COMPOSITION OF THE INTERFACE OF CARBOXYLATE SOAP SOLUTIONS

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Thermodynamical equations are derived that permit the evaluation of the total soap adsorption, the carboxylate ion adsorption, and the carboxylic acid adsorption at the interface of aqueous carboxylate soap solutions by means of interfacial tension measurements. The method is applied to evaluate the interfacial composition of buffered potassium laurate solutions, at concentrations slightly below the critical micellar concentration, against air and against n-dodecane in the pH range 7.47-9.33.

It is well-known that hydrolysis occurs in aqueous solutions of carboxylate soaps at pH values below 11, resulting in the presence of both carboxylate ions and free fatty acid at their interfaces.¹⁻³ As was first indicated by Loos,⁴ it is possible to obtain quantitative data on the interfacial composition of such solutions under well-defined conditions by means of thermodynamical methods. In the first part of this paper, formulae will be developed that permit the evaluation of the adsorption of carboxylate ions, that of free fatty acid, and the sum of these adsorptions independently from sets of surface tension measurements. In the second part, these results will be applied to evaluate the surface composition of buffered potassium laurate solutions at various interfaces.

THERMODYNAMICS

We consider an aqueous solution at constant temperature, containing potassium carboxylate soap KZ at a total concentration $C_{\rm T}$, a potassium borate-boric acid buffer to establish a H⁺ ion activity $a_{\rm H}$, and KCl to establish a K⁺ ion activity $a_{\rm K}$. The hydrolysis of the soap is represented by

$$a_{\rm Z}a_{\rm H}/a_{\rm HZ} = D,\tag{1}$$

where

 $a_{\rm Z} = f_{\rm Z} C_{\rm Z}$ = activity of the carboxylate ions,

 $a_{\rm HZ} = f_{\rm HZ}C_{\rm HZ}$ = activity of the fatty acid molecules,

D =dissociation constant.

We assume $f_{\rm HZ} = 1$, and consequently, $a_{\rm HZ} = C_{\rm HZ}$. Further, we will consider the adsorptions of the potassium ions, the carboxylate ions, and the free fatty acid only; the adsorptions of all other components will be neglected. To establish electroneutrality in each part of the solution

$$\Gamma_{\rm K} = \Gamma_{\rm Z},\tag{2}$$

in which $\Gamma_{\mathbf{K}}$ = the adsorption of the potassium ions relative to water, and

 Γ_z = the adsorption of the carboxylate ions relative to water.

For the system considered, the Gibbs adsorption equation ⁵ reads :

$$-d\gamma/RT = \Gamma_{K}d\ln a_{K} + \Gamma_{Z}d\ln a_{Z} + \Gamma_{HZ}d\ln a_{HZ},$$
(3)

where $\gamma = \text{interfacial tension}$, R = gas constant, T = absolute temperature. 2263

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 Γ_{HZ} = adsorption of free fatty acid relative to water. The total soap concentration C_T is related to the carboxylate ion concentration C_Z by means of the relation :

d ln
$$C_{\rm T}$$
 = d ln $(C_{\rm Z} + C_{\rm HZ})$ = d ln $C_{\rm Z}$ + d ln $[1 + (f_{\rm Z}a_{\rm H}/D)]$. (4)

In our investigation, the value of D is about 10^{-5} , that of $a_{\rm H}$ in the range of 10^{-7} - 10^{-9} , and that of $f_{\rm Z}$ not far below 1. Consequently, all changes in $\ln (1 + f_{\rm Z} a_{\rm H}/D)$ are extremely small, and the last term on the right-hand side of (4) will be neglected in all further considerations.

Substitution of (1) and (4) into (3) results in

$$-d\gamma/RT = \Gamma_{\rm K}d\ln a_{\rm K} + (\Gamma_{\rm Z} + \Gamma_{\rm HZ})d\ln C_{\rm T} + \Gamma_{\rm HZ}d\ln a_{\rm H} + (\Gamma_{\rm Z} + \Gamma_{\rm HZ})d\ln f_{\rm Z}.$$
(5)

Eqn. (5) indicates that changes in the interfacial tension may be caused by changing either the counterion activity $a_{\rm K}$, the total soap concentration $C_{\rm T}$, or the hydrogen ion activity $a_{\rm H}$. It will be the starting point of all further considerations.

