 1200 cm\(^{-1}\). In particular, we may expect that a splitting of the \(\nu_s(PO_2^+)\) mode occurs,
Table 4-4 Observed Raman and calculated frequencies ( cm\(^{-1}\) ) for Na(BHP) samples in the 700 ~ 1250 cm\(^{-1}\) region

<table>
<thead>
<tr>
<th>obsd (^a)</th>
<th>Sample I</th>
<th>Sample II</th>
<th>Sample III</th>
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<td>Coagel</td>
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<td></td>
</tr>
<tr>
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<td>25 °C  -170 °C</td>
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</tr>
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<td>1263vw</td>
<td>1265vw</td>
<td>1266vw</td>
<td>1263vw</td>
<td>(\delta_a)(Skek), w(CH(_2))</td>
</tr>
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<td>1232vww</td>
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<td>1123m</td>
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<td>894s</td>
<td>893w</td>
<td>898m</td>
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</tr>
<tr>
<td>822w,sh</td>
<td>819w,sh</td>
<td>820w,sh</td>
<td>803vw</td>
<td>803vw</td>
<td>803vw</td>
</tr>
<tr>
<td>787m</td>
<td>787m</td>
<td>785m</td>
<td>786m</td>
<td>783m</td>
<td>782m</td>
</tr>
<tr>
<td>748vw</td>
<td>743vw</td>
<td>746vw</td>
<td>747vw</td>
<td>747vw</td>
<td>747vw</td>
</tr>
<tr>
<td>725vw</td>
<td>726vw</td>
<td>725vw</td>
<td>728vw</td>
<td>729vw</td>
<td>728vw</td>
</tr>
</tbody>
</table>

a) s, strong; m, medium; w, weak; v, very weak; sh, shoulder; b, broad

b) δ, deformation; a, antisymmetric; s, symmetric; r, rocking; w, wagging; s, scissoring; t, twisting; τ, torsion
Fig. 4-5. Raman spectra of samples (a) I, (b) II and (c) III in the 700 ~ 1300 cm$^{-1}$ region.
due to coupling with the $\nu$(CC) modes. For sample I, the Raman bands at 1032, 1066 ~ 1067 and 1123 ~ 1125 cm$^{-1}$ are prominent at 25 °C and -170 °C. The former two bands mainly arise from the $\nu$(CC) modes of the extended $n$-butyl and $n$-hexyl chains. The very strong bands at 1123 ~ 1125 cm$^{-1}$ come from the $\nu_s$(PO$_2^-$) mode overlapped with the $\nu$(CO), $\tau$(CH$_2$) and $\nu$(CC) modes, and the band frequencies of the $\nu_s$(PO$_2^-$) mode are very close to that (1120 cm$^{-1}$) for sodium di-\textit{n}-pentyl phosphate. The band frequency originating from the $\nu_s$ mode of the PO$_2^-$ group seems to be dependent on the type of counter ion for the dialkyl phosphate salts (listed in Table 4-5).

For samples II and III in the coagel state, prominent Raman bands at 1030 ~ 1035, 1062 ~ 1065, 1095 ~ 1100, 1122 ~ 1123 and 1151 ~ 1153 cm$^{-1}$ are observed in common and assignments of these bands are summarized in Table 4-4. The former two bands are ascribed to the $\nu$(CC) modes of the extended $n$-butyl and $n$-hexyl chains in the coagel state. The two Raman bands at 1095 ~ 1100 and 1122 ~ 1123 cm$^{-1}$ should be ascribed to the $\nu_s$(PO$_2^-$) mode overlapped with $\nu$(CO), $\tau$(CH$_2$) and $\nu$(CC) modes. These bands are lower in frequency than the $\nu_s$(PO$_2^-$) mode observed at 1123 ~ 1125 cm$^{-1}$ for the dehydrated sample (sample I). This lowering may be ascribed to the difference in conformation about the phosphodiester P-O bonds.

It has already been pointed out by Brown et al. [17] and Jayaram et al. [5] that the band frequency of the $\nu_s$(PO$_2^-$) mode depends upon the conformation about the P-O bonds. However, in the present calculations, conformation dependence of the $\nu_s$(PO$_2^-$) frequency is not so marked. Probably, an increased CH$_2$ chain length results in the small difference of the $\nu_s$(PO$_2^-$) frequency among four conformations, owing to the coupling with the $\nu$(CC) modes. This makes it difficult to discuss conformational change about the P-O bonds using the $\nu_s$(PO$_2^-$) frequency.
4.3.5 The 1400 ~ 1500 and 2800 ~ 3000 cm⁻¹ regions

The CH₂ scissoring mode [ s(CH₂) ] observed in the 1400 ~ 1500 cm⁻¹ region, which is sensitive to molecular interactions, is useful as a monitor of the packing state of the hydrocarbon chain in the gel or crystalline state [18, 19].

Figure 4-6 shows the Raman spectra of samples I, II and III at the different temperatures in this region. A marked difference in the spectral features is found among these three samples. For sample I in the solid state, splitting of the s(CH₂) mode is not observed at 25 °C and -170 °C. However, for samples II and III in the coagel state, splitting of this mode is observed and the separations ( Δν ) between the Raman bands at 1436 ~ 1437 and 1452 ~ 1456 cm⁻¹ are Δν = 16 cm⁻¹ for sample II and Δν = 19 cm⁻¹ for the sample III. These observations can be due to the variation in the packing of the n-butyl and n-hexyl chains caused by the preferential stabilization of a specific conformer about the P-O bonds. The spectral features in this region differ markedly between samples II and III in the coagel state, in particular, in intensity. That is, we may assume that the difference in the chain packing between two coagel states comes from preferential stabilization of a specific isomer about the P-O bonds, reflecting the spectral features.

Figure 4-7 shows the Raman spectra of samples I, II and III at different temperatures in the CH stretching region. For sample I, the Raman bands at 2891 ~ 2892 cm⁻¹ are found to increase in intensity as the sample is cooled to -170 °C. For samples II and III, it is found that the phase transition from the lyotropic liquid crystalline to coagel state brings about a marked variation in the spectral feature of the CH stretching modes. For sample II, it is evident that the relative intensities, I₂893/I₂959-2960 and I₂873-2874/I₂959-2960, increase upon the transition to coagel phase, and moreover, the 2850 cm⁻¹ band newly appears. For sample III, the Raman bands at 2848 and 2884 cm⁻¹ are newly observed, and the 2875 cm⁻¹ band, observed in the lyotropic liquid crystalline state, disappears in the coagel state. Moreover, the relative intensity, I₂907-2909/I₂960-2961, seems to increase rapidly upon such a transition. It should be noted that the Raman bands
Fig. 4-6. Raman spectra of samples (a) I, (b) II and (c) III in the s(CH$_2$) region.
Fig. 4-7. Raman spectra of samples (a) I, (b) II and (c) III in the C-H stretching region.
corresponding to the 2848 ~ 2850 cm\(^{-1}\) bands of samples II and III in the coagel state are not found for sample I. Thus, the extent of hydration of the polar group affects the Raman spectral feature in the CH stretching region. The difference in packing of the \(n\)-butyl and \(n\)-hexyl chains coming from conformational preference about the P-O bonds is reflected in the spectral feature.

**Table 4-5** \(v_4(PO_2^-)\) Frequencies (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Compound</th>
<th>Frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(DMP)(_2)Ba</td>
<td>1098</td>
</tr>
<tr>
<td>(DEP)(_2)Ba</td>
<td>1093</td>
</tr>
<tr>
<td>(DBP)(_2)Ba</td>
<td>1108</td>
</tr>
<tr>
<td>(BPP)(_2)Ba</td>
<td>1106</td>
</tr>
<tr>
<td>(BHP)(_2)Ba</td>
<td>1109</td>
</tr>
<tr>
<td>BHPLi</td>
<td>1123</td>
</tr>
<tr>
<td>BHPNa</td>
<td>1123</td>
</tr>
<tr>
<td>BHPK</td>
<td>1121</td>
</tr>
</tbody>
</table>

DMP : Dimethyl phosphate  
BEP : Diethyl phosphate  
DBP : Di-\(n\)-butyl phosphate  
DPP : Di-\(n\)-pentyl phosphate
4-3-6. Hydration effect on the phosphodiester conformers

Jayaram et al. [5] have assumed the relative conformational free energies of hydration of dimethylphosphate using the hydration shell model, suggesting that the conformational differences for the hydration free energies are within $3 k_B T$. The results may be applied to the case of Na(BHP). Probably, the small conformational differences for hydration free energies enable preference for the $GT$, $TG$ and $TT$ forms owing to the hydration environment in the Na(BHP)-H$_2$O system in the coagel state.

Hydrated water molecules bound at the interface of a bilayer are highly oriented and strongly restricted at the polar moiety. Since a bilayer structure has been confirmed for the Na(BHP)-H$_2$O system in the lyotropic liquid crystalline state by the x-ray diffraction method, it may be expected that the Na(BHP) molecules organize the highly-ordered structure in the coagel state. Therefore, we may assume that the hydration shell in the samples II and III in the coagel state is much more rigid compared with that in the bulk water [18-20]. In such a rigid hydration shell, the available conformational space of Na(BHP) is probably extremely restricted. The restricted conformational space may be associated with the number of water molecules in the rigid shell. Such restriction may cause the preferential stabilization of a specific conformer about the P-O bonds for Na(BHP) in the coagel state, owing to the small conformational differences for the hydration free energies.
4.4 Conclusion

For dehydrated Na(BHP) (sample I) in the solid state and for the Na(BHP)-H₂O system (samples II and III) in the coagel state, Raman bands originating from the accordion-like vibrational mode were observed. Assignment of the accordion-like vibration was made by normal coordinate analysis for four possible conformers (GG, GT, TG, and TT) about the phosphodiester P-O bonds. The two accordion-like vibrational modes arising from the all-trans n-butyl and n-hexyl chains were observed. It was found that the accordion-like band frequency strongly depends upon the conformational difference about the P-O bonds.

For sample I, two Raman bands were observed at 222 ~ 223 and 298 ~ 306 cm⁻¹, and are assigned to the accordion-like vibrational modes of the all-trans n-hexyl and n-butyl chains for the GG form about the P-O bonds, respectively.

For sample II, it was assumed from the accordion-vibrational analysis that the GT form is preferentially stabilized in the coagel phase. Furthermore, for sample III in the coagel state, conformational preference of the TT form was found to occur, indicating directly that the stability of conformation about the P-O bonds depends on the extent of hydration of the PO₄⁻ group.

It was also found that stabilization of such a specific rotational isomer about the P-O bonds is reflected in the observation of bands in the higher frequency region of the Raman spectra.
References

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Chapter 5.

Theory of small angle neutron scattering analysis. The application for colloidal particles

5-1. Introduction

Powerful techniques available for structural determination of macromolecules or self-assemblies in aqueous solutions include light scattering (LS) [1-6], small angle x-ray scattering (SAXS) [7-11] and small angle neutron scattering (SANS) [12-21]. In modern light scattering techniques, both static light scattering (SLS) [1-4] and dynamic light scattering (DLS) [5, 6] are included. Sizes of macromolecules or assemblies in aqueous solutions generally range from about 20 Å up to 10,000 Å. In order to obtain information with regard to size and size distribution, the wavelength of the radiation (λ) used in scattering experiment should match the size range of interest. The scattering vector \( Q \) used in a scattering experiment is given by the following equation.

\[
Q = \frac{4\pi}{\lambda} n \sin\left(\frac{\theta}{2}\right)
\]

where \( \theta \) is the scattering angle and \( n \) is the refractive index of the medium. For the refractive index of light, \( n = 1.33 \) in water, but for x-rays and neutrons, \( n \) is very close to unity. The characteristic size in the real-space \( R \) is reciprocally related to the characteristic width of the intensity distribution in \( Q \) space. Therefore, for a typical aggregate size of \( R \), one needs to do a scattering experiment that spans a \( Q \) range an order of magnitude on each side of the value \( Q_0 = 2\pi/R \). Thus, at the lower end where the radius of a particle \( R \approx 20 \) Å, one should use x-rays or neutrons where \( \lambda \approx 1 \) – 20 Å. At the upper end, where \( R \approx 10,000 \) Å, one should use light with \( \lambda \approx 4000 \) – 8000 Å.

It is also a consequence of this theory that the maximum spatial resolution achievable in a scattering experiment is given in terms of the maximum wave number
covered in the measurement, $Q_{\text{max}}$, by

$$\Delta R = \pi / Q_{\text{max}} \quad (5-2)$$

In a typical SAXS and SANS measurements where $Q < 0.6 \text{ Å}^{-1}$, the maximum spatial resolution achievable is not more than 5 Å. In a typical light scattering experiment $Q \leq 0.003 \text{ Å}^{-1}$, the resolution is not better than 1000 Å.

Although in many ways SANS is similar to the well-known SAXS technique, it has some unique features that distinguish it from SAXS and LS, and it can be used with great advantage in the investigation of macromolecules or self-assemblies in aqueous solutions.

First of all, the scattering power of neutron scattering is greater than x-rays. For neutrons the scattering intensity of the hydrogen-containing molecules can be made to vary greatly by substitution of the protons by deuterons. On the other hand, the application of SAXS technique in determination of the structure of aggregates is rather difficult, because there is no contrast between the solvent and the hydrocarbon part of the aggregate. However, SAXS is a powerful tool for the structural study of the head group region, the counter ion distribution and hydration, since the electron density of metal ions is different from that of solvents.

A change in the coherent scattering length density between the aggregate and the solvent can be achieved by varying the D$_2$O / H$_2$O ratio of the solvent. This technique is called external contrast variation method [12, 14, 17, 18]. Instead of varying the D$_2$O / H$_2$O ratio of the solvent, the internal contrast variation method changes neutron scattering length density of solute by mixing normal-solute with chain-deuterated solute [14]. Using contrast variation methods, one can determine contrast matching point, molecular weight of an aggregate and volume of a surfactant molecule. For SAXS the contrast variation method is rather difficult to apply without changing the chemical and physical properties of solution drastically. Since aggregate formation results from a delicate balance between the hydrophobic interaction and the charge repulsion on the surface of an aggregate, a
small change in solvent condition can induce a pronounced change in the state of an aggregate. In general, for SAXS contrast variation, salts \([7, 8]\) and sucrose \([9, 11]\) are added to vary contrast. But, addition of these compounds changes physical and chemical properties of the solvent and affects the shape and size of aggregates.

Furthermore, the spatial distribution of the particular functional group in the aggregate can be determined by a selective deuteration of a particular functional group in an amphiphilic molecule. Using this procedure, one can obtain information on the chain conformation of the hydrocarbon chain in a micellar core \([12]\).

Thus, SANS has been used successfully to determine the structure of anionic and cationic surfactant micelles in aqueous solutions. In the next section, the procedures for analysis of SANS data are summarized.
5-2. Theory

5-2-1. $Q$-dependent neutron scattering intensity ($d\Sigma(Q)/d\Omega$)

The dependence of the neutron scattering intensity $d\Sigma(Q)/d\Omega$ on the magnitude of a scattering vector ($Q$) can be expressed as a function of both the particle structure factor $P(Q)$, and the size and orientation weighted interparticle structure factor $S'(Q)$, as follows,

$$\frac{d\Sigma(Q)}{d\Omega} = I_0 P(Q) S'(Q) / \text{cm}^{-1} \quad (5-3)$$

where $I_0$ is the extrapolated zero-angle scattering intensity.

