NOTE

Surface-Tension Properties of Novel Phosphocholine-Based Fluorinated Surfactants

Surface- and interface-tension properties of novel fluorinated surfactants containing a phosphocholine group were studied using the Wilhelmy and spinning-drop methods. Using a conventional cationic fluorinated surfactant, we found that the values coming from the Wilhelmy method are not always accurate due to the effect of the wetting angle. The novel fluorinated surfactants show high surface activity not only in water but also in organic solvents such as _m_-xylene and methanol. They seem to be more effective in reducing the surface tension at low pH values. The novel fluorinated surfactants are also effective in reducing the interfacial tension between water and hydrocarbon oil. © 2001 Academic Press

Key Words: **surface tension; spinning-drop method; fluorinated surfactants.**

INTRODUCTION

Fluorinated surfactants cause the largest reduction in the surface tension of water due to the very weak cohesive energy of the fluorocarbon chain (1). Fluorinated surfactants also show surface activity in organic solvents (2–4). Mainly anionic (5), cationic (6), and nonionic (7, 8) fluorinated surfactants have been synthesized but little has been reported concerning zwitterionic or amphoteric fluorinated surfactants. Among amphoteric head groups phosphocholine is very important because of its role as a component of phospholipids such as lecithin. However, phosphocholine has not been used as a head group in fluorinated surfactants.

The Wilhelmy method is widely used to measure the surface tensions of aqueous surfactant solutions. However, since a platinum or glass plate is needed for the measurement, results are often affected by the wetting of the plate with solution. If the contact angle is not negligibly low, the measured surface tension becomes lower than the real value. Since cationic and amphoteric surfactants have a positive charge while the surface of the plate is negatively charged, the contact angle is often large and the surface tension cannot be accurately measured.

The spinning-drop method is widely used to measure low liquid–liquid interfacial tensions, based on the change in the radius of a droplet with the velocity at which it is rotated. If, instead of a liquid drop, an air bubble is introduced into the capillary filled with surfactant solution, the air–liquid surface tension can be measured, as the obtained value does not depend on the contact angle. Since the surface tensions of surfactant solutions are usually above 25 mN/m, a high velocity of rotation is needed for the measurement, making the use of the spinning-drop method difficult. However, the surface tensions of fluorinated surfactant solutions can reach 15 mN/m, facilitating the use of the spinning-drop method.

In this context, we measured the surface tensions of solutions of new fluorinated surfactants having phosphocholine as a head group using both Wilhelmy and spinning-drop methods.

MATERIALS AND METHODS

The molecular structures of the new fluorinated surfactants, designated as T-1 and T-2, are shown in Fig. 1. T-1 was synthesized according to Scheme 1.

Acetonitrile was removed from the reaction product by evaporation and the concentrate was dissolved in tetrahydrofuran. The solution was treated with gel C-200 to adsorb T-1. C-200 was dissolved in methanol and then T-1 was recovered by evaporating the solvent.

T-2 was obtained as illustrated in Scheme 2.

As in the case of T-1, acetonitrile was removed from the reaction product by evaporation and the concentrate was washed with diethylether. The solvent was removed by drying under vacuum to obtain T-2.

A cationic fluorinated surfactant, $C_8F_{17}SO_2NHC_3H_6N^+(CH_3)_3I^-$, designated EF-132, was obtained from Mitsubishi Materials Co.

