# Simultaneous Adsorption of Carboxylate Soaps and Other Surfactants

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The adsorptions <sup>5</sup> of laurate ions and lauric acid at the air/water surface in the presence of laurayl methyl taurate and dodecyl methyl sulphoxide have been measured. The adsorptions of laurate ions and lauric acid at the interface between water and di-n-heptyl ether have also been determined. It has been found that coadsorption of the methyl taurate ions decreases mainly the laurate ion adsorption, whereas the lauric acid adsorption is decreased most by the presence of additional non-ionic hydrophilic groups at the interface.

In a previous publication <sup>1</sup> the laurate ion adsorption and the lauric acid adsorption from aqueous potassium laurate solutions at the interfaces air/solution and n-dodecane/solution was evaluated. It was found that at concentrations slightly below the critical micellar concentration (c.m.c.) the ratio between adsorbed lauric acid and adsorbed laurate ions depended mainly on the pH of the solution, but was slightly affected by changing the interface.

In the present paper is studied how far the presence of other hydrophilic groups at the interface is able to influence this ratio. It has therefore been evaluated how the presence of an ionic additive (potassium lauroyl methyl taurate), of a non-ionic additive (dodecyl methyl sulphoxide) or of ether groups at the interface influence the surface composition of laurate soap solution.

In the presence of taurate ions, and at the interface diheptylether/laurate soap solution, evaluation of the surface composition was based on applying Gibbs' adsorption theorem to appropriate interfacial tension data, by analogy to the method used previously.<sup>1</sup> In the system laurate soap/dodecyl methyl sulphoxide, the latter compound is mainly dissolved by solubilization in the soap micelles. In this case a quantitative analysis was made of a foam of known surface area that was generated slowly from the mixed surfactant solution.

# DETERMINATION OF SURFACTANT ADSORPTIONS BY GIBBS' LAW

On assuming complete ionization of the additive, the various adsorptions at the surface of a mixed carboxylate soap+ionic additive solution can be determined by applying the following formulation of the Gibbs' adsorption law:

$$-d\gamma/RT = \Gamma_{K}d\ln a_{K} + (\Gamma_{Z} + \Gamma_{HZ})d\ln c_{Z} + \Gamma_{HZ}d\ln a_{H} + (\Gamma_{Z} + \Gamma_{HZ})d\ln f_{Z} + \Gamma_{A}d\ln f_{A}c_{A};$$
(1)

 $\gamma$  = interfacial tension;  $\mathbf{R}$  = gas constant; T = absolute temperature;

- $\Gamma_{\rm K}$  = adsorption of cations;  $a_{\rm K}$  = cation activity;
- $\Gamma_z$  = carboxylate soap ion adsorption;
- $\Gamma_{HZ}$  = carboxylic acid adsorption;
  - $c_{\rm Z}$  = carboxylate soap concentration;  $f_{\rm Z}$  = its activity coefficient;  $a_{\rm H}$  = hydrogen ion activity;

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 $\Gamma_{\rm A}$  = adsorption of the ionic additive ions;

 $c_{\rm A}$  = concentration of the additive;  $f_{\rm A}$  = its activity coefficient.

All adsorptions are taken relative to water.

The main assumptions involved in eqn. (1) are that only carboxylate ions, carboxylic acid, additive ions and counter ions are adsorbed, that the activity of the dissolved carboxylate acid is proportional to its concentration, and that the carboxylate ion concentration is high compared with the carboxylic acid concentration.<sup>1</sup>

Starting from solutions containing soap, additive, boric acid—borate buffer, and KCl, we can make such changes in  $c_Z$ ,  $a_H$  and  $c_A$ , that the resultant change in  $\gamma$  can be ascribed to a change of only one of the right-hand-side terms of (1).<sup>1</sup> In this way,  $\Gamma_Z + \Gamma_{HZ}$ ,  $\Gamma_{HZ}$ , and  $\Gamma_A$  can be evaluated separately at constant ionic strength. Then,  $\Gamma_Z$  can be calculated. The change in  $a_K$  on adding KCl to a solution at constant concentrations of the other components can be estimated,<sup>1</sup> so that  $\Gamma_K$  can also be evaluated using (1). According to the assumptions given above,

$$\Gamma_{\rm K} = \Gamma_{\rm Z} + \Gamma_{\rm A}.\tag{2}$$

Consequently, if  $\Gamma_A$  is known,  $\Gamma_Z$  can also be determined using formula (2).

