Surface Tension of Aqueous Solutions of Disodium Monoalkyl Phosphates and Their Mixtures[1)]

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Disodium mono-dodecyl, mono-tetradecyl, and mono-hexadecyl phosphates were synthesized and the surface tension of aqueous solutions of each disodium monoalkyl phosphate (SAP) and of their mixtures were measured. On the basis of the surface tension values thus obtained, the influence of the hydrocarbon chain length of SAP and the effect of the mixing of SAP on the adsorption and the micelle formation were discussed. A modified Szyszkowski equation was derived from the Gibbs adsorption equation and the modified Langmuir adsorption equation by using the activity instead of the concentration. The modified Szyszkowski equation gave calculated values which were in good agreement with the experimental values of the surface tension. It was also found that the energy of adsorption per methylene group, ω, is 682 cal/mol. In mixed solutions, the modified Szyszkowski equation was used to obtain results in good agreement with the measured values of the surface tension, assuming an ideal mixing of SAP in the adsorption layer. Further, the change in the standard free energy was calculated for the micelle formation for each SAP from the hypothetical standard state of the hydrated monomer in solution; it gave the energy of micelle formation per methylene group, ω_m, is 613 cal/mol. The theoretical equation to give the cmc of SAP, was obtained also, assuming the ideal mixing of SAP in the mixed micelle phase; it was proved to be in good agreement with the experimental values of the cmc.

Disodium monoalkyl phosphates (SAP) are interesting materials because they are bi-valent anionic surfactants, in contradistinction to the anionic detergents extensively used, which are mostly uni-valent. This group of surfactants is interesting also as a model compound of phospholipid because it containes a phosphate group, which might have properties different from many other uni-valent polar groups.

Disodium mono-dodecyl and mono-hexadecyl phospates have previously been synthesized in this laboratory, and the degree of hydrolysis of the ester bond measured. As a result, it has been concluded that the aqueous solution of SAP was very stable, at least, at room temperature.[2,3)] The surface tensions of aqueous solutions of these compounds were measured at various concentrations of added salt, and the adsorption amount of SAP at the air-water interface was calculated by applying the Gibbs adsorption equation. It was shown that S-shaped adsorption isotherms were obtained when the adsorption amount was plotted against the concentration, but Langmuir adsorption isotherms of the usual shape were obtained when the same data were plotted against the activity of SAP in the solutions. Furthermore, it was concluded that the activity at the critical micelle concentration was constant, irrespective of the concentration of the added salt.[4,5)]

In the present paper, the influence of the length of the hydrocarbon chain of SAP on the adsorption and the micelle formation will be discussed on the basis of the surface-tension measurements of aqueous solutions of disodium mono-dodecyl, -tetradecyl and -hexadecyl phosphates (SDP, STP and SHP respectively). The adsorption and the micelle formation of mixtures of SAP will also be discussed on the basis of the surface-tension measurements, the latter being performed in 0.01 M sodium hydroxide in order to diminish the binding of H^+ to the long-chain anion in the solutions.[6,7)] By using the experimental values of the surface tension, the modified Szyszkowski equation which is derived from the Gibbs adsorption equation and the modified Langmuir adsorption equation, using the activity instead of the concentration, are tested. A good agreement between the theory and experiments is obtained. As a result, the saturated adsorption amount and the Langmuir coefficients for each SAP are obtained. The theory is then extended to an aqueous solution of mixed SAP.