CALCULATION OF $\Gamma_z + \Gamma_{HZ}$

This value can be calculated from surface tension data on a number of solutions having various soap concentration $C_{\rm T}$, but constant potassium ion concentration and pH. At concentrations below the c.m.c., the activity coefficients $f_{\rm K}$ and $f_{\rm Z}$ will then be approximately the same for all solutions considered, and (5) reduces to

$$-\frac{1}{RT} \left(\frac{\partial \gamma}{\partial \ln C_{\rm T}} \right)_{a_{\rm H}, a_{\rm K}} = \Gamma_{\rm Z} + \Gamma_{\rm HZ}$$
(6)

CALCULATION OF Γ_z

The carboxylate ion adsorption can be determined from the change in surface tension $d\gamma_K$ of solutions with constant values of C_T and a_H , on varying the potassium chloride concentration. After inserting (2), eqn. (5) can be transformed to

$$-d\gamma_{\rm K}/RT - (\Gamma_{\rm Z} + \Gamma_{\rm HZ})d\ln f_{\rm Z} = \Gamma_{\rm Z}(d\ln f_{\rm K}c_{\rm K} + d\ln f_{\rm Z}) - \Gamma_{\rm Z}d\ln f_{\rm Z}.$$
 (7)

According to Brönstedt ⁶ specific effects on the activity coefficients of ions are mainly determined by the nature and the concentration of ions of opposite sign. Since, moreover, the value of the second terms, both on the right-hand side and on the left-hand side of eqn. (7) is small compared with the first terms on either side, the value of d ln f_Z in both second terms may, without serious error, be assumed to equal the value of d ln f_{KCl} found for KCl solutions with corresponding potassium ion concentrations. An analogous assumption was found previously to give satisfactory results in detergent+KCl mixtures.⁷ The value of $\Gamma_Z + \Gamma_{HZ}$ is known from eqn. (6), and the value of (d ln f_Kc_K +d ln f_Z) can be reasonably estimated from experiment (see below). Consequently, Γ_Z can be calculated; combination of the results of eqn. (6) and (7) also yields the value of Γ_{HZ} . The method used here for evaluating Γ_Z is fairly involved, but minimizes the influence of factors in the calculation that are not accessible to measurement.

CALCULATION OF Γ_{HZ}

The adsorption of free fatty acid can be measured independently by measuring the change in surface tension $d\gamma_{\rm H}$ caused by varying the pH at constant potassium ion concentration and constant total soap concentration. Eqn. (5) becomes :

$$-d\gamma/RT = \Gamma_{\rm K}d\ln f_{\rm K} + (\Gamma_{\rm Z} + \Gamma_{\rm H})d\ln f_{\rm Z} + \Gamma_{\rm HZ}d\ln a_{\rm H}.$$
 (8)

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On neglecting the changes in f_K and f_Z , which are only due to the change in buffer composition necessary to change the pH, we obtain

$$-\left(\frac{\partial\gamma}{\partial\ln a_{\rm H}}\right)_{c_{\rm K}c_{\rm T}} = RT\Gamma_{\rm HZ}.$$
(9)

Eqn. (6), (7) and (9) can also be derived on assuming that carboxylate ions, potassium ions and protons are the only components of the system that are adsorbed at the interface and that all protons adsorbed at the interface combine with the carboxylate ions present to form free fatty acid.

DETERMINATION OF ACTIVITY CHANGES BY SURFACE TENSION MEASUREMENTS

In order to apply formula (7) it is essential to know the change in cation activity caused by changing the KCl content of the solution. Because of the complicated nature of the electrolyte mixtures considered, a theoretical estimation cannot be trusted.

By analogy of formula (2) it may be assumed that in solutions of non-hydrolyzing ionic surfactants, the cation adsorption in the range of saturation equals the surfactant ion adsorption. The latter, $\Gamma_{\rm NH}$, can be evaluated from surface tension measurements on surfactant solutions, to which electrolyte has been added to maintain constant cation activity.⁷

On comparing solutions with different salt content and equal surfactant concentration, in the range of saturation adsorption, the change in surface tension due to the change in electrolyte concentration is given 7 by

$$-\frac{\Delta\gamma}{RT} = \Gamma_{\rm NH} \Delta \left(\ln \frac{a_{\rm K1}}{a_{\rm K2}} + \ln \frac{f_{\rm NH1}}{f_{\rm NH2}} \right), \tag{10}$$

in which $f_{\rm NH1}$, $f_{\rm NH2}$ represent the activity coefficient of the non-hydrolyzing surfactant ion at the cation activities $a_{\rm K1}$ and $a_{\rm K2}$ respectively. If $\Gamma_{\rm NH}$ is known, and suitable assumptions are made regarding the activity coefficients, $\Delta \gamma$ may be calculated with an average accuracy better than 5 %.7 Conversely, if $\Gamma_{\rm NH}$ and

 $\Delta \gamma$ are known, it should be possible to evaluate the factor $\Delta \left(\ln \frac{a_{\rm K1}}{a_{\rm K2}} + \ln \frac{f_{\rm NH1}}{f_{\rm NH2}} \right)$

to within 5 %.

