Effects of pH on Foam Stability of Dimethyldodecylamine Oxide and N-dodecyl-2-aminopropionic Acid in Aqueous Solutions

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ABSTRACT

Foam stability of aqueous solutions of dimethyldodecylamine oxide (DMAO) and N-dodecyl-2-aminopropionic acid (DAPA) has been studied in relation to pH by means of the dynamic method. The foam of DMAO solution is stabilized in the acidic pH region, while with the DAPA solution, the foam is stable in either the acidic or basic pH range and unstable between them. The results suggest that the foam stability of the solutions of these two surfactants is governed by the formation of ionic species of the surfactants. It can be presumed that the adsorption of the ionic species of the surfactant molecules at the surface of foam films establishes an electric double-layer which makes the foams stable.

INTRODUCTION

A number of workers have investigated the physicochemical properties of the liquid thin films formed by aqueous solutions of ionic surfactants (1-6). The results obtained from their studies show that the stability or an equilibrium thickness of the liquid film is determined by a balance between double-layer repulsion given by the adsorbed surfactant molecules and attractive forces which arise from hydrodynamic pressure and van der Waals attraction (6). This idea for the thin liquid films can be, of course, applied to the foam stability of aqueous surfactant solutions. On the other hand, it is well known that the ionic form of dimethyldodecylamine oxide and N-dodecyl-2-aminopropionic acid molecules is changeable in aqueous solutions depending on pH (7-11). Thus, it is interesting, in these points of view, to study the foam stability of these surfactants in relation to pH of the solutions. In the present work, the relationship between foam stability of aqueous solutions of these two surfactants and the pH values of the solutions has been studied.

MATERIALS AND METHODS

Dimethyldodecylamine oxide (DMAO) was prepared by H_2O_2 oxidation of dimethyldodecylamine (7,12) which was shown to be 96% pure by gas chromatography. The crude product was purified by recrystallization three times from an acetone-benzene mixture. N-dodecyl-2-aminopropionic acid (DAPA) was a kind gift from T. Okumura of our research laboratories and was the same as used in his previous work (11).

The dynamic method (13) was employed to determine the average lifetime of foams. The air thermostated and saturated with water vapor was bubbled from a single glass orifice into a sample solution which was present in a graduated glass foaming tube. The rate of air flow was controlled with a needle bulb. A steady state was obtained within several tens of minutes after air injection starts. The foam volume at the steady state was proportional to the rate of air flow which was below 50 ml/min. The proportional constant, τ, gives an average lifetime of the foam (13). The foaming tube was maintained at 30 C by circulating thermostated water. The pH of the sample solutions was adjusted with hydrochloric acid and was determined with Horiba type N-5 pH meter at 30 C.

RESULTS

Figures 1 and 2 show some examples of τ vs. pH curves of DMAO and DAPA solutions containing 0.1 M NaCl, respectively. The foam of DMAO solution is abruptly stabilized at a definite pH value which depends on the concentration of DMAO. On the other hand, in the case of DAPA, the foam is stabilized at both higher and lower pH regions. These results strongly suggest that the ionic nature of DMAO and DAPA in aqueous solutions governs the stability of their foams.

DISCUSSION

The thinning of liquid film takes place spontaneously by the attractive force between two surfaces of the liquid film which arises mainly from gravity and capillary suction (6). The liquid film is, therefore, unstable without any resistance against the spontaneous thinning. Electrical double-layer repulsion gives the opposing force to resist the thinning in ionic surfactant solutions (1-6). In the case of DMAO and DAPA solutions, the double-layer repulsive force in the liquid film should depend upon the pH of the solutions because of the following equilibria (7-11).

$$RN(CH_3)_2O \xrightleftharpoons{H^+} RN(CH_3)_2OH^+ \qquad \text{(I)}$$

$$RNHCH_2CH_2COO^- \xrightleftharpoons{H^+} R\overset{+}{N}H_2CH_2CH_2COO^- \xrightleftharpoons{H^+} R\overset{+}{N}H_2CH_2CH_2COOH \qquad \text{(II)}$$

The results shown in Figures 1 and 2 may be ascribed to the above equilibria since the electric double-layer cannot be formed by the nonionic form of DMAO or the zwitterionic form of DAPA.