Experimental

Synthesis of Monoalkyl Phosphoric Acid and Preparation of the Solution of Disodium Salts. Monoalkyl phosphoric acid is synthesized from pyrophosphoric acid and an alcohol of the corresponding chain length, C_{12}, C_{14} or C_{16} in benzene,

$$\mathrm{ROH+H_4P_2O_7=ROPO(OH)_2+H_3PO_4}$$

where R is a hydrocarbon chain. Alcohol (0.5 mol) and pyrophosphoric acid (0.7 mol) are dissolved in 200 ml of benzene in an Erlenmeyer flask, after which the mixture is allowed to stand for 4 days at room temperature. The benzene is then evaporated, and the viscous liquid produced dissolved in 300 ml of ether. The ether solution is then added to 500 ml of 1.5 M NaOH solution to extract the product, after which the ethereal layer is separated from the aqueous layer. The pH of the aqueous solution, 12.5, is then changed to 0.5 by the addition of concentrated HCl. The monoalkyl phosphoric acid thus precipitated is extracted with 300 ml of ether. The ether is then evaporated, and the crude product is vacuum-desiccated. Recrystallization from hexane gives a white, crystalline product. Found: C, 54.22; H, 10.13; P, 11.59%. Calcd for $C_{12}H_{26}O_4P$: C, 54.14; H, 10.15; P, 11.70%; mol wt, 265.1. Found: C, 57.24; H, 10.50; P, 10.44%. Calcd for $C_{14}H_{30}O_4P$: C, 57.14; H, 10.54; P, 10.54%; mol wt, 293.1. Found: C, 59.73; H, 10.82; P, 9.50%. Calcd for $C_{16}H_{34}O_4P$: C, 59.62; H, 10.87; P, 9.63%; mol wt. 321.1.

The melting points are 58, 68, and 78 °C respectively in good agreement with the values reported in the litetrature.[8)] An aqueous solution is prepared by dissolving a known amount of monoalkyl phosphoric acid in an adequate amount of NaOH solution. In the final solution, an excess of NaOH (0.01 M) should be remained to prevent the hydrolysis of di-valent phosphate.

Surface-tension Measurements. The surface-tension is measured by the capillary-rise method at 25 °C in 0.01 M NaOH as the solvent. The Willhelmy method was also tested, but it gave values which were different not only from those obtained by the capillary-rise method but also from those reported in the literature. Therefore, the capillary-rise method is adopted in this work, because it gave the surface tension values which are in good agreement with the reported values.[9] The values of the surface-tension γ, can be calculated from the ratio of the heights of the meniscus above the surface for the solution (h) to that for pure water (h_0). According to the Sugden theory,[10]

$$\gamma = \gamma_0 \times \frac{h\rho}{h_0\rho_0} \times \left(\frac{b}{b_0}\right)$$

Here, γ_0 is the surface tension of pure water and is 71.96 dyn/cm at 25 °C. (b/b_0) is the ratio of the principal radii at the bottom of the meniscus of the solution to that of pure water, the value is obtained from Sugden's table.[10] In our experiments, (b/b_0) is 1.0013 for the solution which had the lowest surface tension. (ρ/ρ_0) is the ratio of the density of the solution to that of pure water; its value was, at most, 1.01. The capillary is washed in a chromic acid-sulfuric acid mixture for a day. It can thus be confirmed that solutions wet the wall of the capillary very well. The solution was once raised by an air pump and then lowered freely in the capillary; the equilibrium value of the height was then read within 15 min at most. The error in the readings for the solution of the same concentration was less than 1%.

Results

Surface Tension of SAP Solutions. The surface tensions of aqueous solutions of SAP were measured in the presence of surface-inactive electrolytes. The concentration of SAP is expressed by C (in M). In the case of a mixed solution of two kinds of SAP, C is used for the total concentration, while the concentrations of the individual SAPs are expressed by C_1 and C_2, where $C_1+C_2=C$. The sodium-ion concentration from the surface-inactive electrolytes is expressed by C'(M), so that the total sodium-ion concentration in the solution is $(2C+C')$. When the added electrolyte is NaOH only, C' is equal to its concentration, but when NaOH and Na_2SO_4 are added, C' is equal to $[NaOH]+2[Na_2SO_4]$.

The surface tension measured as a function of the logarithm of the SAP concentration, C, at the added sodium-ion concentration, $C'=0.01$ M, is given in Fig. 1 for a solution of disodium mono-dodecyl, -tetradecyl, or -hexadecyl phosphotes. When comparison is made at a constant concentration, the surface tensions of SDP, STP, and SHP are found to decrease with the increase in chain length. The kink point for each curve is considered to be the critical micelle concentration (cmc); the values of cmc thus obtained are given in Table 1.