Consequently, solutions containing potassium undecylsulphonate, KCl and buffer substances were prepared in which the amount of buffer and the potassium ion concentration were identical to those in the laurate solutions under investigation, and the change in surface tension by identical increases of the KCl concentration were measured.

After determining $\Gamma_{\rm NH}$, the factor $\Delta \left(\ln \frac{a_{\rm K1}}{a_{\rm K2}} + \ln \frac{f_{\rm NH1}}{f_{\rm NH2}} \right)$ can be calculated from the measurements on the sulphonate series by means of eqn. (2) and (10).

In our experiments, the surfactant ion concentration is always less than 10 % of the total anion concentration. Therefore, it is assumed that the potassium ion activity in the sulphonate solutions is equal to that in the laurate solutions at equal buffer concentration and potassium ion concentration. It was established previously,⁷ that the same values for the activity coefficients could be used both for K-undecylsulphonate solutions and for K-laurate solutions at high pH to calculate the change in surface tension on adding KCl. In consequence, we may expect that, under similar conditions, the assumption $f_{\rm NH} = f_Z$ will be sufficiently accurate for the present purpose. Then the value of the factor $\sqrt{12} \frac{q_{\rm K1}}{q_{\rm K1}} = \frac{f_{\rm NH1}}{q_{\rm K1}}$ schemed from the sulphonate solutions can be substituted

 $\Delta \left(\ln \frac{a_{\rm K1}}{a_{\rm K2}} + \ln \frac{f_{\rm NH1}}{f_{\rm NH2}} \right) \text{ obtained from the sulphonate solutions can be substituted}$

for the factor
$$\Delta \left(\ln \frac{a_{\text{K1}}}{a_{\text{K2}}} + \ln \frac{f_{\text{Z1}}}{f_{\text{Z2}}} \right)$$
 in eqn. (7).

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EXPERIMENTAL

The foregoing theory will now be applied to evaluate the interfacial composition of buffered potassium laurate solutions at concentrations near their critical micellar concentration (c.m.c.) in the pH range 7.4-9.4, both at the interfaces with air and with n-dodecane. Potassium undecylsulphonate was employed as non-hydrolyzing surfactant for the activity measurements.

MATERIALS

Potassium laurate was prepared by dissolving lauric acid (m.p. 43.7° C, composition : 96.6 % lauric acid, 0.7 % myristic acid, 0.2 % capric acid, 2.5 % caprylic acid from gas/ liquid chromatographic analysis) in absolute ethanol, and neutralizing to phenolphthalein with 1 N KOH dissolved in 50 % ethanol. The precipitate was filtered off, dried at 105°C, recrystallized from boiling absolute ethanol, washed with acetone (analytical grade) and finally dried overnight at 70°C.

POTASSIUM UNDECYLSULPHONATE, obtained by reacting undecylbromide and potassium sulphite, was purified by repeated recrystallization from methanol, and prolonged extraction with light petroleum, diethyl ether, and acetone. c.m.c. = 0.016 mole/l. at 20°C from surface tension measurements.

n-DODECANE (b.p., 144.8°C/100 mm Hg; $n_{\rm D}^{25\cdot5}$, 1.4192; d_4^{22} , 0.7471) was obtained by hydrogenating n-dodecene.

POTASSIUM TETRABORATE, $K_2B_4O_7$, was prepared by heating K_2CO_3 (analytical grade) with twice the equivalent amount of boric acid (analytical grade) in a quartz vessel until the evolution of carbon dioxide ceased.

POTASSIUM CHLORIDE (analytical grade) ex Merck was used.

WATER was double-distilled in a quartz still. All vessels used were cleaned by steam from distilled water.