When interactions between micelles can be neglected, the interparticle structure factor is reduced to unity ($S'(Q) = 1$). Therefore, equation (5-3) takes the following form,

$$\frac{d\Sigma(Q)}{d\Omega} = I_0 P(Q) / \text{cm}^{-1} \quad (5-4)$$

$I_0$, $P(Q)$ and $S'(Q)$ can be determined experimentally and theoretically by using the following procedures.
5-2-2. Radius of gyration (R_g)

When S'(Q) is equal to unity, the Guinier approximation [22] can be used to determine the radius of gyration of a particle (R_g) and I_0. In the small angle scattering region (Q R_g < 1), the terms in equation (5-4) can be expanded to give equation (5-5),

$$\frac{d\Sigma(Q)}{d\Omega} = I_0 \exp(-R_g^2 Q^2/3) \quad (5-5)$$

Equation (5-5) is quite valid for the general particle, expressed in terms of the radius of gyration, and for convenience can be written in the following form,

$$\ln \left( \frac{d\Sigma(Q)}{d\Omega} \right) = \ln I_0 - \frac{R_g^2}{3} Q^2 \quad (5-6)$$

Thus, a plot of ln[dΣ(Q)/dΩ] vs. Q^2 (Guinier plot) provides a straight line with a slope equal to -(R_g^2/3). The R_g value can be given in terms of the geometrical parameters for a particle. For a particle consisting of double layers, R_g is given by the following form [14]

$$R_g^2 = \frac{W_1 R_{g1}^2 + W_2 R_{g2}^2}{W_1 + W_2} \quad (5-7)$$

$$W_1 = (\rho_b - \rho_c)V_c \quad (5-8)$$

$$W_2 = (\rho_s - \rho_p)V_p \quad (5-9)$$

(i) Prolate ellipsoid particle with semiaxes a, b, b and thickness of the Stern layer t Å.

$$R_{g1}^2 = \frac{a^2 + 2b^2}{5} \quad (5-10)$$

$$R_{g2}^2 = \frac{[(a+t)^2 + 2(b+t)^2] \left[ (a+t)(b+t)^2 - (a^2 + 2b^2)ab \right]}{5 \left[ (a+t)(b+t)^2 - ab^2 \right]} \quad (5-11)$$

$$V_c = \frac{4\pi}{3} ab^2 = nV_{tail} \quad (5-12)$$

$$V_m = V_c + V_p = \frac{4\pi}{3} (a+t)(b+t)^2 \quad (5-13)$$
(ii) Oblate ellipsoid particle with semiaxes $a$, $a$, $b$ Å and thickness of the Stern layer $t$ Å.

$$R_{g1}^2 = \frac{2a^2 + b^2}{3} \quad (5-14)$$

$$R_{g2}^2 = \frac{\left[ 2(a + t)^2 + (b + t)^2 \right] \left[ (a + t)^2(b + t) - (2a^2 + b^2)a^2b \right]}{5[(a + t)^2(b + t) - a^2b]} \quad (5-15)$$

$$V_c = \frac{4\pi}{3} a^2 b = nV_{\text{tail}} \quad (5-16)$$

$$V_m = V_c + V_p = \frac{4\pi}{3} (a + t)^2(b + t) \quad (5-17)$$

(iii) Circular cylinder (or circular disk) with radius $R$ Å, height $h$ Å and thickness of the Stern layer $t$ Å.

$$R_{g1}^2 = \left( 2R^2 + \frac{h^2}{3} \right) / 4 \quad (5-18)$$

$$R_{g2}^2 = \left( 2(R + t)^2 + \frac{(h + 2t)^2}{3} \right) / 4 \quad (5-19)$$

$$V_c = \pi R^2 h = nV_{\text{tail}} \quad (5-20)$$

$$V_m = V_c + V_p = \pi (R + t)^2(h + 2t) \quad (5-21)$$

where $V_c$ Å$^3$, $V_p$ Å$^3$ and $V_m$ Å$^3$ are the volumes of the micelle core, the polar shell and overall micelle, respectively. $\rho_c$ Å$^{-2}$, $\rho_p$ Å$^{-2}$ and $\rho_s$ Å$^{-2}$ are the average neutron scattering length densities of the hydrophobic core, polar shell and solvent, respectively. $n$ is the average aggregation number of a micelle.

$$\rho_c = \frac{\Sigma_{\text{tail}}}{V_{\text{tail}}} \quad (5-22)$$

$$\rho_p = \frac{n(\Sigma_{\text{head}} + rc(1 - \alpha)b_{\text{ion}} + N_s\Sigma_{\text{solvent}})}{V_p} \quad (5-23)$$
\[ \alpha_s = \frac{\Sigma b_{\text{solvent}}}{V_{\text{solvent}}} = \frac{(1 - x_H)\Sigma b_{\text{D}_2\text{O}} + x_H\Sigma b_{\text{H}_2\text{O}}}{V_{\text{solvent}}} \]  

(5-24)

where \( V_{\text{tail}} \) is the volume of the hydrocarbon tail per surfactant molecule constituting the micellar core and \( V_{\text{solvent}} \) is the volume of a water molecule. \( \Sigma b_{\text{tail}} \) is the total scattering lengths of the hydrocarbon tail per surfactant molecule constituting the micellar core, \( \Sigma b_{\text{head}} \) is the total scattering lengths of the polar heads in the Stern layer per surfactant molecule excluding the counterion and \( b_{\text{ion}} \) is the scattering length of a counterion. \( \alpha \) is the degree of ionization of a micelle. \( \Sigma b_{\text{D}_2\text{O}} \) and \( \Sigma b_{\text{H}_2\text{O}} \) are the total scattering lengths of a \( \text{D}_2\text{O} \) and a \( \text{H}_2\text{O} \), respectively. \( rc \) is the number ratio of [counterion]/[surfactant molecule]. \( x_H \) is the volume fraction of \( \text{H}_2\text{O} \). The averaged hydration number per surfactant polar head \( N_s \) is defined by the following equation,

\[ N_s = \frac{V_p - n(V_{\text{head}} + rc(1 - \alpha)V_{\text{ion}})}{n V_{\text{solvent}}} \]  

(5-25)

where \( V_{\text{head}} \) and \( V_{\text{ion}} \) are the volume of the polar heads in the Stern layer per surfactant molecule excluding the counterion and the volume of a counterion, respectively.
Fig. 5-1. $P(Q)$ vs. $Q$ plots calculated for model (A) and (B). Model (A): prolate ellipsoid $a = 29.1 \, \text{Å}$, model (B): oblate ellipsoid $a = 21.8 \, \text{Å}$ with $b = 10 \, \text{Å}$, $t = 5 \, \text{Å}$, $\rho_s = -0.4 \times 10^{-6} \, \text{Å}^{-2}$, $\rho_p = 6.0 \times 10^{-6} \, \text{Å}^{-2}$, $\rho_c = -0.4 \times 10^{-6} \, \text{Å}^{-2}$ and $R_g = 15 \, \text{Å}$. 


5-2-3. Zero-angle scattering intensity (I₀)

The zero-angle scattering intensity I₀ does not depend on the micellar shape. But, I₀ is a function of the average aggregation number n. I₀ is given by the following form

\[ I₀ = n_p 10^{-16} \left[ (\rho_p - \rho_c)V_c + (\rho_s - \rho_p)V_m \right]^2 / \text{cm}^{-1} \quad (5-26) \]

\( n_p \) denotes the number density of the particles,

\[ n_p = \frac{(C - CMC)N_A}{1000n} / \text{cm}^{-3} \quad (5-27) \]

where \( C \) mol l⁻¹ and \( CMC \) mol l⁻¹ are the total concentration of surfactant and critical micellar concentration, respectively. \( N_A \) is Avogadro’s constant (6.022 × 10²³ mol⁻¹).

If one can determine I₀ by using Guinier approximation, the average aggregation number can be calculated by following equation

\[ n = \frac{1000I₀}{(C - CMC)N_A 10^{-16}} \times \frac{1}{\left( \left( \Sigma_{tail} + \Sigma_{head} + rc(1 - \alpha)b_{ion} \right) + \left( V_{tail} + V_{head} + rc(1 - \alpha)\Sigma_{ion} \right) \left( \frac{1 - x_H}{V_s} \Sigma_{D,D,O} + x_H \Sigma_{D,H,O} \right) \right)^2} \]

(5-28)
5-2-4. Particle structure factor ( \( P(Q) \) )

The particle structure factor ( \( P(Q) \) ) can be calculated for a few simple cases. The micellar model for \( P(Q) \) is illustrated in Fig.5-2[A].

(I) \( P(Q) \) of ellipsoid is expressed by the following form,

\[
P(Q) = \int_0^1 |F(Q, \mu)|^2 \, d\mu \quad (5-29)
\]

\[
F(Q, \mu) = x \left( \frac{3(\sin(QR_1) - QR_1 \cos(QR_1))}{(QR_1)^3} \right) + (1 - x) \left( \frac{3(\sin(QR_2) - QR_2 \cos(QR_2))}{(QR_2)^3} \right)
\]

\[x = \frac{(\rho_p - \rho_c)V_c}{(\rho_p - \rho_c)V_c + (\rho_s - \rho_p)V_m} \quad (5-30)
\]

where \( \mu \) is the cosine of the angle between the scattering vector \( Q \) and the micellar axis \( b \).

(i) For the prolate ellipsoid particle, \( R_1 \) and \( R_2 \) are given by

\[
R_1 = \left[ a^2 \mu^2 + b^2 (1 - \mu^2) \right]^{1/2} \quad (5-32)
\]

\[
R_2 = \left[ (a + t)^2 \mu^2 + (b + t)^2 (1 - \mu^2) \right]^{1/2} \quad (5-33)
\]

(ii) For the oblate ellipsoid particle, \( R_1 \) and \( R_2 \) are given by

\[
R_1 = \left[ a^2 (1 - \mu^2) + b^2 \mu^2 \right]^{1/2} \quad (5-34)
\]

\[
R_2 = \left[ (a + t)^2 (1 - \mu^2) + (b + t)^2 \mu^2 \right]^{1/2} \quad (5-35)
\]

(II) \( P(Q) \) of circular cylinder ( or disk ) is expressed by the following form,

\[
P(Q) = \int_0^{\pi/2} |F(Q, \varphi)|^2 \, d\varphi \quad (5-36)
\]
Fig. 5-2. Schematic micellar model of an ionic micelle for calculation of $P(Q)$ (A) and $S(Q)$ (B). The scattering length density profile corresponding to $P(Q)$ model is also shown.
\[
F(Q, \varphi) = \left( \frac{\sin(Q(h/2)\cos\varphi)}{Q(h/2)\cos \varphi} \right) \frac{2J,Q \sin \varphi}{Q \sin \varphi} \sin^{1/2} \varphi \\
+ (1 - x) \left( \frac{\sin(Q(h/2 + t)\cos \varphi)}{Q(h/2 + t)\cos \varphi} \right) \frac{2J(Q(R + t) \sin \varphi)}{Q(R + t) \sin \varphi} \sin^{1/2} \varphi
\]

(5-37)

where \( \varphi \) and \( J_1 \) are the angle between the axis of the cylinder and bisectrix and a Bessel function of order 1, respectively.

The examples of theoretically calculated \( P(Q) \) are shown in Fig. 5-1 [B].
5.2.5. Size and orientation weighted interparticle structure factor ($S'(Q)$)

For micellar solution systems having interparticle interactions, the interaction peak appears in the SANS intensity spectrum. Therefore, in order to interpret the SANS data, it is necessary to calculate $I_0$, $P(Q)$ and $S'(Q)$ on the basis of a micellar model.

The size and orientation weighted interparticle structure factor $S'(Q)$ can be calculated approximately by use of the following equation

$$S'(Q) = 1 + \beta(Q, \mu)[S(Q) - 1] \quad (5-38)$$

$$\beta(Q, \mu) = \frac{|F(Q, \mu)|^2}{|F(Q, \mu)|^2} \quad (5-39)$$

and $S(Q)$ is the interparticle structure factor.

Figure 5-2[B] illustrates how the micellar model for $P(Q)$ translates into the model for $S(Q)$. In this model, the micelle is assumed to be a spherical macroion of an effective diameter $\sigma$ [23, 24], interacting through a repulsive screened Coulomb potential. The diameter $\sigma$ is set equal to:

(i) For the prolate ellipsoid particle

$$\sigma = \left(2(f + 1)(a + t)(b + t)^2\right)^{1/3} \quad (5-40)$$

(ii) For the oblate ellipsoid particle

$$\sigma = \left(2(f + 1)(a + t)^2(b + t)^2\right)^{1/3} \quad (5-41)$$

where

$$f = \frac{3}{4} \left(1 + \frac{\sin^{-1}p}{p\left(1 - p^2\right)^{1/2}}\right) \left[1 + \frac{1 - p^2}{2p} \ln\left(\frac{1 + p}{1 - p}\right)\right] \quad (5-42)$$
When micellar shape is spherical, \( \sigma = (a + t) = (b + t) \).

A macroion solution consisting of macroions and counterions in a solvent of dielectric constant \( \varepsilon \), in which one of the ionic species, the macroion, is large enough to dominate many of the solution properties. The counterions and solvent are treated as a uniform background characterized by their inverse Debye-Hückel screening length \( \kappa \).

The interparticle structure factor \( S(Q) \) can be calculated according to standard liquid theoretical methods. For spherical macroions having a hard core, the most successful statistical mechanical theory is based on solving the Ornstein-Zernike equation [25]. In the mean spherical approximation (MSA) [26], the total correlation function \( h(x) \) of an effective one component of the macroion is expressed by the following form:

\[
h(x) = c(x) + n_p \sigma^3 \int h(|x - y|) \varepsilon(y) dy \quad (5-44)
\]

where \( c(x) \) and \( c(y) \) are direct correlation functions.

The repulsive potential between two identical spherical macroions, neglecting the weak van der Waals' attraction, is usually modelled by the standard potential [27].

\[
U(r) = \frac{\pi \varepsilon \varepsilon_0 \sigma^2 \varphi_0^2 \exp[-\kappa (r - \sigma)]}{r} \quad r > \sigma \quad (5-45)
\]

where \( \varphi_0 \) is the surface potential, \( \varepsilon_r \) is the dielectric constant of the solvent (\( \varepsilon_r(D_2O) = 78.25, \varepsilon_r(H_2O) = 78.54 \) at 25 °C), \( \varepsilon_0 \) is the permittivity of free space (\( 8.854 \times 10^{-12} \) C² J⁻¹ m⁻¹), \( r \) is the interionic center-center distance, and \( \kappa \) is the Debye-Hückel inverse screening length.

The surface potential \( \varphi_0 \) is related to the electronic charge \( Z_m \) of the macroion by

\[
\varphi_0 = \frac{Z_m}{\pi \varepsilon \sigma (2 + \kappa \sigma)} \quad / V \quad (5-46)
\]

\[
Z_m = n r c \alpha e \quad (5-47)
\]
where $e$ is the electronic charge ($1.602 \times 10^{-12}$ C). The inverse Debye-Hückel screening length $\kappa$ m$^{-1}$ is calculated from the ionic strength $I$ of the solution, by using of the following equation

$$\kappa = \left( \frac{2000N_Ae^2I}{\varepsilon_0\varepsilon_r k_B T} \right) \quad (5-48)$$

where $k_B$ is the Boltzmann constant ($1.3806 \times 10^{-23}$ J K$^{-1}$) and $T$ is the absolute temperature. The ionic strength $I$ mol l$^{-1}$ is calculated by

$$I = \frac{1}{2} \sum_I Z_i^2 C_i \quad (5-49)$$

for example, $S^\pm : \text{Cl}^\pm$ type surfactant ($S^\pm$ and $\text{Cl}^\pm$ indicate surfactant molecules and counterion, respectively).

$$I = \frac{1}{2} CMC + \frac{1}{2} CMC + \frac{1}{2} \alpha(C - CMC) \quad (5-50)$$

$S^{2\pm} : 2\text{Cl}^\pm$ type surfactant

$$I = 2CMC + CMC + \alpha(C - CMC) \quad (5-51)$$

$2S^{\pm} : \text{Cl}^{2\pm}$ type surfactant

$$I = CMC + 2CMC + 2\alpha(C - CMC) \quad (5-52)$$

The problem is usually formulated in dimensionless units, setting $x = r/\sigma$, $k = \kappa\sigma$ and $K = Q\sigma$, so we write

$$\beta U(x) = \gamma \exp(-kx)/x \quad x > 1 \quad (5-53)$$

where $\beta = 1 / k_B T$ and $\gamma\exp(-k) = \beta\pi\varepsilon_0\varepsilon_0\sigma^2$ is the contact potential for a macroion pair, in units of $k_B T$. The solution is entirely characterized by $\gamma$, $\kappa$ and volume fraction $\eta = n_p\pi\sigma^3 / 6$.