Surface-tension measurements were carried out at 25°C using a Wilhelmy type CBVP-Z surface balance with a $23.85 \times 52 \times 0.15$ mm platinum plate (Kyowa Interface Science, Japan) and using a spinning-drop tensiometer Site 04 (Krüss GmbH, Germany) with a speed range of 0–10,000 rpm. In the latter case, the surface tension was obtained with Vonnegut's equation,
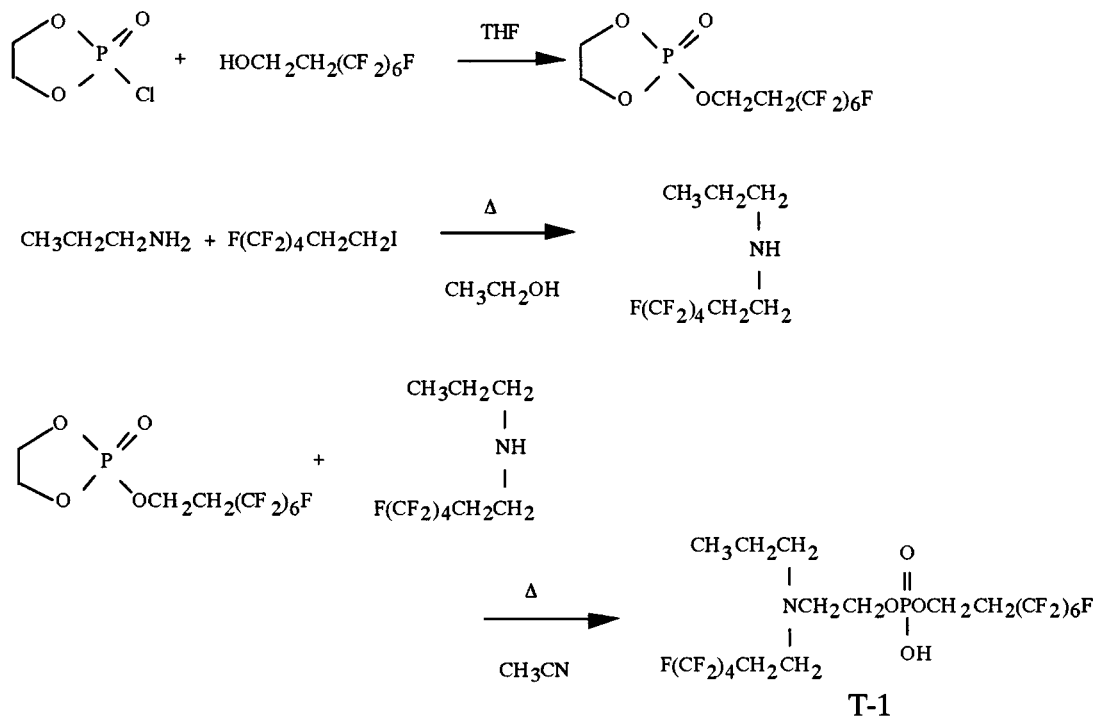
$$\gamma = \Delta\rho\omega^2 r_o^3, \qquad [1]$$

where γ is the interfacial tension, $\Delta\rho$ is the density difference between air and the surfactant solution, ω is the angular velocity, and r_o the radius of a cylindrical bubble.

Double-distilled water was used in the preparation of the samples.

RESULTS AND DISCUSSION

Experimental values for surface tension γ versus the logarithm of surfactant concentration in aqueous solutions of EF-132 are shown in Fig. 2a. It can be seen that the minimum values obtained using the Wilhelmy plate method are, although reproducible, smaller than that corresponding to the spinning-drop method, which suggests that the surfactant solution is not wetting the platinum plate properly (contact angle larger than zero). Therefore, the values coming from the spinning-drop method are more reliable since they are independent on the contact angle. It is thought that very low surface tensions previously reported for fluorinated surfactants (4, 9) might be misleading due to the use of the Wilhelmy plate method. It is known that the cohesive energy for –CF$_2$– is about 15 mN/m while that of –CF$_3$– is about 6 mN/m (10). Since EF-132 has many –CF$_2$– groups in its hydrophobic chain, the expected minimum surface tension is around 15 mN/m.

Surface-tension results for T-1 and T-2 are shown in Fig. 2b. The curve corresponding to T-1 show a break point indicating the formation of aggregates at the critical micelle concentration, whereas for T-2, γ monotonically decreases with no discontinuity until a macroscopic phase separation occurs. This separation corresponds to the precipitation of vesicles, as it was observed by optical microscope.
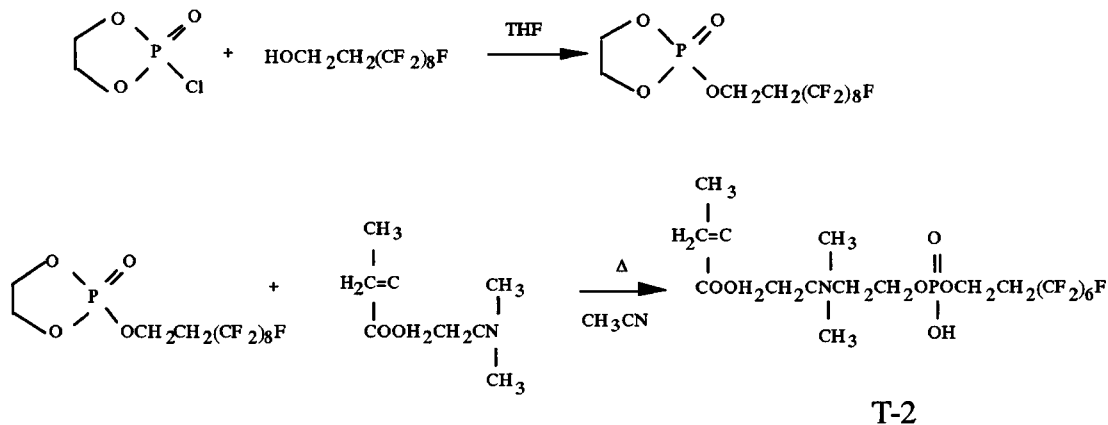
SCHEME 1