The surface tensions measured as functions of the total concentration, C, are also given in Fig. 1. These solutions contain SDP and SHP at various mole fractions of mixing. The concentration of SDP is $C_1=CX_1$, and that of SHP, $C_2=C(1-X_1)$. X_1 is the mole fraction of mixing. When comparsion is made at a constant total concentration, C, the increase in X_1 increases the surface tension. In other words, the total concentration needed to give a constant surface tension increases with X_1. At $X_1=0.5$, the total concentration of a mixture is smaller than the concentration of STP for the same surface tension, as is shown in Fig. 2. The kink points are also considered as cmc.

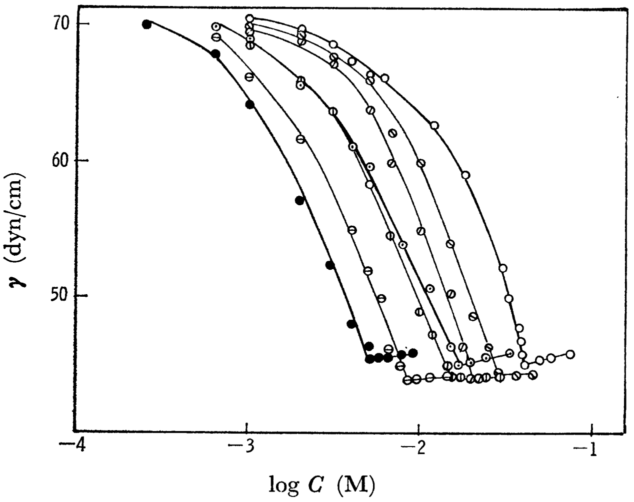

Fig. 1. Surface tension, γ *vs.* log C.
○; SDP, ⊙; STP, ●; SHP, ⦶; $X_1=0.5$, ⊖; $X_1=0.8$, ⊘; $X_1=0.90$, ⦸; $X_1=0.95$. 25 °C, $C'=0.01$ M.

Table 1. The values of the Langmuir coefficient, k, and the critical micelle concentration (CMC)

	k	CMC (M)
SDP	4.5×10^5	4.0×10^{-2}
STP	4.8×10^6	1.7×10^{-2}
SHP	3.3×10^7	6.0×10^{-3}
$X_1=0.5$	—	1.0×10^{-2}
$X_1=0.8$	—	1.5×10^{-2}
$X_1=0.9$	—	2.0×10^{-2}
$X_1=0.95$	—	3.0×10^{-2}

Figure 3 shows the surface tension of an aqueous solution containing SDP and SHP as a function of the concentration of one of them, while the concentration of the other is kept constant. Moreover, both the total sodium-ion concentration, $(2C+C')$, and the ionic strength, J, are kept constant by using a mixture of NaOH and Na_2SO_4 as the added electrolyte. The

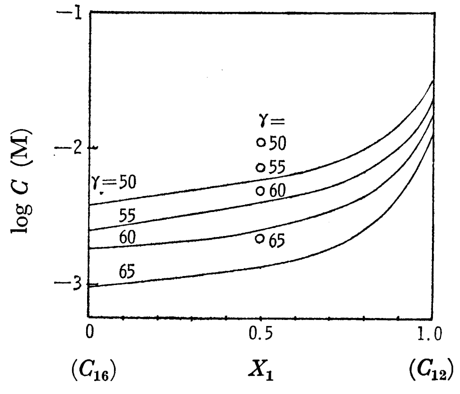

Fig. 2. logarithm of total concentration *vs.* mole fraction of mixing.
The parameter; γ (dyn/cm), ○; STP.