If we take the macroion to have a hard core, then
\[ \beta U(x) = \infty \quad x < 1 \] (5-54)

Taking the mean spherical approximation as the closure relation, then

\[ c(x) = -\beta U(x) \quad x > 1 \] (5-55)

\[ h(x) = -1 \quad x < 1 \] (5-56)

This potential \( U(x) \), used in conjunction with the MSA closure relation, yields an analytical solution of the OZ equation and allows us to obtain a convenient algebraic form for \( S(Q) \).

In our particular solutions, the Coulomb coupling is generally strong (\( \gamma > 1 \)), but volume fractions are low so MSA can yield, sometimes, to unphysical values of the pair distribution function. To overcome this difficulty, we have increased the particle diameter from its physical value \( s \) to an effective hard core value \( s' \), maintaining the Coulomb coupling constant. This means we calculate the structure for a rescaled potential with \( \gamma' = \gamma s \) and \( k' = ks \), where \( s = \alpha / \alpha' \). The structure factor \( S(\eta, \gamma, k; K) \) of the physical system may thus be accurately calculated by evaluating \( S(\eta', \gamma', k'; K') \) for the rescaled system and then rescaling the result by the contraction of the reduced wavenumber \( K' = Qs' \) to the scale \( K = Qs = k's \).

The determination of \( s' \) for the rescaled MSA (RMAS) has been made by generalizing the criterion of Gillan [28] and following the method in ref. [29] to obtain the MSA contact value at the volume fraction \( \eta \):

\[ g_{\eta}^{MSA}(r = \sigma) = -(p_1 + p_2C + p_3F) \] (5-57)

Constants \( A, B, C \) and \( F \) are given by Hayter and Penfold [30].

\[ C = -\left( \omega_{16} F_2 + \omega_{15} F + \omega_{14} \right) / \left( \omega_{13} F + \omega_{12} \right) \] (5-58)

\[ B = b_1 + b_2 C + b_3 F \] (5-59)

\[ A = a_1 + a_2 C + a_3 F \] (5-60)
where $F$ is a root of

$$w_4 F^4 + w_3 F^3 + w_2 F^2 + w_1 F + w_0 = 0 \quad (5-61)$$

The coefficients are given in the appendix of this chapter.

The structure factor $S(Q)$ is obtained by Fourier transforming $\beta(Q)$ using the following expression for the direct correlation function $c(x)$

$$c(x) = A + B + \frac{1}{2} \eta A x^3 + \frac{C \sinh Kx}{x} + \frac{F \cos Kx - 1}{x} \quad x < 1$$

$$= -\gamma \exp(-Kx) \quad x < 1 \quad (5-62)$$

The results for $S(Q)$ is

$$S(Q) = \frac{1}{[1 - 24\eta a(Q)]} \quad (5-63)$$

with $a(Q)$ also given by Hayter and Penford.

$$a(Q) = A \left[ \sin(Q) - \sigma Q \cos(Q) \right] / (\sigma Q)^3$$

$$+ B \left[ 2 / (\sigma Q)^2 - 1 \right] \sigma Q \cos(Q) + 2 \sin(Q) - 2 / (\sigma Q) \right] / (\sigma Q)^3$$

$$+ \eta A \left[ 24 / (\sigma Q)^3 + 4 \left[ 1 - 6 / (\sigma Q)^2 \right] \sin(Q) \right]$$

$$- \left[ 1 - 12 / (\sigma Q)^2 + 24 / (\sigma Q)^4 \right] \sigma Q \cos(Q) / \left[ 2 (\sigma Q)^3 \right]$$

$$+ C \left[ k \cosh(k) \sin(Q) - \sigma Q \sinh(k) \cos(Q) \right] / \left[ \sigma Q \left[ (\sigma Q)^2 + k^2 \right] \right]$$

$$+ F \left[ k \sin(k) \sin(Q) - \sigma Q \left[ \cosh(k) \cos(Q) - 1 \right] \right] / \left[ \sigma Q \left[ (\sigma Q)^2 + k^2 \right] \right]$$

$$+ F \left[ \cos(Q) - 1 \right] / (\sigma Q)^2$$

$$- \gamma \exp(-k) \left[ k \sin(Q) + \sigma Q \cos(Q) \right] / \left[ \sigma Q \left[(\sigma Q)^2 + k^2 \right] \right]$$

$$\quad (5-64)$$

This procedure of computing $S(Q)$ has been shown to produce excellent agreement with SANS data from ionic micellar solutions. The examples of calculated $S'(Q)$ are shown in Fig.5-3 [A] and [B].
Fig. 5-3[A]. $S'(Q)$ vs. $Q$ plot using data of ref. 31 Fig. 3. Parameters are $C = 0.312$ mol l$^{-1}$, $\sigma = 45.3$ Å, $\kappa\sigma = 4.050$, $D = 78.0$ and $\alpha = 0.391$.

[B]. $S'(Q)$ vs. $Q$ plot using data of ref. 17 Fig. 7. Parameters are $C = 2$ g dl$^{-1}$, $\sigma = 45.0$ Å, $Z_m = -11.57e$ and $\eta = 0.034$. 

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5.2.6. Contrast variation method

We have analyzed the scattering intensity curves taken from sample solutions of different H$_2$O-D$_2$O mixtures. For non-interacting micellar systems, the square root of $I_0$ ($\pm I_0^{1/2}$) is a linear function of the scattering length density of the H$_2$O-D$_2$O mixed solvent ($\rho_s$) or volume fraction of H$_2$O ($x_H$), and the volume of a surfactant molecule $V_{\text{molecule}}$ and average aggregation number $n$ can be determined. For interacting micellar systems, we substitute the square root of $Q$-dependent quantity ($\pm A(Q)^{1/2}$) for $\pm I_0^{1/2}$, $A(Q)$ is given by Sheu et al. [18].

$$A(Q) = \left[ (d\Sigma(Q)/d\Omega)/P(Q)/S'(Q) \right]$$

(5-65)

$A(Q)$ can be calculated from the observed SANS spectra combined with the model calculations of $P(Q)$ and $S'(Q)$. The quantity $\pm A(Q)^{1/2}$ is also linearly proportional to the scattering length density of the [D$_2$O] / [H$_2$O] mixed solvent or volume fraction of H$_2$O. Therefore, the contrast matching point, where the scattering intensity vanishes, can be determined by extrapolating the $\pm I_0^{1/2}$ (or $\pm A(Q)^{1/2}$) vs. $x_H$ curve to zero. From the contrast matching point, the volume of a surfactant molecule can be calculated. At the contrast matching point,

$$(\rho_c - \rho_p)V_c + (\rho_p - \rho_s)V_m = 0$$

(5-66)

and the equation (5-66) becomes

$$n\left(\Sigma b_{\text{tail}} + \Sigma b_{\text{head}} + rc(1 - \alpha)b_{\text{ion}}\right)$$

$$+ n\left(V_{\text{tail}} + V_{\text{head}} + rc(1 - \alpha)V_{\text{ion}}\right)\left(\frac{1 - x_H}{V_s}\Sigma \Sigma \Sigma + x_H \Sigma \frac{V_{\text{H2O}}}{V_s}\right) = 0$$

(5-67)

Thus, the volume of a surfactant molecule ($V_{\text{molecule}}$ Å$^3$) is given by following equation.
\[ V_{\text{molecule}} = V_{\text{tail}} + V_{\text{head}} + rc(1 - \alpha)V_{\text{ion}} \]
\[ = \left( \sum \delta_{\text{tail}} + \sum \delta_{\text{head}} + rc(1 - \alpha)\delta_{\text{ion}} \right) \left( \frac{V_{s}}{1 - x_{H} \Sigma \delta_{D_{2}O} + x_{H} \Sigma \delta_{H_{2}O}} \right) \]  
\[ \tag{5-68} \]

The contrast variation curve can be used to obtain the average aggregation number of a micelle \( n \). The slope of contrast variation curve (slope cm\(^{-1/2}\)) is

\[ \text{slope} = \left( \frac{(C \cdot \text{CMC})N_{4}}{1000n} \right)^{1/2} 10^{-9}n \left( V_{\text{tail}} + V_{\text{head}} + rc(1 - \alpha)V_{\text{ion}} \right) \left( \frac{V_{s}}{\Sigma \delta_{D_{2}O} + \Sigma \delta_{H_{2}O}} \right)^{2} \]
\[ \tag{5-69} \]

Thus, \( n \) is given by following equation

\[ n = \frac{1000 \text{slope}^{2}}{(C \cdot \text{CMC})N_{4}10^{-16} \left( V_{\text{tail}} + V_{\text{head}} + rc(1 - \alpha)V_{\text{ion}} \right)^{2} \left( \frac{V_{s}}{\Sigma \delta_{D_{2}O} + \Sigma \delta_{H_{2}O}} \right)^{2}} \]  
\[ \tag{5-70} \]
5-2-7. Appendix

The coefficients appearing in equations (5-58), (5-59) and (5-60) are listed below.

Set
\[ \delta = 1 - \eta \]
\[
\begin{align*}
\alpha_1 &= -(2\eta + 1) \frac{\delta}{k} \\
\alpha_2 &= (14\eta^2 - 4\eta - 1) \frac{1}{k^2} \\
\alpha_3 &= 36\eta^2 \frac{1}{k^4} \\
\beta_1 &= -(\eta^2 + 7\eta + 1) \frac{\delta}{k} \\
\beta_2 &= 9\eta (\eta^2 + 4\eta - 2) \frac{1}{k^2} \\
\beta_3 &= 12\eta (2\eta^2 + 8\eta - 1) \frac{1}{k^4} \\
\nu_1 &= - (\eta^3 + 3\eta^2 + 45\eta + 5) \frac{\delta}{k} \\
\nu_2 &= (2\eta^3 + 3\eta^2 + 42\eta - 20) \frac{1}{k^2} \\
\nu_3 &= (2\eta^3 + 30\eta - 5) \frac{1}{k^4} \\
\nu_4 &= \nu_1 + 24\eta \nu_3 \\
\nu_5 &= 6\eta (\nu_2 + 4\nu_3) \\
\phi_1 &= 6\eta \frac{1}{k} \\
\phi_2 &= \delta - 12\eta \frac{1}{k^2} \\
\tau_1 &= (\eta + 5) \frac{1}{5k} \\
\tau_2 &= (\eta + 2) \frac{1}{k^2} \\
\tau_3 &= -12 \eta \gamma \exp(-k)(\tau_1 + \tau_2) \\
\tau_4 &= 3 \eta k^2 (\tau_1^2 + \tau_2^2) \\
\tau_5 &= 3 \eta (\eta + 8) / 10 - 2 (2\eta + 2)^2 / k^2
\end{align*}
\]

Then
\[
\begin{align*}
a_1 &= \{24 \eta \gamma \exp(-k) [\alpha_1 + \alpha_2 + (1 + k) \alpha_3] - (2\eta + 2)^2\} / \delta^4 \\
a_2 &= 24 \eta [\alpha_3 (\sinh k - k \cosh k) + \alpha_2 \sinh k - \alpha_1 \cosh k] / \delta^4 \\
a_3 &= 24 \eta [(2\eta + 1)^2 / k^2 - \delta^2 / 2 + \alpha_3 (\cosh k - 1 - k \sinh k)]
\end{align*}
\]
- \( \alpha_1 \sinh k + \alpha_2 \cosh k \)/\( \delta^4 \)

\[ b_1 = \{ 3\eta (\eta + 2)^2/2 - 12\eta \gamma \exp (-k) [\beta_1 + \beta_2 + (1 + k) \beta_3] \}/\delta^4 \]

\[ b_2 = 12\eta [\beta_3 (k \cosh k - \sinh k - \beta_2 \sinh k + \beta_1 \cosh k)]/\delta^4 \]

\[ b_3 = 12\eta [\delta^2 (\eta + 2)^2/2 - 3\eta (\eta + 2)^2/k^2 - \beta_3 (\cosh k - 1 - \sinh k) \]

\[ + \beta_1 \sinh k + \beta_2 \cosh k]/\delta^4 \]

\[ v_1 = [(2\eta + 1)(\eta^2 - 2\eta + 10)/4 - \gamma \exp (-k)(v_1 + v_2)]/5 \delta_4 \]

\[ v_2 = (v_4 \cosh k - v_5 \sinh k)/5 \delta^4 \]

\[ v_3 = [(\eta^3 - 6\eta^2 + 5) \delta - 6\eta (2\eta^3 - 3\eta^2 + 18\eta + 10)/k^2 \]

\[ + 24\eta v_3 + v_4 \sinh k - v_5 \cosh k]/5 \delta^4 \]

Define

\[ p_1 = \gamma \exp (-k)(\phi_1 - \phi_2)^2 - (\eta + 2)/2]/\delta^2 \]

\[ p_2 = [(\phi_1^2 - \phi_2^2) \sinh k - 2\phi_1 \phi_2 \cosh k]/\delta^2 \]

\[ p^3 = [(\phi_1^2 - \phi_2^2) \cosh k + 2\phi_1 \phi_2 \sinh k + \phi_1^2 - \phi_2^2]/\delta^2 \]

\[ t_1 = t_3 + t_4 a_1 + t_5 b_1 \]

\[ t_2 = t_4 a_2 + t_5 b_2 + 12\eta(t_1 \cosh k - t_2 \sinh k) \]

\[ t_3 = t_4 a_3 + t_5 b_3 + 12\eta[t_1 \sinh k - t_2 (\cosh k - 1)] - 2(\eta + 10)/5 - 1 \]

\[ \mu_1 = t_2 a_2 - 12\eta v_2^2 \]

\[ \mu_2 = t_1 a_2 + t_2 a_1 - 24\eta v_1 v_2 \]

\[ \mu_3 = t_2 a_3 + t_3 a_2 - 24\eta v_2 v_3 \]

\[ \mu_4 = t_1 a_1 - 12\eta v_1^2 \]

\[ \mu_5 = t_1 a_3 + t_3 a_1 - 24\eta v_1 v_3 \]

\[ \mu_6 = t_3 a_3 - 12\eta v_3^2 \]

\[ \lambda_1 = 12\eta p_2^2 \]

\[ \lambda_2 = 24\eta p_1 p_2 - 12b_2 \]

\[ \lambda_3 = 24\eta p_2 p_3 \]

\[ \lambda_4 = 12\eta p_1^2 - 2b_1 \]
\[ \lambda_5 = 24 \eta p_1 p_3 - 2 b_3 - k^2 \]
\[ \lambda_6 = 12 \eta p_3^2 \]

Then the coefficients of the quartic are
\[
\begin{align*}
    w_4 &= \omega_{16}^2 - \omega_{13} \omega_{36} \\
    w_3 &= 2 \omega_{16} \omega_{15} - \omega_{13} (\omega_{35} + \omega_{35}) - \omega_{12} \omega_{36} \\
    w_2 &= 2 \omega_{15}^2 + \omega_{16} \omega_{14} - \omega_{13} (\omega_{34} + \omega_{25}) - \omega_{12} (\omega_{35} + \omega_{26}) \\
    w_1 &= 2 \omega_{15} \omega_{14} - \omega_{13} \omega_{24} - \omega_{12} (\omega_{34} + \omega_{25}) \\
    w_0 &= \omega_{14}^2 - \omega_{12} \omega_{24}
\end{align*}
\]

where \( \omega_{ij} = \mu_i \lambda_j - \mu_j \lambda_i \). We also have by direct calculation \( \lambda_3^2 = 4 \lambda_1 \lambda_6 \), and hence \( \omega_4 = (\mu_1 \lambda_6 - \lambda_1 \mu_6 - \lambda_3 \mu_3/2)^2 \geq 0 \).
References

Chapter 6.