Suppose the binding process of H^+ ions in bulk phase to DMAO molecules at the surface of the solution is similar to that of Langmuir adsorption, and the degree of ionization or protonation, θ, of the molecules could be related to the concentration of H^+ ion, $[H^+]$, in the bulk phase as Equation (III).

$$\theta = k[H^+]/(1 + k[H^+]) \qquad \text{(III)}$$

where k is a constant. The surface excess of total and protonated DMAO molecules being designated as Γ and Γ_+, respectively, the next equation can be written.

$$\Gamma_+ = \Gamma\theta \qquad \text{(IV)}$$

It is reasonable to assume that the foam of DMAO solution is stabilized when Γ_+ goes up to a just enough amount, $\Gamma_{+,\circ}$, to make the double-layer repulsive force overcome the spontaneous thinning pressure at a definite concentration of H^+ ion, $[H^+]_\circ$. At $[H^+]_\circ$, we obtain Equation (V) from Equations (III) and (IV).

$$\Gamma = (\Gamma_{+,\circ}/k[H^+]_\circ) + \Gamma_{+,\circ} \qquad \text{(V)}$$

The total surface excess, Γ, is related to the concentration, C, of DMAO by the Gibbs adsorption equation.

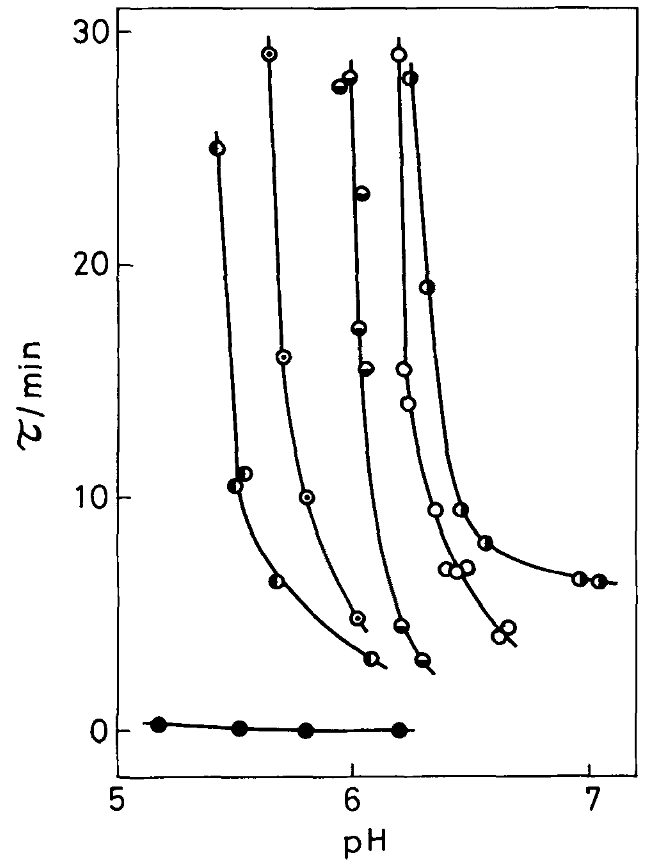

FIG. 1. Average lifetime τ vs. pH curves of DMAO solutions containing 0.1 M NaCl. DMAO concentration; 0.5 mM (●), 0.8 mM (◐), 0.9 mM (◎), 1.0 mM (◒), 2.0 mM (○), and 4.0 mM (◑).

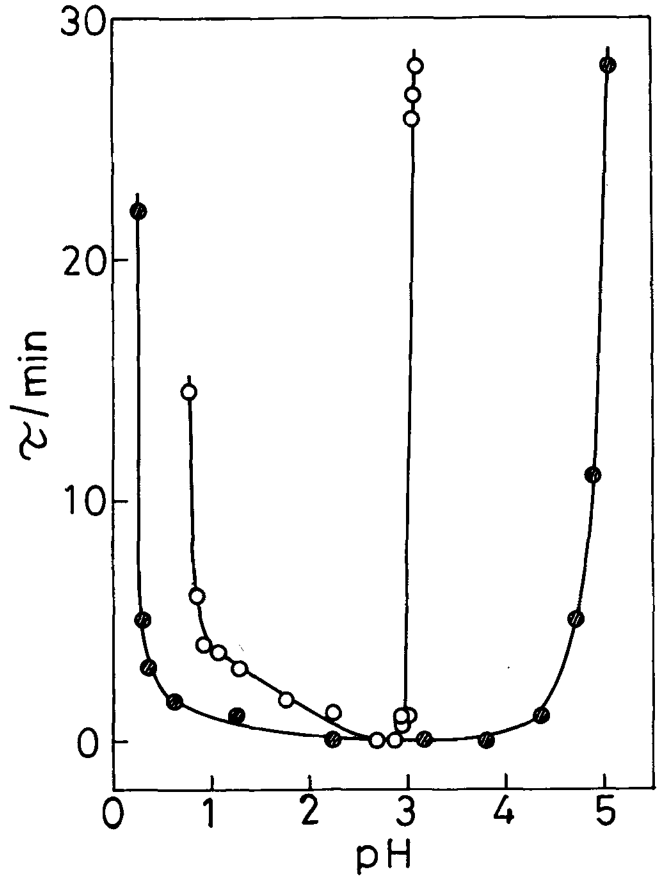

FIG. 2. Average lifetime τ vs. pH curves of DAPA solutions containing 0.1 M NaCl. DAPA concentration; 0.7 mM (●) and 1.0 mM (○).