## EXPERIMENTAL

#### MATERIALS

The preparation and purity of the potassium laurate, potassium tetraborate and potassium chloride used was described earlier.<sup>1</sup>

POTASSIUM LAUROYL METHYL TAURATE was prepared by reacting potassium methyl taurine with lauroyl chloride in an acetone+water mixture. After completion of the reaction, lauric acid was removed by acidifying and extracting with light petroleum. The product was recrystallized from 90 % ethanol. The c.m.c. was 4.4 mmole/l. The stock solution was foam fractionated before use.

n-DIHEPTYL ETHER.—(b.p.  $135^{\circ}$ C/16 mm Hg;  $n_D^{20} = 1.4275$ ;  $d_4^{20} = 0.801$ ) was prepared from n-heptanol at 198°C in the presence of H<sub>2</sub>SO<sub>4</sub>. The product was distilled in vacuum and then twice from metallic sodium.

S<sup>35</sup>-LABELLED DODECYL METHYL SULPHOXIDE (DMS) was synthesized by means of the following reaction scheme:

 $C_{12}H_{25}Br + S^*C(NH_2)_2 \longrightarrow C_{12}H_{25}S^*C \longrightarrow NH_2 \cdot HBr \xrightarrow{NaOH} \\ \parallel \\ NH \\ C_{12}H_{25}S^*H \xrightarrow{CH_3I, NaOH} C_{12}H_{25}S^*CH_3 \xrightarrow{H_2O_2} C_{12}H_{25}S^*CH_3. \\ \parallel \\ O$ 

Gas-chromatography of the  $C_{12}H_{25}Br$  used did not reveal the presence of any impurities. After dilution with inactive material the final product had a m.p. of  $61.5^{\circ}C$  and a specific activity of  $1.87 \times 10^{6}$  C/mg min.

SODIUM LAURATE.—The lauric acid described earlier was reacted with the calculated amount of 0.4 N NaOH solution. The foam-generating solutions were prepared by dilution of this stock solution.

#### SURFACE AND INTERFACIAL TENSION MEASUREMENTS

Surface and interfacial tensions were measured at room temperature  $(20^{\circ}C)$  by means of the drop-weight method. An extensive description of the method and the corrections used has been given elsewhere.<sup>1</sup> Again, equilibrium between the laurate solutions and n-diheptyl

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ether was established by shaking each laurate solution with a small amount of the ether. The final laurate concentration of the aqueous phase was determined by acidifying the equilibrated solution with HCl, followed by chloroform extraction. After washing, the chloroform solution was evaporated. The residue was taken up in absolute alcohol and titrated potentiometrically with alcoholic KOH solution. From control experiments this method was found to be accurate to within 1 %.

All measurements were made in the range of saturation adsorption, which had been determined in advance. The cation concentrations chosen were the same as used in an earlier investigation,<sup>1</sup> allowing the use of previous estimates of the changes in the ionic activities on adding KCl.

### RESULTS

The surface tension data on solutions of potassium laurate containing also potassium lauroyl methyl taurate, and interfacial tension data of potassium laurate solutions against di-n-heptyl ether are collected in table 1.

TABLE 1.—SURFACE TENSIONS OF POTASSIUM LAURATE (KZ) SOLUTIONS IN THE PRESENCE OF POTASSIUM LAUROYL METHYL TAURATE (KA), AND INTERFACIAL TENSIONS AGAINST DI-N-HEPTYL ETHER

buffer comp.	pH	[K+] m equiv./l.	C <sub>Z</sub> m equiv./l.	C <sub>A</sub> m equiv./l.	surface tension, dynes/cm
58.4 mmole/l. H <sub>3</sub> BO <sub>3</sub>	8.05	45	2.00	1.00	36-4
5.4 mmole/l. $K_2B_4O_7$		45	2.00	2.00	33-3
,		45	2.00	1.25	35.3
		45	3.00	1.25	30.9
		80	1.60	1.25	33.4
		80	2.56	1.25	28.6
14.8 mmole/l. K <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	9.44	45	<b>4</b> ∙00	1.25	42.6
,		45	<b>6</b> ∙00	1.25	39.85
		80	<b>4·00</b>	1.25	38.8
		80	<b>6</b> ∙ <b>0</b> 0	1.25	36-2
		80	4.00	0.475	42.2
		80	<b>4·00</b>	1.01	38.9
					interf. tension
					against di-n-
					heptyl ether,
					dynes/cm
58·4 mmole/l. H <sub>3</sub> BO <sub>3</sub>	<b>8</b> ∙20	45	2.52		15.28
$5.4 \text{ mmole/l. } K_2B_4O_7$		45	1.48		19.78
		80	1.425		17.38
		80	2.46		12.80
14.8 mmole/l. K <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	9.43	45	3.44		18·98
10.3 mmole/l. KOH		45	5.49		15.56
		80	3.39		15.63
		80	5.70		11.52