A small angle neutron scattering study of the identical and mixed chain di-
n-alkyl phosphate micelles in water

6-1. Introduction

Much attention has been given to structural studies of dialkyl phosphates having
two long n-alkyl chains in an aggregated state [1-11]. Synthesized amphiphiles, such as
didecyl, didodecyl and dihexadecyl phosphates, have been shown to form vesicles and
lamellar structures that possess physicochemical characteristics similar to those of
biomembranes [2, 3].

When such an organized structure of surfactant molecules is formed in aqueous
solution, conformational change of a hydrocarbon chain and environmental variation of
the hydrated polar groups should occur. The structural change at the interface may be
associated with the functional appearance of a biomembrane. However, such detailed
studies have been very few although they are highly desirable. For dialkyl phosphate
molecules having long n-alkyl chains, both the solubility and the critical micelle
concentration (CMC) in aqueous solution are very low. These properties prevent making
a detailed study of any conformational change of surfactant molecules occurring below and
above the CMC. However, for simple dialkyl phosphate molecules both the solubility and
the CMC in aqueous solutions are very high. Therefore, we may then make a direct
investigation of the conformational change of the surfactant molecules and of the
structural variation at the micellar interface which are a consequence of micellization.

Conformational studies on dialkyl phosphates in the aggregated state are important
for understanding the aggregation structure of phospholipid bilayers. Thus far, the
conformation of simple dialkyl phosphate anions in aqueous solution has been mainly
investigated by infrared and Raman spectroscopic methods [12-14]. Raman studies of
dibutyl phosphate anions [14] have provided direct evidence that micelle formation of the dialkyl phosphate anions brings about an increase in population of the all-\emph{trans} hydrocarbon. Similar observations have already been reported for aqueous solutions of simple soap molecules. For potassium \emph{n}-butanoate, \emph{n}-pentanoate and \emph{n}-hexanoate in the solid state and in aqueous solution, Raman scattering spectra have also been measured, and the concentration dependence of the molecular conformations of these molecules has been investigated in detail by the use of the accordion vibrations derived from the all-\emph{trans} hydrocarbon chains [15, 16]. The results have indicated that the percentage of the all-\emph{trans} hydrocarbon chains increases with an increase in concentration above the CMC. Such a conformational change, seen when simple surfactants undergo micellization, must be closely associated with the structure of aggregates.

We have synthesized the lithium salts of ethyl(\emph{n}-octyl) phosphate, \emph{n}-propyl(\emph{n}-heptyl) phosphate, \emph{n}-butyl(\emph{n}-hexyl) phosphate and di-\emph{n}-pentyl phosphate. The phase diagrams and phase structures of these double chain di-\emph{n}-alkyl phosphate-water systems were discussed in chapter 2. These mixed double chain anionic surfactants have different packing parameters characteristic of each molecule. The problem of the relationship between the geometrical packing properties and factors such as the structure of an aggregate formed by these surfactants in water remains as a challenge to our interest.

Recently, for the barium-salts of ethyl(\emph{n}-octyl) phosphate (EOP) in water, the phase diagram and phase structure have been determined [17, 18]. In particular, self-diffusion coefficient vs. inverse concentration plots could be explained by a simple two-site model and a single monomer $\leftrightarrow$ micelle equilibrium [19, 20], and provided the CMC value which was in good agreement with that determined by $^{31}$P NMR chemical shift vs. inverse concentration plots [17]. The, x-ray low angle diffraction data have supported the evidence for the structural change in the aggregate system at low water-content, which has been assumed from the self-diffusion behavior [18]. Moreover, the conformation of EOP anions in EOP-water system has been investigated by $^{13}$C NMR, infrared and
Raman spectroscopic methods [17, 21]. The phase diagram and phase structure of the sodium di-\(n\)-pentyl phosphate (DPP)-water binary system was discussed in chapter 3, using \(^1\)H pulsed-gradient NMR self-diffusion, \(^{31}\)P NMR and x-ray diffraction data. However, shape and size of an EOP and DPP micelle remain unresolved.

In this chapter, the micellar structures formed by the barium- and lithium-salts of EOP and the sodium-salt of DPP in water are discussed in detail, using small angle neutron scattering spectra and their analyses. In particular, the micellar structure is discussed in connection with the molecular conformation of the DPP anion.
6-2. Experimental

6-2-1. Materials

Barium salts of ethyl(n-octyl) phosphate (EOP), Ba(EOP) were prepared by neutralization of phosphoric acid ethyl(n-octyl) ester with aqueous solutions of barium hydroxide. The preparation of phosphoric acid ethyl(n-octyl) ester was described in chapter 2-2-1. Products were analyzed by $^1$H and $^{13}$C NMR and by elemental analysis. Anal. C$_{20}$H$_{44}$O$_8$P$_2$Ba : Calcd: C, 39.26; H, 7.25 ; Found: C, 39.12; H, 7.29. The preparation of the lithium salt of ethyl(n-octyl) phosphate, Li(EOP), and the sodium salt of di-n-pentyl phosphate, Na(DPP), are described in chapters 2 and 3, respectively.

A series of identical chain di-n-alkyl phosphate lithium salts ($\text{(CH}_3\text{CH}_2\text{nO)}_2\text{PO}_2\text{Li}^+$, n = 0, 1, 2, 3, 4 and 5; $\text{Li}^+(\text{R-O})_2\text{PO}_2\text{Li}^+$) was similarly prepared using phosphorylchloride and the corresponding n-alcohols, by the same procedures. The identification of these products was also established by $^1$H and $^{13}$C NMR spectra and elemental analysis. The agreement between the calculated and observed values of elemental analysis was within 0.5 %.

The solvents were D$_2$O ( Wako Pure Chemical Industries, LTD. ), 99.8 atom % of deuterium, and a deionized and twice-distilled H$_2$O.

6-2-2. Molal volume determination

The apparent molal volumes ($\Phi_{app}$) of a series of identical chain di-n-alkyl phosphate lithium salts were calculated from the densities of the sample-H$_2$O and -D$_2$O solutions, measured with an Anton Paar vibrating tube digital densitometer Model DMA 602/60 at 298.15 ± 0.01 K. The thermal stability of the liquid flowing through the jacket around the density measuring cell was maintained within ± 0.01 K by a temperature controller. The densitometer was calibrated with the known densities of air and water. Reproducibility of the density measurements was better than 3 ppm. The apparent molar
volume $\Phi_{\text{app}}$ may then be calculated from the density ($d$, g cm$^{-3}$) of the solution using equation (6-1),

$$
\Phi_{\text{app}} = \frac{1}{m} \left[ \frac{1000 - mM}{d} - \frac{1000}{d_s} \right] \quad (6-1)
$$

where $m$ is the molarity, $d_s$ the density of the solvent and $M$ the molar weight of the solute.

### 6-2-3. SANS measurements

The small angle neutron scattering (SANS) measurements were carried out by small and medium angle neutron scattering instruments (SAN and WINK) installed at the pulsed neutron source KENS at National Laboratory for High Energy Physics, Tsukuba, Japan [22, 23]. The sample solutions were placed in a quartz cell of 1 or 2 mm path length. The scattering length density ($\rho$) of each component was calculated using the following equation,

$$
\rho = \frac{\sum b_i}{V} \quad (6-2)
$$

where $b_i$ is the scattering length of atom $i$ and $V$ is the molecular volume. The scattering length densities used for the SANS data analysis were quoted from ref.24. The magnitude of the momentum transfer ($Q$) is given by equation (6-3),

$$
Q = \frac{4\pi}{\lambda} \sin \left( \frac{\theta}{2} \right) \quad (6-3)
$$

where $\lambda$ is the incident wavelength ($3 \sim 11$ Å for SAN and $1 \sim 16$ Å for WINK) and $\theta$ the scattering angle. The intensity of scattered neutrons was recorded on a position-sensitive 2-D detector. Scattering intensity from the sample solutions were corrected for detector background and sensitivity, empty cell scattering, incoherent scattering, and sample transmission. Solvent intensity was subtracted from that of the sample. The resulting corrected intensities were converted to radial averages versus $Q$, using programs
provided by the KENS. Normalization of the data to an absolute intensity scale was made by using the transmission of a 1 mm water sample. Corrections for multiple scattering were also made [25].

The SANS measurements were made at three different temperatures (23, 40, 50 °C) for the Ba(EOP) samples and at 23 °C for the Li(EOP) and Na(DPP) samples. Thermal stability was maintained within ± 0.1 °C.
6-3. Results and discussion
6-3-1. Phase diagrams

A phase diagram of the binary Ba(EOP)-water system consists of four regions (I, II, III and IV) [17], as shown in Fig. 6-1. Region I is a homogeneous aqueous solution, in which the EOP anions are in the monomeric state below 1.2 wt% (0.029 M), the critical micelle concentration (CMC) [17]. In particular, it should be noted that the monomer ⇆ micelle equilibrium region is very narrow and the micellar concentration is very small. Region II is a two-phase solution, in which regions I and III coexist. Region III is a lyotropic liquid crystalline phase. It has been deduced from the x-ray diffraction study [18] that the lamellar-like aggregate is preferentially stabilized in this region and that its structure strongly depends on the concentration. In region IV, hydrated crystals and solution coexist.

The phase diagram of the Li(EOP)-water system and Na(DPP) are described in chapter 2 and 3, respectively. In the present study, the aggregate structures in regions I which is a homogeneous aqueous solution, have been investigated by SANS analysis.

6-3-2. Partial molal volume determination

In order to determine the limiting partial molal volume (\( \Phi^0 \)) of a PO_4^- group, the apparent molal volumes (\( \Phi_{app} \)) for a series of identical chain di-n-alkyl phosphate lithium salts (\( \text{Li}^+(R-O)_2\text{PO}_2^- \)) were determined at 298.15 K from density measurements. Fig. 6-2[A] shows concentration dependence of \( \Phi_{app} \) for a series of di-n-alkyl phosphate lithium salts in H_2O with increased chain length. The \( \Phi^0 \) values for these solutes in water were evaluated from the apparent molal volumes by means of equation (6-1).

As shown in Fig. 6-2[B], the CH_2-number dependence of the \( \Phi^0 \) value for a series of samples in water provided a linear relationship (\( \Phi^0 = 76.22 + 15.71 N \)) between the \( \Phi^0 \) value and the CH_2-number (\( N \)). The \( \Phi^0 \) value 15.71 ± 0.30 cm^3 mol^{-1} for the CH_2 group was evaluated from the slope and is very close to the \( \Phi^0(CH_2) \) value which has
Fig. 6-1. Phase diagram of the Ba(EOP)-H₂O system. Region I: homogeneous transparent solution; region II: two-phase solution; region III: homogeneous solution; region IV: solid Ba(EOP) and its solution.
already been reported [26]. Extrapolation to the intercept provides summation (φ₀^sum = φ₀(PO₄⁻) + φ₀(Li⁺) + 2φ₀(H⁻)) of the φ₀ value of a PO₄⁻ group, a Li⁺ ion and that of two protons belonging to the terminal CH₃ groups. The φ₀ value of a PO₄⁻ group can be calculated from the observed φ₀(CH₂) and φ₀^sum values, the known φ₀(CH₃) values and φ₀(Li⁺) value [27], using the additive rule. Thus, in the present study, the φ₀ value 23.43 ± 0.41 cm³ mol⁻¹ for a PO₄⁻ group was obtained and is used for the SANS analysis.

In order to estimate the isotope effect on the φ₀ value of a PO₄⁻ group, density measurements were also made for the sodium di-n-pentyl phosphate-H₂O and D₂O solutions. Figure 6-2[C] shows concentration dependence of φ_app for the sodium di-n-pentyl phosphate-H₂O and D₂O solutions. The isotope effect was found to be about 0.3%, using Fig.6-2[C] data. Thus, the φ₀ value of a PO₄⁻ group, obtained for a series of identical chain di-n-alkyl phosphate lithium salts in H₂O, was used for a SANS analysis.

The volume and the neutron scattering length density of all species using for SANS analysis are listed in Table 6-1.

<table>
<thead>
<tr>
<th>Species</th>
<th>V, Å³</th>
<th>Σb_coh × 10⁻⁴, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>42.6*</td>
<td>-0.457</td>
</tr>
<tr>
<td>CH₂</td>
<td>28.2*</td>
<td>-0.083</td>
</tr>
<tr>
<td>PO₄⁻</td>
<td>39.1</td>
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</tr>
<tr>
<td>Ba²⁺</td>
<td>11.5</td>
<td>0.528</td>
</tr>
<tr>
<td>Li⁺</td>
<td>2.0**</td>
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</tr>
<tr>
<td>Na⁺</td>
<td>3.6**</td>
<td>0.363</td>
</tr>
<tr>
<td>D₂O</td>
<td>30.2**</td>
<td>1.918</td>
</tr>
<tr>
<td>H₂O</td>
<td>29.9**</td>
<td>-0.165</td>
</tr>
</tbody>
</table>

* ref.26, ** ref.27
Fig. 6-2[A]. Concentration dependence of $\Phi_{\text{app}}$ for a series of identical chain di-$n$-alkyl phosphate lithium salts-H$_2$O solutions. (a): di-methyl phosphate, (b): di-ethyl phosphate, (c): di-$n$-propyl phosphate, (d): di-$n$-butyl phosphate, (e): di-$n$-penty phosphate and (f): di-$n$-hexyl phosphate.
Fig. 6-2[B]. The CH$_2$ number dependence of the $\phi^0$ value for a series of identical chain di-$n$-alkyl phosphate lithium salts.
Fig. 6-2[C]. Concentration dependence of $\Phi_{\text{app}}$ for sodium di-$n$-pentyl phosphate-$\text{H}_2\text{O}$ (●) and -$\text{D}_2\text{O}$ (○) solutions.
6-3-3. Micellar structure of Ba(EOP)

In the present study, emphasis is given to discussion of the phase structures in region I, as a result of the SANS analysis.

For region I, two sample solutions, 1.0 wt% (below the CMC) and 2.0 wt% (above the CMC), were used for the SANS measurements. At concentrations above 2.0 wt%, a phase separation occurs and region II newly appears. Therefore, for the sample solution in region I, the 2.0 wt% concentration is close to the maximum concentration, for which SANS measurements are possible.

Figure 6-3[A] shows the data of $I(Q)$ against $Q$ observed at concentrations of 1.0 and 2.0 wt% for the Ba(EOP)-D$_2$O system. It is evident that the $I(Q)$ values for the 1.0 wt% solution arise from the monomers in solution, and that the neutron scattered intensities obtained at the higher concentration contain contributions from both monomers and micelles. The peak arising from the intermicellar interactions disappears in the intensity spectrum, indicating that the micellar concentration is very low and the intermicellar interaction can be neglected in region I. Therefore, the interparticle structure factor is reduced to unity.