$$\Gamma = -(1/RT)(\partial\gamma/\partial \ln C) = -(C/RT)(\partial\gamma/\partial C) \qquad \text{(VI)}$$

where γ is the surface tension, R and T are the gas constant and the absolute temperature, respectively. The measured surface tension of the DMAO solutions was related linearly to the concentration in the 0.7 to 1.1 mM region at 30 C. Thus, we obtain the next equation.

$$\Gamma = aC \qquad \text{(VII)}$$

where a (= $-(1/RT)(\partial\gamma/\partial C)$) is a proportional constant and evaluated to be 4.34 x 10^{-4} cm from the surface tension data. Eliminating Γ from Equations (V) and (VII), we obtain

$$C = (C_o/k[H^+]_o) + C_o \qquad \text{(VIII)}$$

where $\Gamma_{+,o}/a$ is rewritten as C_o. Figure 3 shows the C vs. $1/[H^+]_o$ plot obtained from the τ vs. pH curves in Figure 1 taking the concentration of H^+ ion at τ =15 min as $[H^+]_o$. The values of C_o and k can be estimated as 0.73 mM and 2.7 x 10^6 M^{-1}, respectively, from the slope and the intercept of the straight line below 1.1 mM. The break point at 1.1 mM indicates the critical micelle concentration which is in fair agreement with the reported value (7). As is clear from the definition of C_o, the foam of DMAO solutions will never be stabilized at the concentrations below C_o,(=0.73 mM). The data at 0.5 mM in Figure 1 seem to support this conclusion. Incidentally, the surface excess at 0.73 mM can be calculated from Equation (VII) to be 3.2 x 10^{-10}mol/cm^2 which should be compared with the saturated amount of adsorption of sodium dodecyl sulfate; 3.19 x 10^{-10} mol/cm^2 (14), and DAPA; 3.73 x 10^{-10}mol/cm^2 (15).

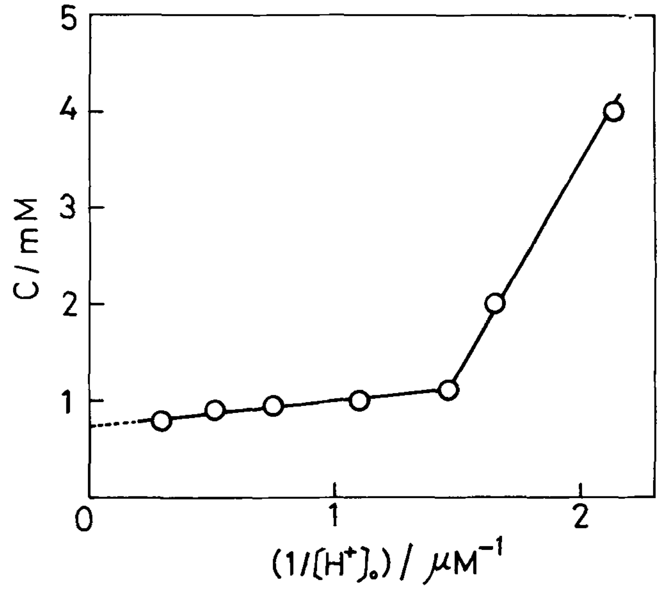

FIG. 3. The C vs. $1/[H^+]_o$ plot for DMAO solutions. Details are in text.

The foaminess of sodium salt of DAPA was measured in relation to pH by Andersen (16) whose data showed a minimum point at pH=4 in the foam volume vs. pH curve. He has proposed that amphoteric surfactants almost always exhibit a marked decrease in foaming in the isoelectric range. Similar minimum point was also observed in aqueous solutions of some proteins presumably because of the amphoteric nature of the proteins (17). The considerations similar to the above may be applicable to the pH dependence of the foam stability of DAPA solutions shown in Figure 2. Foam stabilization at the lower and the higher pH value could be attributed to the protonation of carboxyl group and the deprotonation of amino group of zwitterionic DAPA molecules respectively, although the minimum points in the τ vs. pH curves in Figure 2 disagree with the reported isoelectric point of DAPA, 6.8-7.0 (11). A possible reason for this discrepancy is the difference between pk values of DAPA molecules at the surface and those in bulk phase. When the pH moves from the minimum point, the foam of DAPA solution becomes stable more steeply in the higher pH region than it does in the lower region, which is remarkable especially in 1.0 mM solutions. This might be interpreted as showing that the binding constant k of the protons (see Equation III) to the amino group is different from that to the carboxyl group.

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