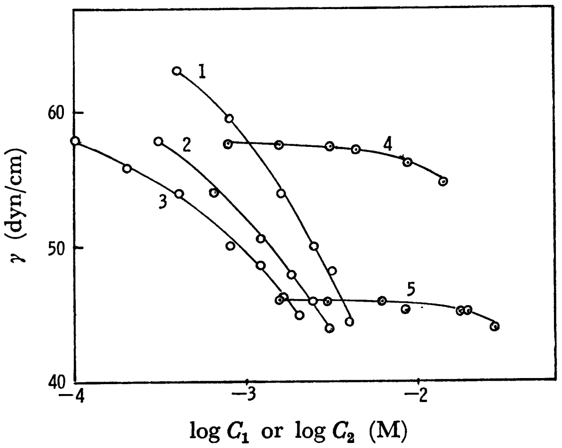

Fig. 3. Surface tension, γ, *vs.* log C_1 or log C_2.
○; γ *vs.* log C_2. Curve 1; $a_1=9.17\times10^{-7}(C_1=4\times10^{-3}$, $C+[Na_2SO_4]=8\times10^{-3})$, 2; $a_1=5.07\times10^{-6}(C=1.2\times10^{-2}$, $C+[Na_2SO_4]=1.5\times10^{-2})$, 3; $a=1.04\times10^{-5}(C_1=1.8\times10^{-2}$, $C+[Na_2SO_4]=2\times10^{-2})$.
⊙; γ *vs.* log C_1. Curve 4; $a_2=3.17\times10^{-7}(C_2=7.5\times10^{-4}$, $C+[Na_2SO_4]=1.5\times10^{-2})$, 5; $a_2=1.36\times10^{-6}$ $(C_2=1.5\times10^{-3}$, $C+[Na_2SO_4]=3\times10^{-2})$.

surface tension changes more with the concentration of SHP, C_2 (Curves 1, 2 and 3) than with that of SDP, C_1 (Curves 4 and 5).

Discussion

Effect of the Chain Length on Adsorption. As is well known,[5,11)] the Gibbs adsorption equation is a general equation relating adsorption amount, Γ, surface tension, γ, and activity, a.

$$\Gamma=\frac{-1}{RT}\left(\frac{\partial\gamma}{\partial\ln a}\right)_{T,\,P} \tag{1}$$

The activity of SAP in a single solution, a, is defined as:

$$a=\gamma_\pm{}^3C(2C+C')^2 \tag{2}$$

where γ is the mean ionic activity coefficient and can be calculated from the Güntelberg approximation of the Deby-Hückel theory:

$$\log\gamma_\pm=\frac{-A\sqrt{J}}{1+\sqrt{J}} \tag{3}$$

Here, J is the ionic strength and A is a constant, whose value is 1.022 for SAP at 25 °C.[12)] As has already been stated in our previous papers,[4,5)] the modified Langmuir adsorption equation using activity instead of concentration is written as:

$$\Gamma=\frac{\Gamma_s ka}{1+ka} \tag{4}$$

where Γ_s is the saturated adsorption amount and where k is the Langmuir coefficient. Equation (1) is integrated with equation (4) to give the modified Szyszkowski equation:

$$F=\gamma_0-\gamma=\Gamma_s RT\ln(1+ka) \tag{5}$$

F is the surface pressure and γ_0, the surface tension of pure water. A proper numerical value, k, could give a linear relation between F and ln $(1+ka)$.