Figure 6-3[B] shows the $I(Q)$ vs. $Q$ plots for the 2.0 wt% sample solution at different temperatures. In these spectra, the scattered intensities arising from the monomers were subtracted from the observed intensities. Therefore, the scattered intensities, shown in Fig.6-3[B], pertain only to the micelles. As shown in Fig.6-4, within the temperature range studied a Guinier plot ($\ln(I(Q))$ vs. $Q^2$) provides a straight line in the small $Q$ region, indicating that the intermicellar interaction can be neglected. Table 6-2 lists the $R_g$ values of the 2.0 wt% sample at different temperatures. The Guinier radius tends to increase with an increase in temperature, indicating a temperature dependence of micellar size.

The shape and size of a Ba(EOP) micelle have been determined on the basis of the radius of gyration obtained from the Guinier plot. For the Ba(EOP) micellar model, we
Fig.6-3[A]. SANS spectra of the Ba(EOP)-D$_2$O solutions ( a : 1.0 wt% and b : 2.0 wt% at 50 °C ).
Fig. 6-3[B]. Temperature dependence (a: 23 °C, b: 40 °C, c: 50 °C) of the scattered intensity for the 2.0 wt% sample, in which the scattered intensities of the 1.0 wt% solution were subtracted from the observed intensities, and fitted scattering intensity profiles (solid lines) in the $Q$ range 0.03 – 0.40 Å$^{-1}$. 
Fig. 6-4. $\ln(I(Q))$ against $Q^2$ plots for the 2.0 wt% Ba(EOP)-D$_2$O solution at different temperatures (a: 23 °C, b: 40 °C, c: 50 °C).
have assumed that a micelle consists of a hydrophobic core and a Stern layer (hydrophilic layer) having a thickness \( t \) equal to the diameter \( 4.2 \text{ Å} \) of the PO4 group. SANS intensity profiles for oblate spheroid, cylinder-like and disk-like models were also tested. However, the prolate spheroid model provided the best fit. For the minor axis \( b \) of the hydrophobic core, the assumed values of \( b \) were equal to the length \( 11.6 \text{ Å} \) of the all-trans \( n \)-octyl chain (obtained from the Tanford's equation [28]) and 0.81 times [29] \( b = 0.81 \times 11.6 \text{ Å} \) that for the extended \( n \)-octyl chains. Calculations have been made to provide the best fit between the radius of gyration obtained from the Guinier plots and theoretically-calculated results, as shown in Fig.6-3[B]. The calculated intensity profile for the prolate spherical micelle having a minor axis \( b = 11.6 \text{ Å} \) has provided the best fit between the observed data points and the calculated results. Thus, for the micelles of Ba(EOP) in water, we have found that the shape is prolate and the \( a/b \) ratio depends on temperature. The aggregation number \( n \) tends to increase with an increase of temperature. The results are summarized in Table 6-2.

### Table 6-2 The results of the Ba(EOP) SANS data analysis

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>23</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_g ), Å</td>
<td>14.0 ± 0.5</td>
<td>14.5 ± 0.4</td>
<td>14.9 ± 0.4</td>
</tr>
<tr>
<td>( n )</td>
<td>48.5 ± 2.1</td>
<td>50.7 ± 1.9</td>
<td>52.8 ± 2.1</td>
</tr>
<tr>
<td>( a ), Å</td>
<td>26.7 ± 1.2</td>
<td>27.9 ± 1.1</td>
<td>29.0 ± 1.1</td>
</tr>
<tr>
<td>( a/b )</td>
<td>2.29 ± 0.10</td>
<td>2.40 ± 0.09</td>
<td>2.49 ± 0.10</td>
</tr>
</tbody>
</table>
6-3-4. Micellar structure of Li(EOP)

Figure 6-5 shows the neutron scattering intensity spectra of the Li(EOP)-D2O samples in region I. In these spectra, the scattered intensities arising from the monomers were subtracted from the observed intensities. Very broad peaks are seen in the SANS spectra within the concentration range 4 - 10 wt%, indicating the presence of intermicellar interactions in this system. The interaction peak increases steadily in intensity, and shifts to higher Q values as the concentration increases. Therefore, it seems that interactions between micellar particles are enhanced with an increase in concentration.

We may assume that a structural model of the Li(EOP) micelle is similar to that of the Ba(EOP) micelle. For the SANS analysis, prolate spheroid, oblate spheroid, cylinder-like and disk-like shapes have been used as models, assuming mono-dispersity of the micelles. We have found that the prolate-spheroid model provides the best fit to the observed data, as shown in Fig.6-5[A]. The results are summarized in Table 6-3, together with the fitting parameters (n and a). The average percentage deviation per datum point was ± 4 % for all spectra.

As is seen in Table 6-3[A], it is evident that the average aggregation number (n) increases with an increase in concentration. A ladder model of micellar growth [30], which has been successfully applied to SANS studies of micellar systems in many investigations [31-35], may be applied to the formation of the micelle in this system. Figure 6-6 shows n as a function of the square root of the monomer concentration (molar fraction) forming the micelle in region I. All the n values fall on a straight line, thus suggesting a ladder model. Moreover, it can be seen that an a/b ratio of the prolate spheroidal micelle decreases as the concentration approaches the CMC. The result indicates that the micellar shape varies with an increase in micellar concentration. Extrapolation of the linear (X - X_{CMC})^{1/2} vs. n plots provides the minimum aggregation number (n = 19.7) of a micelle at the CMC. For a micelle having the minimum aggregation number n = 19.7, an a/b ratio is 1.0, indicating that the minimum micelle
Fig. 6-5. Observed scattering intensity spectra ( ○ ) for the Li(EOP)-D₂O system. a : 10 wt%, b : 9 wt%, c : 8 wt%, d : 7 wt%, e : 6 wt%, f : 5 wt% and g : 4 wt%, and fitted scattering intensity profiles ( solid lines ) in the Q range 0.06 ~ 0.40 Å⁻¹.
Table 6-3 The results of the Li(EOP) SANS data analysis

[A] Concentration dependence

<table>
<thead>
<tr>
<th>C, wt%</th>
<th>4.0</th>
<th>5.0</th>
<th>6.0</th>
<th>7.0</th>
<th>8.0</th>
<th>9.0</th>
<th>10.0</th>
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<tbody>
<tr>
<td>n</td>
<td>28.5</td>
<td>31.0</td>
<td>33.7</td>
<td>34.7</td>
<td>36.2</td>
<td>37.5</td>
<td>38.9</td>
</tr>
<tr>
<td>a/b</td>
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<td>1.47</td>
<td>1.59</td>
<td>1.64</td>
<td>1.71</td>
<td>1.77</td>
<td>1.84</td>
</tr>
<tr>
<td>α</td>
<td>0.46</td>
<td>0.45</td>
<td>0.43</td>
<td>0.43</td>
<td>0.43</td>
<td>0.42</td>
<td>0.42</td>
</tr>
<tr>
<td>N_s</td>
<td>14.0</td>
<td>13.6</td>
<td>13.1</td>
<td>13.0</td>
<td>12.8</td>
<td>12.6</td>
<td>12.4</td>
</tr>
<tr>
<td>σ, Å</td>
<td>35.1</td>
<td>36.0</td>
<td>36.9</td>
<td>37.3</td>
<td>37.8</td>
<td>38.2</td>
<td>38.7</td>
</tr>
<tr>
<td>κ, Å</td>
<td>8.85</td>
<td>8.51</td>
<td>8.23</td>
<td>7.95</td>
<td>7.69</td>
<td>7.50</td>
<td>7.29</td>
</tr>
<tr>
<td>η</td>
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<td>0.061</td>
<td>0.082</td>
<td>0.104</td>
<td>0.125</td>
<td>0.146</td>
<td>0.168</td>
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</table>

[B] Contrast variation

<table>
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<tr>
<th>D_2O %</th>
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<th>80</th>
<th>70</th>
<th>60</th>
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<tbody>
<tr>
<td>n</td>
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<td>37.7</td>
<td>39.3</td>
<td>38.3</td>
<td>37.5</td>
</tr>
<tr>
<td>a/b</td>
<td>1.84</td>
<td>1.78</td>
<td>1.86</td>
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<td>1.77</td>
</tr>
<tr>
<td>α</td>
<td>0.42</td>
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<td>0.41</td>
<td>0.40</td>
<td>0.42</td>
</tr>
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<td>N_s</td>
<td>12.4</td>
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<td>12.4</td>
<td>12.5</td>
<td>12.6</td>
</tr>
<tr>
<td>σ, Å</td>
<td>38.7</td>
<td>38.3</td>
<td>38.8</td>
<td>38.5</td>
<td>38.2</td>
</tr>
<tr>
<td>κ, Å</td>
<td>7.29</td>
<td>7.29</td>
<td>7.33</td>
<td>7.37</td>
<td>7.30</td>
</tr>
<tr>
<td>η</td>
<td>0.168</td>
<td>0.168</td>
<td>0.168</td>
<td>0.168</td>
<td>0.168</td>
</tr>
</tbody>
</table>

n : The average aggregation number of a micelle.
a/b : Micellar axis ratio, b = 11.6 Å.
α : The degree of ionization of a micelle.
N_s: The number of water molecules associated with a PO₄ group.
σ : The macro-ion diameter.
κ : The inverse screening length of Debye-Hückel theory.
η : Volume fraction of macro-ion.
Fig. 6-6. A plot of $n$ as a function of the square root of monomer concentration-forming-micelles for Li(EOP)-D$_2$O system.
may be spherical. Accordingly, for region I we may assume that both the micellar growth and the sphere to prolate shape variation occur with an increase in micellar concentration.

The SANS intensity spectra for the Li(EOP) 10 wt% solution at different $[{\text{D}_2\text{O}}] / [{\text{H}_2\text{O}}]$ ratios have also been measured, and are shown in Fig.6-7. The used parameters ($n$ and $\alpha$) of fit and the extracted parameters are also listed Table 6-3[B]. For the observed intensity spectra, contrast variation analysis has been made using the $Q$-dependent quantity $A(Q)$ described at chapter 5-2-6. $A(Q)$ can be calculated from the observed SANS spectra and substitution of the theoretical calculations of $P(Q)$ and $S'(Q)$. Since, $\pm A(Q)^{1/2}$ is linearly proportional to the scattering length density of the $\text{D}_2\text{O}-\text{H}_2\text{O}$ mixed solvents, the contrast matching point, where the scattering intensity vanishes, can be determined by extrapolating the $\pm A(Q)^{1/2}$ vs. $x_H$ (volume fraction of $\text{H}_2\text{O}$) curve to zero. Figure 6-7 also shows the fitted curves of the scattering intensity vs. $Q$ plots at various $[{\text{D}_2\text{O}}] / [{\text{H}_2\text{O}}]$ ratios. Agreement between the observed intensities and the calculated results is excellent for all samples. The contrast variation plot is shown in Fig.6-8. We have found that the contrast matching point occurs at a ratio of $[{\text{D}_2\text{O}}] / [{\text{H}_2\text{O}}] = 0.874 / 0.126$. The mean aggregation number ($n$) and volume value ($V_{\text{mol}}$) of an EOP molecule obtained from the slope and matching point are 37.3 and 352 Å$^3$, respectively.

The contrast matching point has been calculated, taking into account the mean value ($\alpha = 0.41$) for the degree of ionization, and has been found to occur at a ratio of $[{\text{D}_2\text{O}}] / [{\text{H}_2\text{O}}] = 0.876 / 0.124$. The calculated and observed matching point values are almost identical.
Fig. 6-7. Observed scattering intensity spectra (○) for the 10 wt% Li(EOP) solution at various D$_2$O % in the solvent: a: 100 % D$_2$O, b: 90 % D$_2$O, c: 80 % D$_2$O, d: 70 % D$_2$O and e: 60 % D$_2$O, and fitted scattering intensity profiles (solid lines) in the $Q$ range 0.06 ~ 0.40 Å$^{-1}$, assuming that the micelles are mono-dispersed.
Fig. 6-8. External contrast variation plots for the 10 wt% Li(EOP) solution.
6-3-5. Micellar structure of Na(DPP)

For the micellar solution of Na(DPP) in water, the SANS experiment has been carried out at 23 ± 0.1 °C in the concentration range 6.0 ~ 10.0 wt%. The structural model of the Na(DPP) micelle is assumed similar to that of Li(EOP) micelle.

In the present study, both prolate and oblate spheroid models for DPP micelles have been calculated by assuming mono- and poly-dispersity. We have found that the prolate spheroid model provides consistently better fits to the observed SANS data than does the oblate spheroid model. The results analyzed on the basis of mono-dispersity are summarized in Table 6-4[A]. In the SANS analysis, the intensity spectrum of a DPP solution measured at concentrations below the CMC was subtracted from the intensity spectra of the solutions containing micelles in the $Q$ range 0.06 ~ 0.60. The intensity spectra obtained for the DPP micellar solutions are shown in Fig.6-9. The scattered intensities $d\Sigma(Q)/d\Omega$ observed in this concentration region are weak, because of low molecular weights. However, the experimental uncertainty of the results is of the order of ± 2 %. In the curve of $d\Sigma(Q)/d\Omega$ against $Q$ obtained in the concentration range 7.0 ~ 10.0 wt%, very broad peaks are observed, showing that there are interactions between the micelles. As the concentration is changed from 7.0 wt% to 10.0 wt%, the interaction peak increases steadily and shifts slightly to higher $Q$ values, indicating an enhanced interparticle structure factor with increasing micellar concentration. The closeness of fit between the observed data points and the theoretically calculated results is excellent (Fig.6-9) and the average percentage deviation per data point was ± 5 % for all spectra. The parameters ($n$ and $\alpha$) of fit are also listed in Table 6-4[A].