By applying formulae (1) and (2) to these data, the adsorptions of laurate ions  $(\Gamma_Z)$ , of lauric acid  $(\Gamma_{HZ})$ , and lauroyl methyl taurate ions  $(\Gamma_A)$  were calculated using the methods described earlier.<sup>1</sup> The results are collected in table 2. The lauric acid adsorption was also determined from the change of surface (interfacial) tension with pH. In both systems, the values found were intermediate between those reported in table 2 at the limits of the relevant pH range. The adsorption data on laurate ions and lauric acid in the absence of taurate under comparable conditions are also included for comparison (bracketed figures).

		<b>()K</b> +1	Г <sub>А</sub>	Г <sub>НZ</sub>	Γ <sub>z</sub>
interface	pH	m equiv./l.	mole/cm <sup>2</sup> 10 <sup>10</sup>		
air	<b>8</b> ∙05	45-80	1.84	2.5 (2.95)	1.85(3.15)
	9.44	45-80	1.82	1.35(2.2)	1.4 (3.55)
di-n-heptyl	<b>8</b> ·20	45-80		1.1	2.4
ether	9.43	45-80		0	3.1

TABLE 2.—Adsorption of laurate ions, lauric aicd, and of lauroyl methyl taurate ions

# MEASUREMENTS OF SURFACTANT ADSORPTIONS AT THE AIR/WATER INTER-FACE OF THE SYSTEM Na-laurate/dodecyl methyl sulphoxide by means of the foaming method

The principle of this method and the apparatus used have been described earlier.<sup>2</sup> From the composition of the foam after collapse, the relative surface excess of each component was calculated as the difference between the amount found by this analysis and that present in a sample of the generating liquid containing the same weight of water.

The area of the foam was estimated from a count of the number of bubbles present in the foam, and its volume. The volume/surface ratio was put equal to that of the regular dodecahedron.<sup>3</sup> The pH of the generating solution was adjusted by means of a borax+boric acid buffer (4.75 g/l. Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, 10 H<sub>2</sub>O in expt. 1 and 2 of table 3; 3.698 g/l. Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and 0.0744 g/l. H<sub>3</sub>BO<sub>3</sub> in expt. 3-8) at a value of 9.2. CO<sub>2</sub>-free nitrogen gas was used to generate the foam. The change in composition of the generating solution during foaming is neglected as less than 1 % of the surfactant present in the solution was withdrawn in the foam.

## ANALYSIS OF THE FOAM

An aliquot part of the collapsed foam was titrated first potentiometrically with KOH in alcoholic solution to determine the amount of free fatty acid; then, mannitol was added and the titration repeated to determine the amount of boric acid. Finally, the total amount of soap and boric acid was found by titrating with HCl. After collapse of the foam, the fatty acid reacts with the borate to yield boric acid and sodium soap. On assuming that the [borate]/[boric acid] ratio in the foam itself equals that in the generating solution, the original composition of the foam can be calculated. The  $S^{35}$  labelled dodecyl methyl sulphoxide used was determined by tracer analysis.

### RESULTS

The data obtained are collected in table 3. In all experiments the foam volume was 8-10 l., the number of bubbles was about 50,000 and the weight of the collapsed foam 300-500 mg. The foaming rate was  $20 \text{ cm}^3/\text{min}$ .