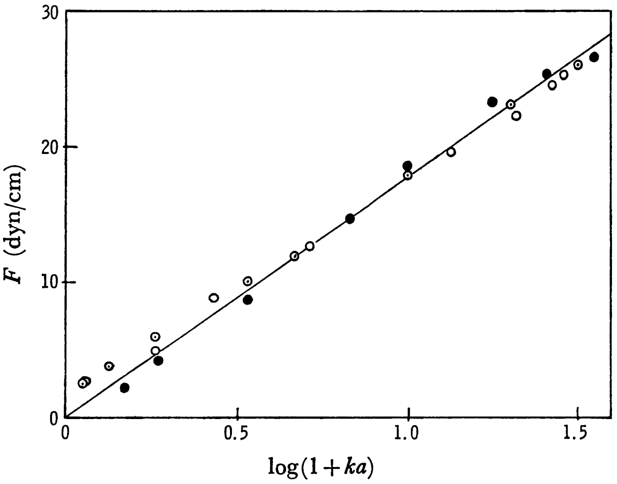

Fig. 4. Surface pressure, F, *vs.* log(1+*ka*).
○; SDP, ⊙; STP, ●; SHP

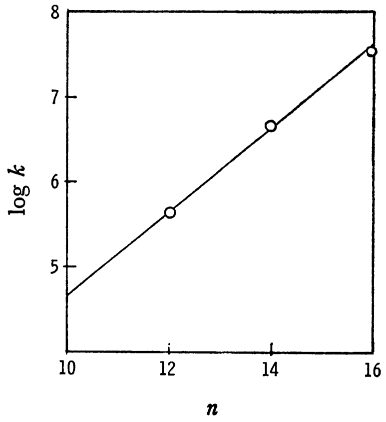

Fig. 5. Logarithm of Langmuir coefficient, log k, *vs.* hydrocarbon length, n.

In Fig. 4, F is plotted against ln(1+*ka*). When we used the Langmuir coefficients, the k values of 4.5×10^5, 4.8×10^6, and 3.3×10^7 for SDP, STP, and SHP respectively, the data for these three SAP solutions, plotted in this way, fell on a straight line. The value of Γ_s is 3.1×10^{-10} mol/cm^2, independent of the hydrocarbon-chain length. This corresponds to 53 Å^2 of the area occupied by one molecule. It is shown in Fig. 5 that the logarithm of the Langmuir coefficient, k, changes linearly with the number of carbon atomes in the hydrocarbon-chain, n. This means that the energy of adsorption per methylene group, ω, is constant, because the standard adsorption free energy $\Delta G°$, is given by the following equation:

$$\Delta G°=-RT\ln k \tag{6}$$

The value of ω obtained from the inclination of the straight line in Fig. 5 is 682 cal/mol. This result agrees with Traube's value ($\omega=650$ cal/mol).[13)]

Mixed Adsorption of Disodium Monoalkyl Phosphates. Not much works has been reported on the adsorption from aqueous solutions of mixed detergents because of difficulty involved in the calculation of the adsorption amount of each component. It has been shown in our previous paper, moreover that the adsorption amount calculated directly from the Gibbs adsorption equation and from the modified Szyszkowski equation, which is based on the modified Langmuir adsorption equation, agreed well with each other for an aqueous solution of a single SAP. In this paper, the modified Langmuir adsorption equation is extended to a mixture of the disodium monoalkyl phosphates. Assuming that the mixing of these homologous surfactants in the adsorption layer is ideal, and remembering that Γ_s is independent of the number of carbon atoms, as has been stated in the previous section, the modified Langmuir adsorption equation for a mixed solution may be written as:

$$\Gamma_1 = \frac{\Gamma_s k_1 a_1}{1+k_1a_1+k_2a_2} \tag{7}$$

$$\Gamma_2 = \frac{\Gamma_s k_2 a_2}{1+k_1a_1+k_2a_2} \tag{8}$$

where a_1 and a_2 are the activities of SDP and SHP, where $a_1 = \gamma_\pm^3 C_1(2C+C')^2$, and, where $a_2 = \gamma_\pm^3 C_2(2C+C')^2$. On the other hand, the Gibbs adsorption equation of a mixed solution is:

$$-\mathrm{d}\gamma = \Gamma_1 RT\,\mathrm{d}\ln a_1 + \Gamma_2 RT\,\mathrm{d}\ln a_2 \tag{9}$$

Equation (9) is integrated with Equation (7) and (8) to give:

$$F = \gamma_0 - \gamma = \Gamma_s RT \ln(1+k_1a_1+k_2a_2) \tag{10}$$

$\ln(1+k_1a_1+k_2a_2)$ is calculated using the values of the Langmuir coefficients, k_1 and k_2, which have previously been obtained for each single solute solution. They are given in Table 1. When F is plotted against $\ln(1+k_1a_1+k_2a_2)$, the linear relation shown in Fig. 6 is obtained. From this slope, the value of $\Gamma_s = 3.1\times10^{-10}$ mol/cm^2 is obtained, exactly the same value as was obtained from Fig. 4.