The aggregation number of a Na(DPP) micelle is shown in Fig.6-10 as a function of the square root of the monomer concentration (molar fraction) attributable to formation of micelles. We may assume that the aggregation number ($n$) tends to become small with a decrease in concentration ($n = 12$ at 7.0 wt% and $n = 15$ at 10.0 wt%). Moreover, all the $n$ values fall on a straight line. Therefore, a ladder model of micellar
Fig. 6-9. Observed scattering intensity spectra ( \( \bigcirc \) ) for the Na(DPP)-D\(_2\)O system. a: 10 wt\%, b: 9 wt\%, c: 8 wt\% and d: 7 wt\%, and fitted scattering intensity profiles (solid lines) in the \( Q \) range 0.06 ~ 0.60 Å\(^{-1}\), assuming that the micelles are mono-dispersed.
Table 6-4 The results of the Na(DPP) SANS data analysis

[A] Concentration dependence (mono-dispersed)

<table>
<thead>
<tr>
<th>C, wt%</th>
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</tr>
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<tbody>
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<td>α</td>
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</tr>
<tr>
<td>Ns</td>
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<td>20.1</td>
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<td>κ, Å</td>
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<td>29.7</td>
<td>30.1</td>
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<tr>
<td>η</td>
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<td>0.089</td>
<td>0.113</td>
<td>0.138</td>
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</table>

[B] Contrast variation

<table>
<thead>
<tr>
<th>D2O %</th>
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<th>40</th>
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<td>14.6</td>
<td>14.6</td>
</tr>
<tr>
<td>a/b</td>
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</tr>
<tr>
<td>α</td>
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<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
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<td>30.3</td>
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<tr>
<td>η</td>
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</tr>
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</table>

[C] Concentration dependence (poly-dispersed)

<table>
<thead>
<tr>
<th>C, wt%</th>
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<th>10.0</th>
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<tbody>
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<td>16</td>
</tr>
<tr>
<td>n_min</td>
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<td>8</td>
</tr>
<tr>
<td>n_max</td>
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<td>21</td>
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<td>24</td>
</tr>
<tr>
<td>α</td>
<td>0.50</td>
<td>0.49</td>
<td>0.45</td>
<td>0.42</td>
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</table>

n : The average aggregation number of a micelle.
a/b : Micellar axis ratio b = 7.8 Å.
α : The degree of ionization of a micelle.
Ns : The number of water molecules associated with a PO₄ group.
σ : The macro-ion diameter.
κ : The inverse screening length of Debye-Hückel theory.
η : Volume fraction of macro-ion.
Fig. 6-10. A plot of $n$ as a function of the square root of monomer concentration-forming-micelles for Na(DPP)-D$_2$O system.
growth can be applied to the micellar formation of Na(DPP) anions [30]. Furthermore, as can be seen in Table 6-4[A], the shape of a Na(DPP) micelle is prolate and the $a/b$ ratio has a tendency to decrease as the concentration approaches the CMC. Therefore, we may assume that the micellar shape changes at concentrations above the CMC. The SANS spectra of sample solutions at concentrations near the CMC will be very weak in intensity, making it very difficult to obtain the particle structure factor of the nascent micelle. However, we can assume a minimum aggregation number ($n = 7$) for a micelle at the CMC by extrapolation of the linear $(X - X_{\text{CMC}})^{1/2}$ vs. $n$ plots, as shown in Fig.6-10. Under these conditions, an $a/b$ ratio of 1.1 can be calculated, showing that the minimum micelle is spherical. Thus, for the micellar system of DPP anions it can be assumed that micellar growth and variation from the spherical to the prolate shape occurs with an increase in concentration above the CMC. The rationale for proposing a minimum micelle of aggregation number $n = 7$ can be seen from the following geometrical consideration.

The hydrocarbon core volume of a Na(DPP) micelle having an aggregation number $n = 7$ is 2173 Å³, since the volume of the two $n$-pentyl chains of a DPP molecule is 311 Å³. If we assume that the shape of a Na(DPP) micelle is spherical and that the radius of the micellar core is equal to the length (7.8 Å) of a pentyl chain taking up the all-trans form, (given by Tanford's equation [28]), then the volume of the micelle will be 2010 Å³, and we can calculate an aggregation number of 6.5, by dividing the volume of 2010 Å³ by the volume (311 Å³) of the two pentyl chains. This value is almost the same as the minimum aggregation number $n = 7$.

As has already been demonstrated directly in our preceding papers [15, 16], for the aqueous solutions of simple soap molecules (potassium $n$-pentanoate and $n$-hexanoate) and barium dibutyl and dipentyl phosphate molecules, the percentages of rotational somers containing the gauche-forms are relatively high below the CMC, compared with that of the all-trans-form. However, micellization brings about preferential stabilization of the all-trans hydrocarbons. These experimental results are consistent with a micellar
model having the extended structure of hydrocarbon chains outlined above.

Micelles of the double-chain anionic surfactant AOT have been studied in aqueous solutions by Sheu et al. [34] by using SANS. They assumed that the minimum aggregation number at the CMC was 15 ± 1 and that the micellar shape was spherical. Furthermore, it was assumed that the AOT micelles grew as the concentration increased and were transformed from a spherical to an oblate spherical shape. For the micellar solutions of ammonium octanoate in aqueous solution [36], it has already been found from SANS that the aggregation number depends upon the concentration: \( n = 7 \) at 0.36 mol l\(^{-1}\) and \( n = 12 \) at 0.48 mol l\(^{-1}\).

We have analyzed the scattering intensity curves taken from sample solutions of different H\(_2\)O-D\(_2\)O mixtures. The contrast variation method at finite \( Q \) used in the present study is based on a \( Q \)-dependent quantity \( A(Q) \) described at chapter 5-6-2. \( A(Q) \) can be calculated from the observed SANS spectra combined with the model calculations of \( P(Q) \) and \( S'(Q) \). \( \pm A(Q)^{1/2} \) is linearly proportional to the scattering length density of the [D\(_2\)O] / [H\(_2\)O] mixed solvent. Therefore, the contrast matching point, where the scattering intensity vanishes, can be determined by extrapolating the \( \pm A(Q)^{1/2} \) vs. \( x_H \) curve to zero.

Figure 6-11 shows the experimental and fitted curves of the scattering intensity vs. \( Q \) plots for the DPP solution (10.0 wt%) at various [D\(_2\)O] / [H\(_2\)O] ratios. The agreement is excellent across the whole range of samples. The used parameters (\( n \) and \( \alpha \)) of fit and the extracted parameters are also listed in Table 6-4[B]. Figure 6-12 shows the contrast variation (\( \pm A(Q)^{1/2} \) vs. \( x_H \)) plots. It is found by extrapolation that the contrast matching point occurs at a ratio of [D\(_2\)O] / [H\(_2\)O] = 0.142 / 0.858. The mean aggregation number (\( n \)) and volume value (\( V_{mol} \)) of a DPP molecule obtained from the slope and matching point are 14 and 348 Å\(^3\), respectively.

The contrast matching point has been calculated, taking into account the mean value (\( \alpha = 0.40 \)) for the degree of ionization, and has been found to occur at a ratio of [D\(_2\)O] / [H\(_2\)O] = 0.139 / 0.861. The calculated and observed matching point values are almost
Fig. 6-11. Observed scattering intensity spectra (○) for the 10 wt% Na(DPP) solution at various D$_2$O % in the solvent. a: 100 % D$_2$O, b: 80 % D$_2$O, c: 60 % D$_2$O and d: 40 % D$_2$O, and fitted scattering intensity profiles (solid lines) in the Q range 0.06 ~ 0.60 Å$^{-1}$, assuming that the micelles are mono-dispersed.
Fig. 6-12. External contrast variation plots for the 10 wt% Na(DPP) solution.
identical.

The SANS analysis provides the degree ($\alpha$) of ionization of a micelle (Table 6-4[B]), associated with the electric-double layer at the interface. As the concentration increases, the $\alpha$ value tends to decrease. It should be noted that the $\alpha$ value becomes very small (0.3) at a concentration of 10 wt%, which is very close to the second $CMC$ (10.7 wt%) determined by the concentration dependence of the self-diffusion coefficient (discussed in chapter 3-3-2). Accordingly, in the concentration region above the second $CMC$ (17 wt%), determined by the $^{31}$P NMR chemical shift (discussed in chapter 3-3-3), we may expect that the degree of ionization for the aggregate system will become extremely small compared with that at 10 wt%. For the Na(DPP)-water solution, it may be assumed from the results of the $^{31}$P NMR and x-ray low angle diffraction patterns (discussed in chapter 3-3-3 and 3-3-4) that a highly-organized structure, similar to a lamellar structure, is formed at high concentrations. It is very difficult to estimate the degree of ionization at the lamellar interface by SANS analysis. However, we may speculate that most of the counter ions are condensed at the interface of a lamellar structure.

Usually, we may assume that micelles in equilibrium with each other in solution have a finite distribution of sizes about some mean value. In the present study, the scattering intensity ($d\Sigma(Q)/d\Omega$) was also calculated by considering the polydispersity and use was also made of the interparticle structure factor $S'(Q)$.

For the size-dispersed system of charged hard particles, the scattering intensity can be expressed in the following form,

$$
\frac{d\Sigma(Q)}{d\Omega} = \left( \sum_{i_{\text{max}}}^{i_{\text{min}}} n_p(i) \left[ (\rho_p(i) - \rho_v(i))V_v(i) + (\rho_v(i) - \rho_p(i))V_m(i) \right] \right)^2 P(i, Q) S'(Q)
$$

(6-18)

$$
n_p = \frac{(C - CMC)d(i)N_A}{1000i} \text{ / cm}^{-3}
$$

(6-19)
where $i$ denotes the particles having aggregation number $i$, and $d(i)$ is the concentration distribution function of the monomer. It is assumed that $d(i)$ is a Gaussian function with standard deviation (square root of mean average aggregation number) [36].

The calculated $d\Sigma(Q)/d\Omega$ profiles are not shown here. The average aggregation number ($n_{ave}$), and the minimum and maximum values of the aggregation number are listed in Table 6-4[C]. It can be seen that the $n_{ave}$ values are very similar to the aggregation number calculated by assuming monodispersity.
6-3-6. Molecular conformations in the Na(DPP) micelle

For di-n-butyl or di-n-pentyl phosphate anions in water, we have already demonstrated that the all-trans form of the alkyl group is preferentially stabilized upon micellization [13, 14]. Therefore, in the SANS spectral analysis, the assumption that the radius of the micellar core is equal to the length of an extended pentyl chain is well supported by these experimental results.

Furthermore, for the conformations about the two PO-CC single bonds, it has been found that micellization brings about preferential stabilization of the trans form [37]. Accordingly, in the DPP micelle, we may assume that the pentyloxy segments are in an extremely restricted state.

However, in the Na(DPP)-micellar system, conformations about the two phosphodiester P-O bonds seem to play an important role. As shown in Fig.6-13, for the DPP molecule only three molecular forms (GG, GT and TT) about the P-O bonds can be considered: four mirror images (G'T, TGG and TGT) can be omitted and the GG' and G'T forms are also omitted because of their instability due to steric hindrance. In our previous paper [14], for Raman spectra of DPP the accordion vibrational mode has provided evidence that preferential stabilization of a specific molecular form about the P-O bonds occurs even in the solid state, depending upon the content of hydrated water molecules about the PO₄⁻ group.

In the present study, the accordion vibrational modes, which reflect directly the conformation about the P-O bonds, has been measured for the micellar solution of the Na(DPP)-water system. The very broad Raman band at 270 cm⁻¹, which derives from the GT form [14], has been found, indicating that the GT form about the P-O bonds is stabilized in the micellar state. However, the broadness of the 270 cm⁻¹ band may indicate that two other molecular forms (GG and TT) also coexist in addition to the GT form, although their populations are low.
Fig. 6-13. Schematic representation of three rotational isomers (GG, GT and TT) about the P-O bonds. The conformations about every CH$_2$-CH$_2$ bond and two CH$_2$-O bonds were assumed to be in the trans conformation.
6-4. Conclusion.

Mixed-double chain anionic surfactant molecules, the barium- and lithium-salts of ethyl(n-octyl) phosphate (EOP) and sodium n-pentyl phosphate (DPP) have been synthesized. The microstructure of aggregates in the EOP- and DPP-water binary systems has been studied by SANS spectra.

For the micellar solution of the EOP-barium salt in D$_2$O, it has been found by SANS analysis that the micellar shape is a prolate spheroid and that the aggregation numbers (n) are n = 48 at 23 °C and n = 52 at 50 °C.

For the micellar solution of the EOP-lithium salt in water and the DPP-sodium salt in water, SANS spectra have been measured and intensity profile calculations have been made. Calculations of the SANS data on the Li(EOP) system and Na(DPP) suggested a sphere to prolate transition due to a slight micellar growth.
References

25. Suzuya, K. Ph. D. thesis; Tohoku University, 1992


Chapter 7.

Small-angle neutron scattering study of bis(quaternary ammonium bromide) surfactant micelles in water. Effect of the spacer chain length on micellar structure

7-1. Introduction

Considerable attention has been given to the solution behavior of bis(quaternary ammonium bromide) surfactants [1-11] of general formula

\[
\text{Br}^- (\text{CH}_3)_2N^+ - (\text{CH}_2)_{n_s} - N(\text{CH}_3)_2\text{Br}^- \\
\text{C}_m\text{H}_{2m+1} \quad \text{C}_m\text{H}_{2m+1}
\]

\(n_s = 2, 3, 4 \text{ and } 6\)

in which two alkyl dimethylammonium bromide moieties are connected by a polymethylene chain, referred to as a spacer. These dimeric surfactants continue to attract interest, because of their potent bactericidal activity [12, 13] and peculiar solution behavior [14, 15].

Zhna et al. [9] have reported on the solution behavior of such dimeric surfactants. In aqueous solution, the critical micelle concentration (CMC) was found to go through a maximum at a value of the spacer carbon number (\(n_s\)) apparently equal to 5, as \(n_s\) was increased. At \(n_s \geq 10\), log(CMC) decreased linearly as \(n_s\) increased. These results were explained in terms of conformational change of the surfactant cation and of the spacer location in the micelle.

The surface tension of the dimeric surfactant-water systems has been measured as a function of the surfactant concentration for homologs with varying spacer lengths [15]. The results suggested that the behavior of the surface tension reflects a variation of location of the spacer away from the interface which is in contact with water, to the air.
side of the interface at a value of \( n_s \geq 10 \) when the spacer becomes sufficiently hydrophobic.

Furthermore, Zana et al.\([14]\) have investigated the microstructures of the aggregates of the dimeric surfactant with \( m = 12 \) and \( n_s = 2, 3 \) and 4 in aqueous solution, using cryogenic transmission electron microscopy. It was found that the dimeric surfactants with a short spacer (\( n_s = 2, 3 \)) form long, thread-like and entangled micelles, even at a low concentration, while surfactants with \( n_s = 4 \) form spherical micelles. These observations reveal that the length of a spacer affects the morphology of the aggregates formed by the dimeric surfactant molecules and short spacers promote lower spontaneous curvature in the self-assemblies.

Israelachvili et al.\([16]\) have shown that the type and structure of the self-assembly formed by different surfactants depend upon their geometrical packing parameters. However, a packing property is dependent on many factors. Therefore, in order to discuss quantitatively the relationship between the geometrical packing parameters and morphological characteristics, the effect of perturbation of the local arrangement of a surfactant molecule on its micellar and mesomorphic properties in aqueous solution should be further investigated.

In the present study, for the dimeric surfactants with \( m = 10 \) and \( n_s = 2, 3, 4 \) and 6, the effect of the spacer chain length on the aggregation number and micellar shape in water is discussed in detail, using small angle neutron scattering (SANS) spectra.

The microstructure of \( n \)-alkyl trimethylammonium bromide micelles (so-called \( C_n \text{TAB} \)) has already been investigated in detail by Berr et al., using SANS spectra \([17-19]\). As the bis(quaternary ammonium bromide) surfactants can be considered as "dimers" of the \( C_n \text{TAB} \) molecules, elucidation of the microstructures of \( C_n \text{TAB} \) micelles by SANS will provide useful data for analysis of the SANS spectra of dimeric surfactant micelles.
7-2. Experimental

7-2-1. Materials

Bis(quaternary ammonium bromide) surfactants (DS $m = 10$, $n_s = 2, 3, 4, 6$ and 8) were synthesized as follows [9, 10]. For $n_s = 2, 3, 4, 6$ and 8, reactions of alkanediyl-$\alpha$, $\omega$-bis(dimethylamine) with 1-bromo-$n$-decane were performed in dried ethanol under reflux ($T = 80 \, ^\circ C$) for 48 h in the presence of a $5 \sim 10$% excess of alkyl dimethylamine or alkylbromide, so as to ensure as complete biquaternization as possible. The surfactants thus prepared were recrystallized in various solvent mixtures (ethanol - ethylacetate or acetone - ethylacetate). Sample identity was confirmed by NMR and elemental analyses. The reactants were obtained from Tokyo Kasei Co., and were purified before reaction.