### DISCUSSION

### COMPARISON OF THE RESULTS OF THE DIFFERENT METHODS

Whereas the data obtained by surface tension measurements were obtained at concentrations slightly below the c.m.c., the foaming method results were obtained at concentrations somewhat in excess of the c.m.c. However, the adsorption of surfactants becomes practically constant when their concentration exceeds 30 % of the c.m.c.<sup>2</sup> The adsorption values obtained by foaming buffered laurate solutions

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at a concentration slightly higher than the c.m.c. should therefore nearly equal those at the surface of a laurate solution of the same pH and of comparable ionic strength at a concentration slightly below the c.m.c. The use of Na-laurate (table 3) instead of K-laurate (table 2) is not likely to influence the adsorption values obtained, since the saturation adsorption values of K-laurate and Na-laurate are nearly equal.<sup>4</sup> On comparing the data given in table 2 for K-laurate at the air/water interface at pH 9.3 to those given for Na-laurate in table 3 (expt. 1 and 2)

TABLE 3.—Adsorption of laurate ions ( $\Gamma_Z$ ), lauric acid ( $\Gamma_{HZ}$ ), and dodecyl methyl sulphoxide ( $\Gamma_{DMS}$ ) from buffered sodium laurate solutions at ph 9.2

expt. no.	original	original solutions		Γ <sub>HZ</sub>	Г <sub>DMS</sub>
	NaZ, g/l.	DMS, mg/l.	mole/cm <sup>2</sup> 10 <sup>10</sup>		
1	4.000		3.7	2.5	
2	4.000		<b>4</b> ·3	3.1	
3*	8.000	89.6	3.4	1.7	0.14
4*	8.000	89.6	4.3	1.7	0.20
5*	4.016	242.0	5.35	1.0	1.9
6*	4·016	242.0	5.0	0.8	1.9
7*	4.001	18 <b>0·0</b>	5.8	0.6	1.8
8*	4.001	180.0	5-4	0.85	1.9

\* 17.5 mg/l NaCl added

the adsorption values obtained by the foaming method appear to be high in comparison to those obtained from surface tension measurements, though both types of measurement give about the same ratios of  $\Gamma_{\rm HZ}$  to  $\Gamma_{\rm Z}$ . However, the changes in surface composition found on adding DMS clearly exceed the deviations between the two methods employed.

#### GENERAL

On comparing the laurate ion and lauric acid adsorptions obtained above to their values obtained in the absence of other hydrophilic groups at the interface,<sup>1</sup> the ratio  $\Gamma_{\rm HZ}/\Gamma_{\rm Z}$  is found to be increased by the presence of ionic groups, and decreased by the presence of non-ionic groups at the interface. It is difficult to reconcile this result with the occurrence of specific interaction between the hydrophilic parts of the adsorbed laurate ions and lauric acid.<sup>1</sup> In that case, any change in the laurate ion adsorption would be expected to cause a concomitant change in the lauric acid adsorption.

On comparing the lauric acid adsorption at the interfaces K laurate+K methyl taurate/air, K-laurate/air, K laurate/dodecane<sup>1</sup> and K laurate/heptyl ether, its value appears to decrease with the total surface charge. A deviating behaviour is observed for the system sodium laurate+DMS; here the lauric acid adsorption is strongly decreased, whereas the laurate ion adsorption is raised to values exceeding those obtained for a system containing laurate soap only. This effect might be explained as follows. The adsorption data of table 3 show that part of the water molecules present between the carboxylate groups in expt 1-2 has been replaced in expt. 5-8 by sulphoxide groups. The available area per surfactant molecule is decreased from about 25 Å<sup>2</sup> to 20 Å<sup>2</sup>. Since the dipole moment of the sulphoxide group (3.8 D) is much larger than that of water (1.85D) or carboxylic acid groups ( $\sim 1.8D$ ), such a replacement is likely to increase the dielectric constant in the surface layer. Consequently the electrical repulsion between the adsorbed laurate ions is decreased, so that the energy needed to bring a laurate ion from the solution into

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the surface will be lowered. This may be the cause of the observed increase in laurate ion adsorption with decrease of the lauric acid adsorption. However, it is unlikely that further progress can be made until a theory on the interaction between adsorbed ionic and non-ionic surfactants in the surface layer has been developed.

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- <sup>2</sup> van Voorst Vader, van den Tempel, Int. Congr. Surface Activity (Cologne, 1960), vol. A, p. 248.
- <sup>3</sup> Manegold, *ibid.*, vol. B, p. 522.

<sup>&</sup>lt;sup>1</sup> van Voorst Vader, Trans. Faraday Soc., 1961, 57, 2263.