A small-angle neutron scattering study of the ethyl (n-octyl) phosphate micelles in water

**Summary** Mixed-double chain anionic surfactants, barium- and lithium-salts of ethyl(n-octyl) phosphate (EOP), which are asymmetric in the molecular shape, and a series of identical chain di-n-alkyl phosphate lithium salts have been synthesized. The limiting partial molar volume of a PO₂ group (23.43 ± 0.41 cm³ mol⁻¹) for use in small-angle neutron scattering analysis was determined by density measurements of a series of identical chain di-n-alkyl phosphate lithium salts. For lithium EOP-D₂O system, a critical micellar concentration (2.3 wt%) was determined by ³¹P NMR spectra. The micellar shape and size in the EOP-water binary system has been investigated by using small-angle neutron scattering (SANS) spectra. 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 lithium EOP-micellar system, it has been found that the minimum micelle with an aggregation number n = 21 is spherical and micellar growth and variation from the spherical to the prolate shape might occur with an increase in concentration above the CMC.

**Key words** Ethyl(n-octyl) phosphate – micelle – SANS

**Introduction**

The type and structure of an aggregate formed by different surfactant molecules depend on their geometrical packing properties [1], which can be represented by the characteristic packing parameters of a given surfactant molecule. For surfactant molecules of optimal area a₀, hydrocarbon volume v and critical chain length L₀, Israelachvili et al. [1] have shown that the value of the packing parameter (v/a₀ L₀) determines the shape of an aggregate. A packing property can be easily changed by many factors such as ionic environment, temperature, polar-group size, length and unsaturation of a hydrocarbon chain [2–7]. Therefore, in order to discuss the quantitative details of the relationship between the geometrical packing property of a surfactant molecule and factors affecting the aggregate structure, further systematic studies on the molecular design and synthesis of a surfactant molecule and the aggregate structure are essential.

We have synthesized the lithium salts of ethyl(n-octyl) phosphate, n-propyl(n-heptyl) phosphate and n-butyl(n-hexyl) phosphate, and the phase diagrams and phase structures of these double chain surfactant-water systems have been determined [8]. 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(n-octyl) phosphate (EOP) in water, the phase diagram and phase structure has been determined [9, 10]. In particular, self-diffusion coefficient vs. inverse concentration plots could be explained by a simple two-site model and a single monomer = micelle equilibrium [11, 12], and provided the CMC value which was in good agreement with that determined by $^3$P NMR chemical shift vs. inverse concentration plots [9]. 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 behaviour [10]. Moreover, the conformation of EOP anions in EOP-water system has been investigated by $^3$C NMR, infrared and Raman spectroscopic methods [9, 13]. However, shape and size of an EOP micelle remains unresolved.

EOP anion

Techniques available for structural determination of micellar shape and size in aqueous solutions include quasi-elastic light scattering, small-angle x-ray scattering (SAXS) and small-angle neutron scattering (SANS). Of these, SANS can provide not only size information but more detailed structural information on individual regions of the aggregate. Therefore, SANS has been used successfully to determine the structure of anionic and cationic surfactant micelles [14–17].

In the present paper, the aggregate structures formed by barium- and lithium-salts of EOP in water are discussed in detail, using SANS and their analyses.

**Experimental**

**Materials**

Barium Ba(EOP) and lithium Li(EOP) salts of ethyl(n-octyl) phosphate (EOP) were prepared as follows. Ethylphosphorodichloridate (C$_2$H$_4$OP(O)Cl$_2$, b.p. 65–67°C at 25 mmHg), prepared using phosphoryl chloride and ethyl-alcohol and vacuum-distilled, was converted to ethyl(n-octyl) phosphorochloridate ((C$_2$H$_5$O)(C$_8$H$_{17}$O)P(O)Cl) [18]. The (C$_2$H$_5$O)(C$_8$H$_{17}$O)P(O)Cl sample was vacuum-distilled several times (b.p. 121–123°C at 4 mmHg) and was treated with benzaldehyde (Furuka Chemie AG) by the method of Mukaiyama et al. [19], to yield phosphoric acid ethyl(n-octyl)ester, (C$_2$H$_5$O)(C$_8$H$_{17}$O)PO(O)H. Phosphoric acid ethyl(n-octyl)ester was then neutralized with aqueous solutions of barium or lithium hydroxide.

Products were analyzed by $^1$H and $^{13}$C NMR and by elemental analysis. Anal. C$_{20}$H$_{44}$O$_5$P$_2$Ba: Calcd: C, 39.26; H, 7.25; Found: C, 39.12; H, 7.29; C$_{19}$H$_{32}$PO$_4$Li: Calcd: C, 49.18; H, 9.08; Found: C, 48.86; H, 9.25.

A series of identical chain di-n-alkyl phosphate lithium salts ((C$_2$H$_4$(CH$_2$)$_n$O)$_2$PO$_7$Li, $n = 0, 1, 2, 3, 4$ and $5$; Li$^+$ (R-O)$_2$PO$_7$) was similarly prepared using phosphoryl-chloride 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.

**Molar volume determination**

The apparent molar 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 DDA 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 $\Phi_{app}$ may then be calculated from the density ($d$, g cm$^{-3}$) of the solution using:

$$\Phi_{app} = \frac{1}{m} \left[ \frac{1000 - mM}{d} - \frac{1000}{d_s} \right],$$

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

**$^{31}$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 $^3$P chemical shifts ($\sigma$) of the EOP anions in D$_2$O solution were measured relative to the $^3$P signal of aqueous 85%-H$_3$PO$_4$ solution as an external reference.

**Neutron scattering measurements**

The small-angle neutron scattering (SANS) measurements were carried out by small- and medium-angle neutron