Reaction 1:

$$\text{(cyclic phosphate-Cl)} + HOCH_2CH_2(CF_2)_6F \xrightarrow{THF} \text{(cyclic phosphate-}OCH_2CH_2(CF_2)_6F)$$

Reaction 2:

$$CH_3CH_2CH_2NH_2 + F(CF_2)_4CH_2CH_2I \xrightarrow[CH_3CH_2OH]{\Delta} \begin{array}{c} CH_3CH_2CH_2 \\ | \\ NH \\ | \\ F(CF_2)_4CH_2CH_2 \end{array}$$

Reaction 3:

$$\text{(cyclic phosphate-}OCH_2CH_2(CF_2)_6F) + \begin{array}{c} CH_3CH_2CH_2 \\ | \\ NH \\ | \\ F(CF_2)_4CH_2CH_2 \end{array} \xrightarrow[CH_3CN]{\Delta} \begin{array}{c} CH_3CH_2CH_2 \quad\quad O \\ | \quad\quad\quad\quad || \\ NCH_2CH_2OPOCH_2CH_2(CF_2)_6F \\ | \quad\quad\quad\quad | \\ F(CF_2)_4CH_2CH_2 \quad OH \end{array}$$

T-1

THF=tetrahydrofuran

The values of surface tension obtained at high surfactant concentrations using both Wilhelmy and spinning-drop methods are similar; therefore, we consider the values coming from the Wilhelmy accurate. Judging from the slope of the curves in Fig. 2b, adsorption of T-1 on the liquid–air surface seems more effective than that of T-2. It can be attributed to the higher lipophilicity of T-1, which bears two fluorocarbon chains. The minimum value for γ (approximately 15 mN/m) is similar to that found in other fluorinated surfactant systems (11).

Figure 3 shows variation of surface tension with concentration for T-1 in m-xylene. The solubility of T-2 in m-xylene is very low; therefore, no measurements were carried out in this system. The curve shows a break point at a specific concentration, resembling the critical micelle concentration. The minimum in surface tension is around 18 mN/m, giving a surface pressure of 5.3 mN/m. The ratio of the slopes of the lines, according to the Gibbs' equation, is proportional to the ratio of the surface excess of T-1 in water and m-xylene. It is evident that the adsorption of T-1 molecules at the solvent–air interface is much higher in aqueous medium than in nonaqueous medium.

Figure 4 shows the surface tension curves in methanol solutions. The surface tension does not change significantly on addition of T-1, but addition of T-2 reduces the surface tension to approximately 15 mN/m. This is a remarkable result, since the surface tension of pure methanol is very low and it is difficult
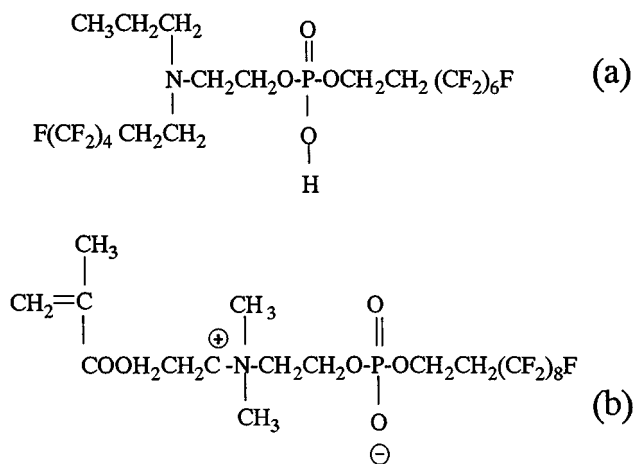
SCHEME 2

$$\text{(cyclic phosphate-Cl)} + HOCH_2CH_2(CF_2)_8F \xrightarrow{THF} \text{(cyclic phosphate-}OCH_2CH_2(CF_2)_8F)$$

$$\text{(cyclic phosphate-}OCH_2CH_2(CF_2)_8F) + \begin{array}{c} CH_3 \\ | \\ H_2C=C \quad\quad CH_3 \\ | \quad\quad | \\ COOH_2CH_2CN \\ | \\ CH_3 \end{array} \xrightarrow[CH_3CN]{\Delta} \begin{array}{c} CH_3 \\ | \\ H_2C=C \quad CH_3 \quad O \\ | \quad\quad | \quad\quad || \\ COOH_2CH_2CNCH_2CH_2OPOCH_2CH_2(CF_2)_6F \\ | \quad\quad | \\ CH_3 \quad OH \end{array}$$

T-2

THF=tetrahydrofuran

FIG. 1. Molecular structure of surfactants: (a) T-1, (b) T-2.