In Fig. 3, the surface tension is measured by holding the activity of one component, $a_2 = \gamma_\pm^3 C_2(2C+2[\mathrm{Na_2SO_4}]+[\mathrm{NaOH}])^2$ or $a_1 = \gamma_\pm^3 C_1(2C+2[\mathrm{Na_2SO_4}]+[\mathrm{NaOH}])^2$, constant; then Equation (9) reduces to either

$$-\mathrm{d}\gamma = \Gamma_1 RT\,\mathrm{d}\ln a_1 \tag{11}$$

or

$$-\mathrm{d}\gamma = \Gamma_2 RT\,\mathrm{d}\ln a_2 \tag{12}$$

These equations are integrated using Eq. (7) or (8) respectively; the same equation as Eq. (10) is obtained in both cases. In Fig. 7, the surface pressure, F, is plotted against $\ln(1+k_1a_1+k_2a_2)$. In Figs. 8 and 9, the adsorption amounts, Γ_1 and Γ_2, are calculated from Eqs (11) and (12) respectively by the direct differentiation of the experimental curves and compared with the theoretical values calculated from Eqs (7) and (8). These experimental results agree well with the theoretical ones. Thus, it may be concluded that the modified Langmuir adsorption equation using the activity is valid also in an aqueous solution of mixed SAP, and that the mixing of these homologous surfactants in the adsorption layer is ideal.

Micelle Formation and Chain Length. Herraman treated micelle formation as phase separation and assumed standard states of the hydrated monomer and

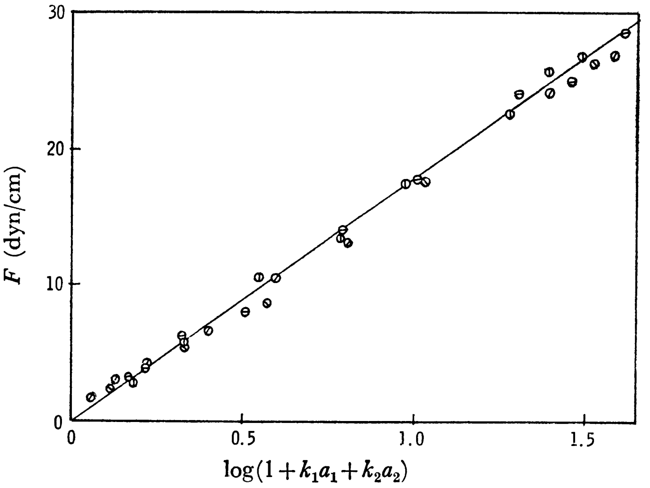

Fig. 6. Surface pressure, F, *vs.* $\log(1+k_1a_1+k_2a_2)$.
⦶; $X_1=0.5$, ⊖; $X_1=0.8$, ∅; $X_1=0.9$, ⦸; $X_1=0.95$.
——; Theory ($\Gamma_s = 3.1\times10^{-10}$ mol/cm^2).