7-2-2. Conductivity measurements

The electrical conductivity method was used to determine the critical micelle concentration ($CMC$) from plots of the specific electrical conductivity $\kappa$ against the surfactant concentration $C$. The degree of ionization of a micelle was taken as the ratio of the values of $d\kappa/dC$ above and below the $CMC$. The electrical conductivities of the sample solutions were measured with a Conductivity Meter CM 11P (TOA Electronics Ltd) at $25.0 \pm 0.1 \, ^\circ C$.

7-2-3. SANS measurements

The small angle neutron scattering (SANS) measurements were carried out using the medium angle neutron scattering instrument (WINK) installed at the pulsed neutron source KENS at the National Laboratory for High Energy Physics, Tsukuba, Japan. The sample solutions were placed in a quartz cell of 1 or 2 mm path length at $23 \, ^\circ C$. The scattering length density ($\rho$) of each component was calculated using the following equation,
\[ \rho = \Sigma b_i / V \quad (7-1) \]

where \( b_i \) is the scattering length of atom \( i \) and \( V \) is the molecular volume. The \( V \) values calculated from partial molar volume data [20] and \( \Sigma b_i \) values quoted from ref. 21 are listed in Table 7-1. The magnitude of the momentum transfer (\( Q \)) is given by equation (7-2),

\[ Q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (7-2) \]

where \( \lambda \) is the incident wavelength (1 ~ 16 Å for WINK). The intensity of scattered neutrons was recorded on a position-sensitive 2-D detector. Normalization of the data to an absolute intensity scale was made by using the transmission of a 1 mm water sample.

**Table 7-1** Volumes (\( V \)) and scattering lengths (\( \Sigma b_{coh} \))

<table>
<thead>
<tr>
<th>Species</th>
<th>( V ), Å(^3)</th>
<th>( \Sigma b_{coh} ), ( \times 10^{-4} ) Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)</td>
<td>42.6</td>
<td>-0.457</td>
</tr>
<tr>
<td>CH(_2)</td>
<td>28.2</td>
<td>-0.083</td>
</tr>
<tr>
<td>N</td>
<td>-30.5</td>
<td>0.936</td>
</tr>
<tr>
<td>Br(^-)</td>
<td>50.0</td>
<td>0.677</td>
</tr>
<tr>
<td>D(_2)O</td>
<td>30.3</td>
<td>1.918</td>
</tr>
</tbody>
</table>
7-3. Results and discussion

7-3-1. Critical micelle concentration

It is well known that the electrical conductivity of surfactant solutions changes with concentration at different rates below and above the CMC. Surfactant molecules are completely dissociated at low concentrations and their conductivities increase linearly with an increase in concentration up to the CMC. Although the conductivity continues to increase as the concentration increases even beyond the CMC, the rate of increase in conductivity is low compared with that below the CMC, because some of the counterions are bound to the micelle, thereby causing a reduction in the effective charge of the micelle. Thus, a plot of conductivity against concentration below and above the CMC furnishes two straight lines which intersect at the CMC.

For a series of DS with $m = 10$, $n_s = 2, 3, 4, 6$ and 8 in aqueous solutions, the specific electrical conductivity ($\kappa$) was measured at various concentrations. The points of inflection in plots of $\kappa$ vs. concentration provide a measure of the values of the CMC. From the slopes of the two straight lines below and above the CMC, average degrees of ionization ($\alpha_{\text{ave}}$) of the micelles were calculated and these are listed in Table 7-2. The CMC values thus obtained for these dimeric surfactants were found to be very close to those reported by Devinsky et al. [31], where a plot of log(CMC) against $n_s$ showed a linear increase with an increase in $n_s$ for the DS series with $n_s = 2 \sim 6$, while the DS series with $n_s$ values above 6 showed a linear decrease in log(CMC) with increasing length of the spacer. Furthermore, it was found that the variation of degree of ionization with the length of the spacer is very close to that found for the DS series with $m = 12$ and $n_s = 2, 3, 4$ and 6 [14].

We can apply the mass-action law to the monomer $\leftrightarrow$ micelle equilibrium in the micellar solutions for a series of DS with $m = 10$ and $n_s = 2 \sim 8$. If we assume that the DS molecules are 2 : 1 electrolytes [9], the ionization process of DS in water may be presented as follows,
\[ nS^{2+} + 2n(1 - \alpha)Br^- \Leftrightarrow \left( S_nBr_{2n(1-\alpha)} \right)^{2n\alpha+} \]  \hspace{1cm} (7.3)

where \( S^{2+} \) and \( Br^- \) denote dimeric surfactant monomer cation and bromide anion, respectively, \( n \) is the aggregation number of a micelle, and \( \alpha \) is the degree of ionization per polar group. If activity coefficients are neglected, the equilibrium constant is given by the following equation,

\[ K = \frac{\left[ \left( S_nBr_{2n(1-\alpha)} \right)^{2n\alpha+} \right]}{\left[ S^{2+} \right]^{n} \left[ Br^- \right]^{2n(1-\alpha)}} \]  \hspace{1cm} (7.4)

Since the Gibbs free energy is \( \Delta G^{0}_{\text{tot}} = -RT \ln K \), the free energy of micellization per monomer for the above equilibrium system may be given by equation (7.5)

\[ \Delta G^0 = \frac{-RT \ln K}{n} \]

\[ \Delta G^0 = \frac{-RT \ln \left( \frac{\left( S_nBr_{2n(1-\alpha)} \right)^{2n\alpha+}}{n} \right)}{n} - \ln \left[ S^{2+} \right] - 2(1 - \alpha) \ln \left[ Br^- \right] \]  \hspace{1cm} (7.5)

When the aggregation number \( n \) is large, the contribution of the term \( \ln \left[ \left( S_nBr_{2n(1-\alpha)} \right)^{2n\alpha+} \right] / n \) to the \( \Delta G^0 \) value is negligible. Thus, the free energy of micellization may be approximately represented as

\[ \Delta G^0 \approx RT \left( \ln \left[ S^{2+} \right] + 2(1 - \alpha) \ln \left[ Br^- \right] \right) \]  \hspace{1cm} (7.6)

When the concentration is very close to the CMC, we may assume \( [S^{2+}] = [Br^-] = CMC \). Therefore, the free energy of micellization per monomer may be written as

\[ \Delta G^0 \approx RT \left( 3 - 2\alpha \right) \ln CMC \]  \hspace{1cm} (7.7)

Thus, the \( \Delta G^0 \) values for micellization of the dimeric surfactants can be calculated by the use of \( \alpha_{\text{ave}} \) and the CMCs measured in the present study. The \( \Delta G^0 \) values are
Thus, the $\Delta G^0$ values for micellization of the dimeric surfactants can be calculated by the use of $\alpha_{\text{ave}}$ and the CMCs measured in the present study. The $\Delta G^0$ values are plotted against the spacer chain length ($n_s$) of the dimeric surfactants in Fig. 7-1 and are also listed in Table 7-2.

It is thus found that the $\Delta G^0$ vs. $n_s$ plots provide two straight lines. The slopes of the lines ($\partial \Delta G^0 / \partial n_s$) are equal to the free energy of transfer of a spacer methylene unit from bulk-water to the micelle. From the slopes of the line ($n_s = 2, 3$ and $4$) and of the line ($n_s = 4, 6$ and $8$), the calculated values of free energy per spacer methylene unit are 3.9 kJ mol$^{-1}$ and 0.05 kJ mol$^{-1}$, respectively. It should be noted that there exists a marked difference between the two free energy values. Thus, for the dimeric surfactants with $n_s = 2, 3$ and $4$, the free energy of transfer of a spacer methylene unit from the bulk phase to the micelle increases with the number of the spacer methylene groups. However, for the dimeric surfactants with a $n_s$ value greater than 6, the free energy of transfer tends to decrease as the spacer length increases.

<table>
<thead>
<tr>
<th>Spacer</th>
<th>CMC, wt%</th>
<th>$\alpha_{\text{ave}}$</th>
<th>$\Delta G^0$, kJ mol$^{-1}$</th>
<th>$-(\Delta - n_0\delta)$, kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.347</td>
<td>0.15</td>
<td>-60.9</td>
<td>-37.2</td>
</tr>
<tr>
<td>3</td>
<td>0.373</td>
<td>0.22</td>
<td>-57.4</td>
<td>-28.7</td>
</tr>
<tr>
<td>4</td>
<td>0.512</td>
<td>0.28</td>
<td>-53.1</td>
<td>-23.5</td>
</tr>
<tr>
<td>6</td>
<td>0.566</td>
<td>0.29</td>
<td>-52.6</td>
<td>-16.6</td>
</tr>
<tr>
<td>8</td>
<td>0.482</td>
<td>0.32</td>
<td>-52.9</td>
<td></td>
</tr>
</tbody>
</table>

* In order to estimate the contribution of the term $\ln[(S\_\alpha Br_{2\alpha(1-\alpha)}^{2+\alpha+\frac{1}{n}})]$ to the $\Delta G^0$ value, the procedure described in ref.19 was used in this study. The errors of the $\Delta G^0$ values were within 1.8 %.
Fig. 7-1. Spacer chain length \( (n_s) \)-dependence of the free energy \( (\Delta G^0) \) of micellization per spacer methylene unit.
7-3-2. Effect of spacer chain length on micellar structure

In the present study, both prolate and oblate spheroid models for the DS micelles have been calculated by assuming mono-dispersity. It has been found that the prolate model provides consistently better fits to the observed SANS intensity data than does the oblate model.

A structural model of the DS micelle, used in the calculation of the single particle form factor $P(Q)$, is shown in Fig.7-2. This model is based on the assumption of the result of the SANS analysis for $n$-alkyl trimethylammonium bromide micelles, made by Berr et al.[17-19]. The shape of the DS micelle is prolate and has a hydrophobic core with a major axis $a$ and minor axis $b$. The $b$ value is set equal to the fully extended length of the portion of the $n$-decyl chain which constitutes the hydrophobic core. The Stern layer, of thickness $t$, consists of the dimethylammonium head groups, associated with bromide counterions and water molecules, spacer methylene groups and the hydrated portion of the $n$-decyl chain. The assumption that the spacer methylene groups are located in the Stern layer comes from the results of surface tension and x-ray scattering investigation made by Alami et al.[10, 15].

The $b$ and $t$ values are given by the following equations [18], which are similar to the equation presented by Tanford [26],

$$b = 2.95 + 1.27 \left(10 - n_{\text{wet}}\right)$$  \hspace{1cm} (7-8)

$$t = 2.95 + 1.27 \left(2 + n_{\text{wet}}\right)$$  \hspace{1cm} (7-9)

where $n_{\text{wet}}$ is the number of hydrated methylene groups for the monomeric-portion of the DS molecules, the number 10 is the number of carbon atoms in a $n$-decyl chain, and the number 2 is the summation of the number of nitrogen atoms and of terminal methyl carbon atoms lying along the molecular axis which includes an $n$-decyl chain. The volume of the hydrocarbon tail constituting the core ($V_{\text{tail}}$) and that of the polar heads in the Stern layer ($V_{\text{head}}$) per one DS molecule, used for calculation of the scattering length densities of the whole micelle, are expressed as follows.
Fig. 7-2. Micellar model used in the calculation of $P(Q)$. $t$ is thickness of the Stern layer, and $a$ and $b$ are major and minor axes, respectively.
\[ V_{\text{tail}} = 2 \left[ V_{\text{CH}_3} + (9 - n_{\text{wet}}) V_{\text{CH}_2} \right] \quad (7-10) \]
\[ V_{\text{head}} = 2 \left( 2V_{\text{CH}_3} + n_{\text{wet}} V_{\text{CH}_2} + V_{\text{N}} \right) + n_s V_{\text{CH}_2} \quad (7-11) \]

where \( V_{\text{CH}_3}, V_{\text{CH}_2} \) and \( V_{\text{N}} \) are the volumes of the methyl and methylene groups and of the nitrogen atom, respectively, and \( n_s \) is the number of spacer methylene groups.

In the SANS analysis, the scattering intensity coming from the DS solution was corrected for the detector background and incoherent scattering. The intensity spectrum of the DS solution measured at concentrations below the CMC was subtracted from those of the micelle solutions in the \( Q \) range 0.06 ~ 0.30 Å\(^{-1}\). The scattering intensity spectra observed for the DS micellar solutions and the theoretically calculated results are shown in Fig.7-3[A] ~ [D]. The closeness of fit between the observed and calculated data is excellent.

Figures 7-3[A] ~ [D] show the observed and the fitted curves of the scattered intensity vs. \( Q \) plots for a series of DS micellar solutions at various concentrations. The observed intensity data were analyzed with the aggregation number (\( n \)), degree of ionization (\( \alpha \)) and the number of hydrated methylene groups (\( n_{\text{wet}} \)) as fitting parameters, and the \( a, b \) and \( t \) values are calculated using \( n_{\text{wet}} \) and \( n \). The extracted parameter values are listed in Table 7-3.

As can be seen in Tables 7-3, the aggregation number for the DS micellar solutions is found to depend upon the length of the spacer methylene chain (\( n_s \)). In fact, as the \( n_s \) value increases, the value of \( n \) tends to decrease. In particular, it should be noted that there exists a marked difference in aggregation number between the two different spacers (\( \text{CH}_2 \)) and (\( \text{CH}_3 \)).

Figure 7-4 shows the average aggregation number (\( n \)) plotted as a function of the square root of the mole fraction of the monomer concentration (\( X - X_{\text{CMC}} \)^{1/2}) attributable to formation of micelles. For a series of the DS micellar solutions, the \( n \) values increases with an increase in micellar concentration, and all the \( n \) values fall on a
Fig. 7-3[A]. Observed scattering intensity spectra (open circle) for the DS ($m = 10$, $n_s = 2$)-D$_2$O system at $23 \, ^\circ\text{C}$. a: 4.0 wt%, b: 3.5 wt%, c: 3.0 wt%, d: 2.5 wt%, e: 2.0 wt%, f: 1.5 wt% and g: 1.0 wt%, fitting scattering intensity profiles (solid lines). The average percentage deviation per datum point was within ±4 % for all spectra.
Fig. 7-3[B]. Observed scattering intensity spectra (open circle) for the DS ($m = 10$, $n_s = 3$)-D$_2$O system at 23 °C. a: 4.0 wt%, b: 3.5 wt%, c: 3.0 wt%, d: 2.5 wt%, e: 2.0 wt%, f: 1.5 wt% and g: 1.0 wt%, fitting scattering intensity profiles (solid lines). The average percentage deviation per datum point was within ±4% for all spectra.
Fig. 7-3[C]. Observed scattering intensity spectra (open circle) for the DS (m = 10, n_s = 4)-D_2O system at 23 °C. a: 4.0 wt%, b: 3.5 wt%, c: 3.0 wt%, d: 2.5 wt%, e: 2.0 wt%, f: 1.5 wt% and g: 1.0 wt%, fitting scattering intensity profiles (solid lines). The average percentage deviation per datum point was within ± 5% for all spectra.
Fig. 7-3[D]. Observed scattering intensity spectra (open circle) for the DS ($m = 10, n_s = 6$)-D$_2$O system at 23 °C. a: 4.0 wt%, b: 3.5 wt%, c: 3.0 wt%, d: 2.5 wt%, e: 2.0 wt% and f: 1.5 wt%, fitting scattering intensity profiles (solid lines). The average percentage deviation per datum point was within ±5% for all spectra.
Fig. 7-4. A plot of $n$ as a function of the square root of monomer concentration-forming-micelles ($X$: molar fraction). ●: DS ($m = 10, n_s = 2$), ■: DS ($m = 10, n_s = 3$), ◆: DS ($m = 10, n_s = 4$) and ▲: DS ($m = 10, n_s = 6$).
straight line, indicating that a ladder model of micellar growth can be applied to the micellar formation of DS cations [28].