TABLE 1
**Change in Surface Tension in 1 g/L Solutions
of T-1 as a Function of pH**

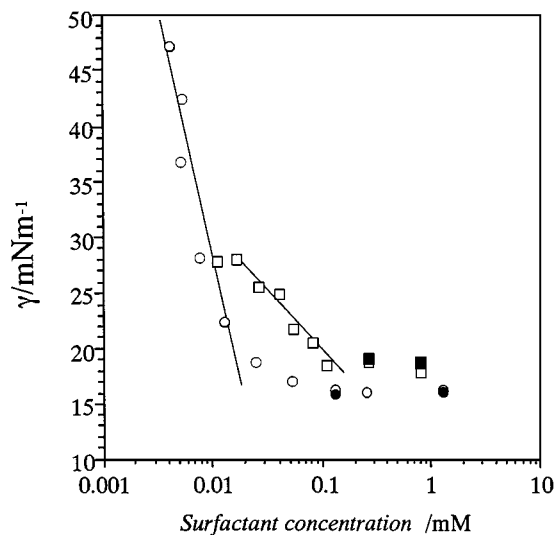| pH	γ (mN/m)
1.9	15.5
4.2	16.3
8	16.6
9	16.9
11.9	18.2

FIG. 3. Surface tension γ vs the logarithm of surfactant concentration in solutions of T-1 in m-xylene ($\square$, $\blacksquare$) and water ($\bigcirc$, $\bullet$). The lines are the best linear fit for the points before the breaking point. Filled symbols indicate values measured using the spinning-drop method.
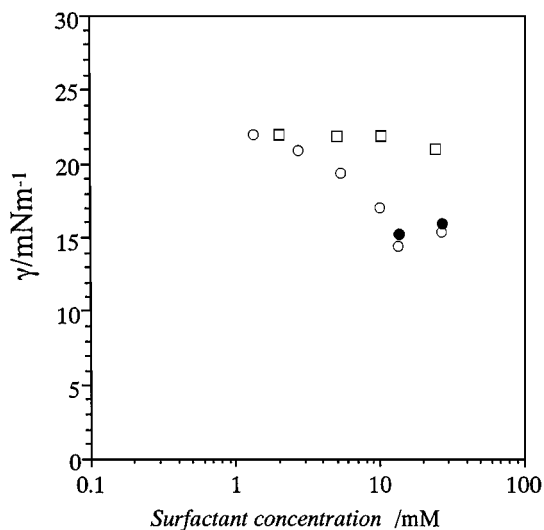

FIG. 2. Surface tension γ vs the logarithm of surfactant concentration in aqueous solutions of fluorinated surfactants: (a) EF-132 ($\blacklozenge$, $\diamondsuit$), (b) T-1 ($\square$, $\blacksquare$) and T-2 ($\bigcirc$, $\bullet$). Filled symbols indicate values measured using the spinning-drop method.

FIG. 4. Surface tension γ vs the logarithm of surfactant concentration in methanol solutions for T-1 ($\square$) and T-2 ($\bigcirc$, $\bullet$). Filled symbols indicate values measured using the spinning-drop method.

TABLE 2
Interfacial Tension between a 2 g/L Aqueous Solution of T-1 and Different Oils ($\gamma_{w/o}$) and Spreading Coefficient (S)

Oil	$\gamma_{w/o}$ (mN/m)	S (mN/m)
Octane	4.5	0.6
Decane	6.8	0.6
m-Xylene	6.2	6.1

to diminish the surface tension of such organic solvents. In general, surfactants show very low surface activity when dissolved in alcohols.

Values of γ as a function of pH for T-1 are shown in Table 1. The surface tension increases with pH, indicating that the adsorption is less effective as the dissociation of the anionic head group increases (high pH).

Table 2 shows the interfacial tension between an aqueous solution of T-2 and different kinds of oils. The spreading coefficient S is defined as $S = \gamma_{a/o} - \gamma_{w/o} - \gamma_{a/w}$, where the subscripts a, o, and w indicate air, oil, and surfactant aqueous solution, respectively. It can be seen that S is positive for all the oils and is particularly large for m-xylene, indicating that the surfactant solution can spread ("float") over the m-xylene surface (12), as we have, in fact, confirmed.

CONCLUSION

The new fluorinated surfactants studied adsorb strongly at the air–liquid interface, causing the surface tension to decrease significantly even in organic solvents or in extreme pH conditions.

The spinning-drop method is a reliable measure of the surface tension in fluorinated surfactant systems.

The novel amphoteric surfactants have the ability to spread over organic liquids, similarly to other fluorinated surfactant systems.

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