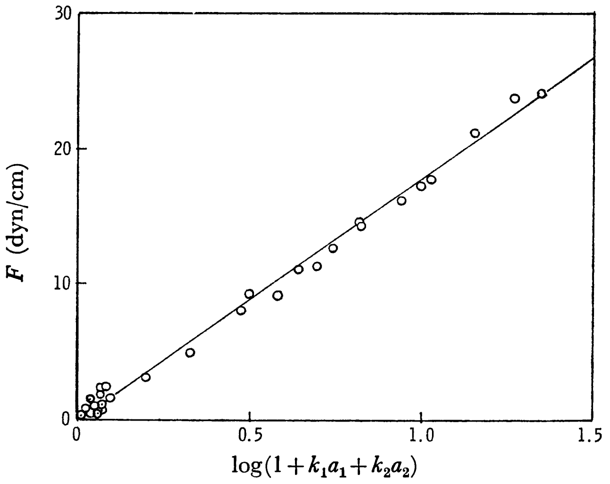

Fig. 7. Surface pressure, F, *vs.* $\log(1+k_1a_1+k_2a_2)$.
——; Theory.

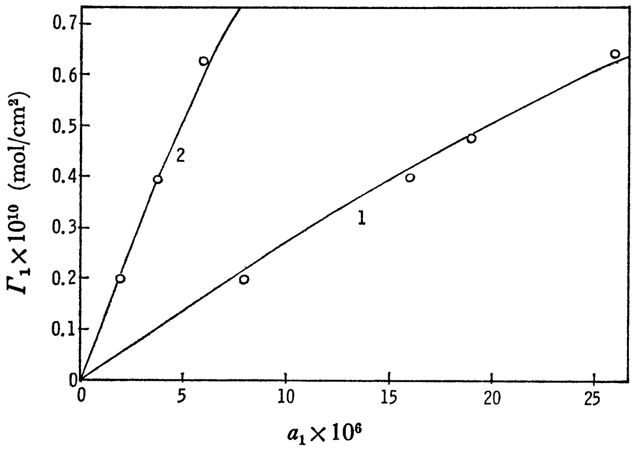

Fig. 8. Adsorption amount Γ_1 *vs.* a_1 (a_2=constant).
1; $a_2 = 1.37\times10^{-5}$, 2; $a_2 = 3.17\times10^{-7}$.
——; Calculated from equation (7).

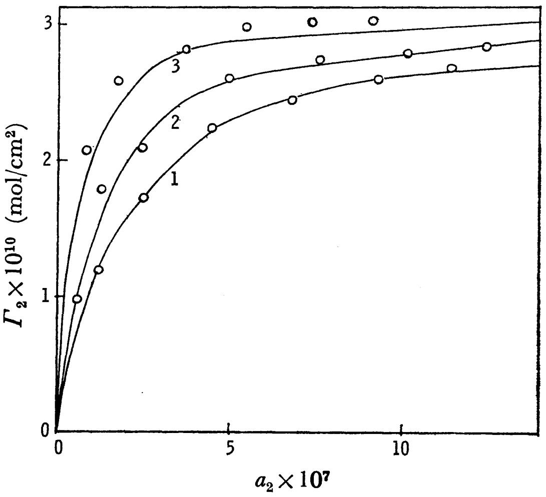

Fig. 9. Adsorption amount Γ_2 *vs.* a_2 (a_1=constant).
1; $a_1=1.05\times10^{-5}$, 2; $a_1=5.07\times10^{-6}$,
3; $a_1=9.17\times10^{-7}$.
——; Calculated from equation (8).

of hydrated micelle in an aqueous solution. Then he showed that the thermodynamic quantities calculated on this basis were in good agreement with the experimental values.[14] Applying his theory to SAP, but using the activity instead of the concentration in Herraman's equation, the standard free energy of the micelle formation, ΔG^*, is written as:

$$\Delta G^* = RT\ln a_{\rm m} \tag{13}$$

where $a_{\rm m}$ is the activity at the critical micelle concentration. In the case of SAP, the activity, $a_{\rm m}$, is given by the following equation:

$$a_{\rm m} = \gamma_\pm{}^3 C_{\rm m}(2C_{\rm m}+C')^2 \tag{14}$$

where $C_{\rm m}$ is the critical micelle concentration of SAP and C' is that of the inorganic salt added to the solution. In our previous paper, it was verified that the micelle formation occurred at a constant activity, irrespective of the added amount of inorganic salt. When the logarithm of $a_{\rm m}$ is plotted against the number of carbon atoms in the hydrocarbon chain, n, for a solution of each SAP, the linear relation shown by the solid line in Fig. 10 is obtained. The energy of micelle formation per methylene group is therefore, constant and is calculated to be ω =613 cal/mol from the slope of the straight line. On the basis of these results, ΔG^* can be expressed as:

$$\Delta G^* = -n\omega_{\rm m} + h \tag{15}$$

where h is a constant. As in a previous discussion of the effect of added salt on micelle formation,[4] the critical micelle concentration, $C_{\rm m}$, of disodium monoalkyl phosphates can be represented as a function of the counter-ion concentration [Na+] and the number of carbon atoms in the hydrocarbon chain, n, by the following equation at 25 °C.

$$\log C_{\rm m} = -31\log\gamma_\pm - 21\log[{\rm Na}^+] - 0.471n + 1.424 \tag{16}$$

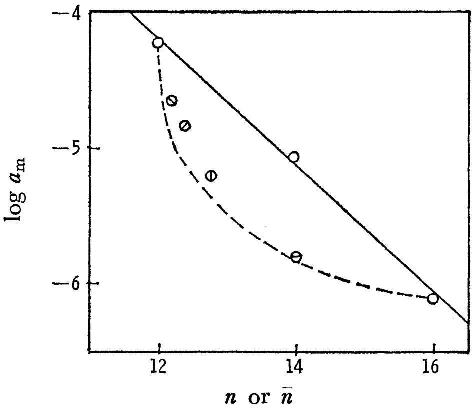

Fig. 10. log $a_{\rm m}$ *vs.* n or $\bar{n}$.
----; Theory, Eq. (18).

Mixed Micelle Formation. Shinoda presented a theory of micelle formation in an aqueous solution of mixed homologous detergents and represented the critical micelle concentration as a function of the hydrocarbon chain length and the mole fraction of mixing.[15] His theory was essentialy based on Hobb's theory[16] and also on the assumption that ideal mixing occurred in a mixed micelle of homologous detergents. In this paper, a theory is derived from a different basis that the activity at the critical micelle concentration is given as a function of the hydrocarbon chain length and the mixing mole fraction of each surfactant.

A mixed micelle is considered to be formed in an aqueous solution of the mixed SAP, and the mixing of the two surfactants in the mixed micelle phase is assumed to be ideal. Then the following equation is obtained:

$$RT\ln a_{\rm m1} = \Delta G^*{}_1 + RT\ln Y_1 \tag{17}$$

where $a_{\rm m1}$ is the activity of SDP at the critical micelle concentration and where y_1 is its mole fraction in the mixed micelle phase. $\Delta G_1{}^*$ is equal to the ΔG^* of Eq. (15) introduced 12 into n. A similar equation can be written for the 2 component, SHP with n=16. When y_1 and y_2 are eliminated, the following equation is readily obtained:

$$a_{\rm m} = {\rm e}^{\rm h}(X_1{\rm e}^{n_1\omega_{\rm m}/RT} + X_2{\rm e}^{n_2\omega_{\rm m}/RT}) \tag{18}$$

where $a_{\rm m}=a_{\rm m1}+a_{\rm m2}$, $a_{\rm m1}=X_1a_{\rm m}$, and $a_{\rm m2}=X_2a_{\rm m}$, because the mean ionic activity coefficients are equal for both components as long as the Güntelberg equation (13) is presumed. Numerical values are introduced into n_1, n_2 and $\omega_{\rm m}$, and the theoretical value of $a_{\rm m}$ is calculated. In Fig. 10, the experimental and theoretical values of $a_{\rm m}$ are compared for various values of the average numbers of carbon atoms:

$$\bar{n} = n_1X_1 + n_2X_2 \tag{19}$$

The experimental results plotted are in good agreement with the theoretical values shown by a broken curve. It is, therefore, verified that the theory of ideal mixing is valid for the mixed micelle phase in an aqueous solution of mixed SAP.

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