Extrapolation of the linear \((X - X_{CMC})^{1/2}\) vs. \(n\) plots provides the minimum aggregation number of a micelle at the CMC. When we compare the minimum aggregation numbers \(n_0\) for DS molecules \((m = 10\) and \(n_s = 2, 3, 4\) and 10\) with each other, the difference during the \(n_0\) values seems to be very small, revealing that the aggregation number of a minimum micelle formed by the DS molecules with \(m = 10\) at the CMC is not so dependent on the length of a spacer methylene chain. This may imply that the main hydrocarbon chain (\(n\)-decyl group) of the DS surfactants plays an important role in formation of a minimum micelle.

Moreover, it can be seen in Table 7-3 that the \((a+t)/(b+t)\) ratio of the prolate spherical micelles decreases as the concentration approaches the CMC. This result indicates that the shape of a DS micelle varies with an increase in micellar concentration. For a new-born micelle having a minimum aggregation number of \(n_0 = 22 \sim 25\), the \((a+t)/(b+t)\) ratio is very close to 1.0, indicating that the minimum micelle may be spherical. Thus, we may assume that both micellar growth and sphere to prolate shape variation occur with an increase in micellar concentration.

We may stress the effect of the spacer chain length on such micellar growth and shape variation. For the sample solutions of DS with \(m = 10\) and \(n_s = 2, 3\) and 4, the slope in the linear plots of \((X - X_{CMC})^{1/2}\) vs. \(n\) tends to decrease with an increase in spacer chain length. This observation reveals that the extent of micellar growth decreases with an increase in spacer chain length. In particular, we may emphasize that there exists a marked difference in the slopes of the two different spacers \((CH_2)_2\) and \((CH_2)_3\), showing that marked growth of the micelle occurs for DS molecules with \(n_s = 2\). However, for DS molecules with \(n_s = 6\), the slope of the linear plots becomes very small or approaches zero, implying that the extent of micellar growth is very small or that no
Table 7-3 Scattering intensity spectra observed for DS micellar solutions and theoretical calculated results

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<th>$b$, Å</th>
<th>$t$, Å</th>
<th>$(a+t)/(b+t)$</th>
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DS($m = 10$, $n_s = 2$)-D$_2$O system at 23 °C

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DS($m = 10$, $n_s = 3$)-D$_2$O system at 23 °C
DS \( (m = 10, n_s = 4) \)-D\(_2\)O system at 23 °C

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DS \( (m = 10, n_s = 6) \)-D\(_2\)O system at 23 °C

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\(n\) : The average aggregation number of a micelle. \(\alpha\) : The degree of ionization of a micelle. In the present SANS analysis, it was assumed that the micellar solution is a one-component macrofluid and the finite size of the counter ion is ignored. Therefore, the \(\alpha\) values listed in Table 7-3 are an apparent charge [27]; \(n_{\text{wet}}\) : the number of hydrated methylene groups in the Stern layer; \(a\) : the major axis of prolate micelle given by \(a = (4\pi n V_{\text{tail}})/(3b^2)\); \(b\) : the minor axis of a prolate micelle given by equation (7-8); \(t\) : the thickness of the Stern layer given by equation (7-9); \(N_S\) : the number of water molecules associated with a DS molecule; \(\kappa\) : the inverse Debye-Hückel screening length; \(\sigma\) : the macroion diameter.
micellar growth occurs. Thus, it is evident that an increase in spacer chain length prevents the growth of the DS micelles.

We can discuss the growth of DS micelles in detail, on the basis of the ladder model [28]. The process of micellization may be assumed as follows. At the CMC, DS molecules form a minimum sized spherical micelle containing $n_0$ monomers in aqueous solutions, and no formation of micelles with aggregation number less than $n_0$ occurs. When the DS micelles with $n > n_0$ are formed in solution, a micelle takes up a prolate spherocylinder and $n_0$ and $n - n_0$ molecules are used for formation of the hemispherical end portions and of the cylinder portion, respectively (Fig. 7-5). According to the ladder model, the formation and growth of micelles are characterized by the aggregation number ($n_0$) of the minimum size micelle, the free energy change ($\delta$) per monomer when a surfactant molecule is inserted into the cylinder portion of a spherocylindrical micelle, and the free energy change ($\Delta$) when $n_0$ surfactant molecules aggregate to form the minimum micelle. The mean aggregation number ($n$) of a spherocylindrical micelle can be approximately given by the following equation

$$n = n_0 + 2K^{1/2}(X - X_{CMC})^{1/2}$$ (7-12)

$$K = e^{(\Delta-n_0\delta)RT}$$ (7-13)

where $X$ and $X_{CMC}$ are the total surfactant concentration and CMC expressed by the molar fraction, respectively. Therefore, the slope in the linear $(X - X_{CMC})^{1/2}$ vs. $n$ plots is equal to $2K^{1/2}$. The magnitude of ($\Delta - n_0\delta$), calculated from the slope ($2K^{1/2}$), represents the difference in free energy between $n_0$ monomers in the two end caps of a spherocylindrical micelle and the same number of monomeric surfactants in the cylinder portion. The calculated energy differences thus obtained are listed in Table 7-2 and are plotted against the spacer chain length in Fig. 7-6. The value of $- (\Delta - n_0\delta)$ provides a measure of the rapidity of micellar growth as the concentration increases. The effect of an
Fig. 7-5. Schematic structure of a prolate spherocylindrical micelle with aggregation number $n$. Two end-caps form a minimum micelle with $n_0$ monomers.
Fig. 7-6. Spacer chain length dependence of the value of $-RT(\Delta - n_0\delta)$. 
increase in spacer chain length is found to cause an exponential increase in the parameter, 
\[-(\Delta - n_0\delta),\] indicating that an increased length of spacer chain prevents micellar growth.

As has already been reported by Zana et al. [14], electron-micrographs of the micelles formed by DS molecules with \(m = 12\) and \(n_s = 2\) and \(3\) in aqueous solutions show long, thread-like and entangled micelles, while, in a micrograph of micelles formed by the surfactant with \(m = 12\) and \(n_s = 4\), the thread-like micelles are no longer present and spherical micelles are seen instead.

The results of SANS analysis for the DS surfactants with \(m = 10\) and \(n_s = 2, 3, 4\) and \(6\) also show that the spacer chain length strongly affects the morphology of aggregates formed by such dimeric surfactants in water.
7-3-3. Micellar shape and molecular packing parameters

We may discuss the relationship between the molecular packing parameters of a dimeric surfactant and micellar shape. For surfactant molecules of optimal area $a_0$, hydrocarbon volume $v$ and critical chain length $l_c$, the packing parameter is defined as $v/a_0l_c$ [29]. The packing parameters calculated for DS molecules with $m = 10$, $n_s = 2, 3, 4$ and 6 are $0.45 \ (n_s = 2)$, $0.36 \ (n_s = 3)$, $0.33 \ (n_s = 4)$ and $0.26 \ (n_s = 6)$. As has been shown by Israelachvili et al. [29], we may expect that surfactant molecules form spherical micelles at $v/a_0l_c < 1/3$, non-spherical micelles at $1/3 < v/a_0l_c < 1/2$, and vesicles or bilayers at $1/2 < v/a_0l_c < 1$ and inverted structures at $v/a_0l_c > 1$. Therefore, for the DS surfactants used in the present study, we may expect from the calculated parameter values that the DS surfactants with $n_s = 2$ and 3 form non-spherical micelles. In particular, the SANS data show that the shape of the micelles of the DS molecules with $m = 10$ and $n_s = 2, 3$ are prolate spheroid and that, for the DS molecules with $m = 10$ and $n_s = 4$, 6, the micellar shape is almost spherical. This results agree with the results of cryogenic transmission electron microscopy study reported by Zana et al. [14], which have showed that DS micelles are spherical only for $m = 12$ and $n_s = 4$, while for $n_s = 2$ and 3, thread-like and entangled micelles form. The packing parameters calculated for DS molecules with $m = 12$, $n_s = 2, 3$ and 4 are $0.46 \ (n_s = 2)$, $0.37 \ (n_s = 3)$ and $0.33 \ (n_s = 4)$. The results are therefore qualitatively in accordance with the theoretical prediction.

However, for nascent micelles, prediction of the shape by use of molecular packing parameters is unsuccessful, since all the minimum micelles formed by the DS molecules with $n_s = 2 \sim 6$ are spherical. The reason may possibly be due to the fact that the packing parameter is determined only from the geometrical data of a surfactant molecule in the crystalline state and the effect of the conformational change of a surfactant molecule upon micellization is not taken into account in the calculations.

Recently, we have already demonstrated in our Raman scattering study of surfactants [30], which measured the concentration dependence of the accordion band
intensity, that a conformational change of surfactant molecules occurs upon micellization. Furthermore, we have confirmed that there is a dependence of the conformational preference about the P-O bonds upon the extent of hydration in di-n-alkyl phosphate-water systems [31]. Thus, micellization brings about preferential stabilization of a specific rotational isomer. For a new-born micelle, the rigidity of the stabilized specific conformation may be not so great, since such a micelle has a small aggregation number. Application of the theory may therefore no longer be applicable. However, the rigidity of a specific conformation increases with an increase in aggregation number. That is, micellar growth may promote preferential stabilization of a conformation similar to that which occurs in the solid state. Therefore, for grown-up micelles we may apply the theory for prediction of the micellar shape.
7-4. Conclusion

Double-headed surfactants in which two quaternary ammonium species \((\text{C}_{10}\text{H}_{21}\text{N}^+\text{(CH}_3)_2)\) are linked at the level of the head groups by a hydrocarbon spacer \((\text{(CH}_2)_n, n_s = 2, 3, 4, 6 \text{ and } 8)\) have been synthesized. For the dimeric surfactant-water systems, the free energies \((\Delta G^0)\) of micellization were calculated from the CMC and the degree of ionization determined by specific electrical conductivity measurements. The \(\Delta G^0\) vs. \(n_s\) plots yielded two straight lines in which the slopes \((\delta\Delta G^0/\delta n_s)\) are equal to the free energy of transfer of a spacer methylene unit from the bulk-phase to the micelle. It has been found that free energy per spacer methylene unit strongly depends upon the chain length of the spacer.

The microstructure and growth of a micelle in the dimeric surfactant-water systems have been studied by SANS spectra. It has been found that the aggregation number of the micelles strongly depends on the length of the spacer methylene chain. Moreover, the aggregation number of a minimum micelle has been found to be almost independent of the spacer chain length. This fact reveals that the main chains of the dimeric surfactant DS molecules play an important role in formation of a minimum micelle.

Furthermore, it has been assumed that both micellar growth and spherical to prolate shape transition occur with an increase in micellar concentration and strongly depend on the spacer chain length. In particular, we may stress that growth of the micelle occurs markedly for DS molecules with \(n_s = 2\) and gradually becomes smaller in extent with an increase in \(n_s\) value, reaching almost zero at \(n_s = 6\). Thus, it may be concluded that an increase in spacer chain length prevents growth of DS micelles in water.
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   103.


    1987, 120, 245.

    308.

    1985, 22, 10.


    London; 1992; Chapter 17.
Chapter 8.

Conclusion

In this study, two different types of surfactant molecule were used, in order to discuss the effect of the characteristic packing parameters \( \nu / a_0 l_c \) on the aggregate structure and the phase structures. One of them is a series of identical and mixed-chain di-\( n \)-alkyl phosphates and the other is a series of bis(quaternary ammonium bromides). The conclusions are summarized as follows.

1. For a series of identical and mixed-chain di-\( n \)-alkyl phosphates, the di-\( n \)-pentyl (DPP), \( n \)-butyl(\( n \)-hexyl) (BHP), \( n \)-propyl(\( n \)-heptyl) (PHP) and ethyl(\( n \)-octyl) (EOP) phosphates, with characteristic packing parameters equal to 0.50, 0.43, 0.37 and 0.33, respectively, were focused. The results of differential scanning calorimetry, \(^{31}\)P NMR and x-ray low angle diffraction, indicate that the stability of the aggregate structure in the lamellar phase increases in the order Li(EOP) < Li(PHP) < Li(BHP) < Li(DPP).

2. The phase diagram of the Na(DPP)-water system consisting of five regions (I, II, III, IV and V) has been determined. The phase structure has been investigated by \(^1\)H pulsed-gradient NMR self-diffusion, \(^{31}\)P NMR and x-ray low angle diffraction methods. The results are summarized as follows. In region I, there exist two critical micelle concentrations (CMC), indicating that this region is in a monomer-micelle equilibrium and that variation in the aggregated state occurs at the second CMC. Region II is a two phase area in which regions I and IV coexist. In region III, hydrated crystals and an aqueous solution of Na(DPP) coexist. Region IV is a homogeneous, transparent and fluid phase and the results of \(^{31}\)P NMR spectra and x-ray diffraction patterns reveal the formation of a highly organized structure, similar to a lamellar-like structure. Region V is a homogeneous, transparent and fluid phase and the self-diffusion coefficient value and \(^{31}\)P NMR spectra show that its phase structure is very similar to that for the concentrated.

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sample in region I.

3. For anhydrous Na(BHP) in the solid state and the Na(BHP)-H2O system in the lyotropic liquid crystalline and coagel states, the Raman scattering spectra arising from the accordion vibrational mode were studied in the temperature range -170 ~ 25 °C. For anhydrous Na(BHP), the GG form about the phospodiestor P-O bonds was preferentially stabilized at lower temperature. In the coagel phase of Na(BHP)-H2O system, preferential stabilization of a specific conformation about the P-O bonds occurred and the species of stabilized molecular form was dependent on the water content: for the 8:2 Na(BHP)-H2O sample in the coagel the GT form was stabilized, while for the 7:3 Na(BHP)-H2O coagel sample the TT form was preferentially stabilized. The stabilization of such a specific conformation was also reflected in the higher frequency region. These results showed that the stability of conformation about the P-O bonds depends on the extent of hydration of the PO4− group and on the temperature.

4. Small angle neutron scattering (SANS) has been used to elucidate the size and shape of a micelle in the Na(DPP), Li(EOP) and Ba(EOP)-water systems. The results are summarized as follows: For the Na(DPP) micelle, the aggregation number (n) depends on the concentration (n = 12 at 7.0 wt% and n = 15 at 10.0 wt%). The minimum micelle is spherical and has an aggregation number n = 7. It has been found that the micelles of barium EOP in water have the shape of a prolate spheroid and aggregation numbers (n) equal to 48 at 23 °C and 52 at 50 °C. For the Li(EOP)-micellar system, it has been found that the minimum micelle with an aggregation number n = 21. For this micellar system, it can be assumed that micellar growth and variation from the spherical to prolate shape occurs with an increase in concentration above the CMC.

5. The microstructure of the self-assembly systems, formed by dimeric surfactants in which two quaternary ammonium species (C_{10}H_{21}N^+(CH_{3})_2) are linked at the polar head groups by a hydrocarbon spacer ( (CH_{2})_{n_s} , n_s = 2, 3, 4 and 6), has been investigated by SANS. The SANS analysis showed that the extent of growth and the
variation of shape of the dimeric surfactant micelles strongly depend on the spacer chain length. In particular, it has been found that for the dimeric surfactant with a short spacer ($n_s = 2$) both micellar growth and shape variation are more pronounced, while for the surfactant with a long spacer ($n_s = 6$) the extent of micellar growth and shape variation becomes very small. We stress that an increase in spacer chain length, within the range of $n_s = 2 \sim 6$, hinders the growth of the micelles formed by the dimeric surfactants in water.

The conclusions 1 $\sim$ 5 suggest that there is a close relationship between the molecular conformation, the characteristic packing parameter, the aggregate structure and the phase structure of aqueous micelles.
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