A New Type of Water Insoluble Surfactant: Molecular Aggregation of Long Chain Phosphonium Salts ($Ph_3P^+\text{-}CH_2CH_2R,I^-$; R = alkyl or fluoroalkyl) in Formamide

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The molecular aggregations of various water insoluble substituted phosphonium salts ($Ph_3P^+\text{-}CH_2CH_2R,I^-$; R = C_4H_9, C_6H_{13}, C_8H_{17}, C_4F_9, C_6F_{13}, or C_8F_{17}) are compared and the results show that the salts have surfactant properties.

Molecular aggregation phenomena in structured non-aqueous solvents have received little attention compared to the number of investigations carried out in water. Molecular aggregation of some surfactants (*e.g.* sodium dodecyl sulphate and cetyltrimethylammonium bromide) has been compared in water and solvents such as formamide.[1] We have demonstrated recently that microemulsions [defined as transparent dispersions of water, oil, and amphiphile(s)[2]] can be prepared in formamide instead of water.[3,4] We have shown that formamide, in contrast to water, solvates large ions preferentially.[4]

We have have therefore carried out a study of molecular aggregation of large ions which are insoluble in water, but which can aggregate in formamide. We chose the long chain substituted phosphonium salts (**2**), which were prepared by heating triphenyl phosphine and various alkyl or fluoroalkyl iodides† (**1**) to 95 °C in the absence of solvent [equation (1)].

$$\mathrm{Ph_3P + ICH_2CH_2R \xrightarrow{95\,°C} Ph_3P^+\text{-}CH_2CH_2R,I^-} \qquad (1)$$

(**1**) (**2**) Yields = 60—90%

a; R = C_4F_9
b; R = C_6F_{13}
c; R = C_8F_{17}
d; R = C_4H_9
e; R = C_6H_{13}
f; R = C_8H_{17}

The phosphonium salts (**2**) were identified by ^1H, ^{13}C, and ^{19}F n.m.r. spectroscopy and by elemental analysis. These compounds are insoluble in water even at high temperatures. They are soluble, however, in formamide, and micellisation was observed by conductimetry.‡ The plots of conductance *vs.* concentration for compounds (**2**) show a sharp change in slope at a given concentration. We considered this to be the point of micelle formation (Figure 1).§

It is noteworthy that the form of discontinuity shown in Figure 1 is not the usual form obtained for micellar aggregation in water. This phenomenon is probably due to the fact that micellar aggregation in formamide is different to that in water. In formamide, with its high dielectric constant (ε = 110), the micelles are probably more dissociated than in water (ε = 80) and so the conductivity increases beyond the critical micelle concentration (c.m.c.). We are now undertaking a study of this phenomenon.

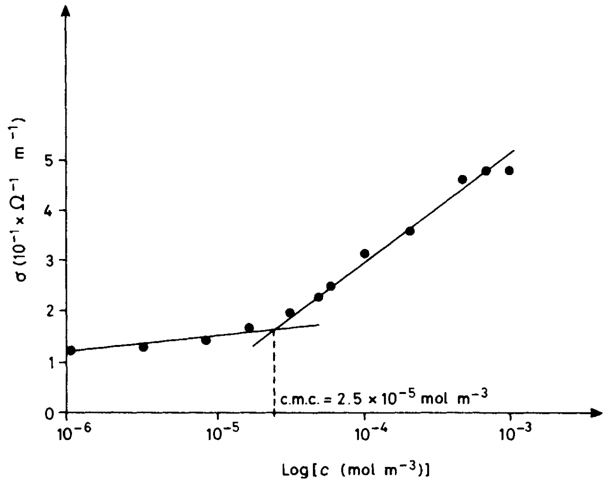

Figure 1. Specific conductance (σ) *vs.* concentration (c) at 64 °C for formamide solutions of (**2c**).

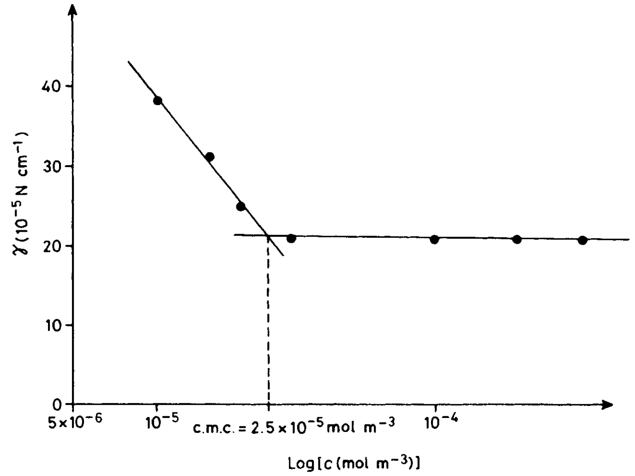

Figure 2. Surface tension (ν) *vs.* concentration (c) at 64 °C for formamide solutions of (**2c**).

However, measurement of surface tension also shows a sharp change at the same concentration (Figure 2).‡ In this case, the form of discontinuity is as is usual for micellar aggregation and indicates the tensioactive properties of the molecules.

The yields and c.m.c.s for the different derivatives (**2**) are shown in Table 1. The results indicate the following: as in the

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† We are grateful to Atochem for supplying the fluoroalkyl iodides.

‡ Conductivity measurements were carried out at 64 °C using a Tacussel CD 6N-G conductimeter (the Krafft points of the derivatives were around 60 °C). Surface tension measurements were carried out at 64 °C using a Prolabo tensiometer (Tensimat n3) with the ring detachment method.

§ The breaks in slope were clear cut, and gave the values of the c.m.c.s (an example is shown in Figure 1). Extrapolation led to a 5% uncertainty in the c.m.c. values. It should be pointed out that the exact nature (true spheres or otherwise) of the aggregates obtained is not known. Morphological studies would be required to provide this information.

Table 1. Characteristics of compounds (**2**).

Compound	Yield (%)	C.m.c. (mol dm^{-3})
(**2a**)	85	0.034
(**2b**)	88	0.030
(**2c**)	60	0.025
(**2d**)	90	0.030
(**2e**)	90	0.022
(**2f**)	90	0.019

case of classical surfactants in water, the c.m.c. decreases with increasing chain length, for both alkyl and fluoroalkyl compounds. In formamide however, the fluorinated compounds have higher c.m.c.s than their alkyl homologues. The reverse is found in water, where the long chain fluorinated compounds have markedly lower c.m.c.s than their alkyl homologues (up to 1.5 times lower for perfluorinated derivatives[5]). The differences are due to the increased hydrophobic nature of the fluorinated compounds.

It would appear from our results that the fluorinated derivatives are considerably less 'solvophobic' in formamide than in water. We have demonstrated for the first time surfactant properties of water insoluble molecules in a structured non-aqueous solvent (formamide) and hence have shown the general nature of the micellisation phenomenon.

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