MEASUREMENTS

ESTABLISHMENT OF EQUILIBRIUM SYSTEMS

Equilibrium between laurate solutions and n-dodecane was obtained by shaking 100 ml of each laurate solution (containing also KCl and buffer salts) during 18 h intermittently with 2-3 ml n-dodecane.

It was verified that equilibrium distribution of the lauric acid was then established by performing control experiments starting from dodecane containing lauric acid and comparing the interfacial tensions of the former systems with the control.

LAURATE DETERMINATION

During the establishment of equilibrium, an appreciable shift in the laurate concentration of the aqueous solution occurs. The final laurate concentration in the latter was determined by inserting its surface tension in the equation

$$\gamma = -A \log c_{\rm T} - B,\tag{11}$$

which was found to be valid in the concentration range investigated. The constants A and B of formula (11) were determined by surface tension measurements on laurate solutions of known laurate concentration, at the same pH and cation content as the equilibrated solution.

MEASUREMENTS OF THE INTERFACIAL TENSION

Interfacial tensions were measured by means of the drop-weight method, using a stainless steel capillary attached to an Agla micrometer syringe by means of a teflon connecting piece.⁸ In view of the small amounts of equilibrated dodecane available, a special drop receiver was used for measurements on this system (fig. 1). The interfacial tensions found on using this receiver agreed within experimental accuracy with those obtained using a conventional receiving vessel. All the measurements were carried out at room temperature (20°C).

In preliminary experiments it was found that at constant cation concentration and pH, the slope of the plot of the surface tension against the logarithm of $c_{\rm T}$ was constant

in the concentration range just below the c.m.c. of the system. Moreover, this slope proved to be independent of the cation concentration chosen. Therefore, in this concentration range saturation adsorption may be assumed.⁷ For the final measurements, only two concentrations within the range of saturation adsorption were used in order to

save time in collecting the results since, even in the presence of a buffer, the pH of the laurate solutions was found to change appreciably in two or three days. All solutions were prepared under a nitrogen blanket. The pH of all measuring solutions was checked with an Electrofact pH meter immediately before starting the interfacial tension measurements. With the equilibrated solutions, a slight shift of the pH was sometimes observed. Therefore, preliminary graphs of the dependence of the surface tension and of the interfacial tension on the value of the pH were constructed after completion of the experiments. From these, all measurements of a given series were corrected to refer to the same pH. In most cases the corrections applied did not exceed a few tenths of a dyne/cm.

The absolute value of the surface tension was found to change up to 0.5 dyne/cm with the batch of potassium tetraborate employed in preparing the buffer. However, the changes in tension caused by changing the laurate concentration, the KCl



FIG. 1.—Micro receiving vessel for interfacial tension measurements; A, dropping tip (d = 1.8 mM); B, cork; C, receiving vessel.

concentration or the pH could be reproduced closely for every batch used. The same batch of tetraborate was used throughout the study of a given system.

RESULTS

EVALUATION OF $\Delta(\ln f_{\rm K}c_{\rm K} + \ln f_{\rm Z})$

Surface tension measurements were made on solutions containing K-undecylsulphonate, the same amounts of buffer salts as present in the measurements on laurate and KCl up to the same K^+ concentration as present in these latter measurements. The K-undecylsulphonate concentrations chosen were such that saturation adsorption at the surface occurred. Their values were comparable to the surfactant concentrations used in the laurate measurements. It follows from (10) that

$$-\frac{\Delta\gamma}{2\cdot 3 RT} = \Gamma_{\rm NH} \Delta(\log_{10} f_{\rm K} c_{\rm K} + \log_{10} f_{\rm Z}). \tag{10A}$$

It was verified for the system water+KCl+K-undecylsulphonate that the value of $\Delta(\log_{10} f_K c_K + \log_{10} f_Z)$ calculated from (10 A) on inserting the value of $\Gamma_{\rm NH}$ found from surface tension measurements at constant cation concentration, was in agreement with theoretical expectation.⁷ For in this system, the value of $\Delta(\log_{10} f_K c_K + \log_{10} f_Z)$ can be estimated from known activity data on KCl.⁹ On changing the cation concentration from 45 mequiv./l. to 80 mequiv./l. at 20°C, the calculated value is 0.208. The experimental results are collected in table 1.

The value for $\Delta(\log_{10} f_{\rm K}c_{\rm K} + \log_{10} f_{\rm Z})$ found in the absence of buffer is in good agreement with the calculated value. Though the scattering of the values of $\Gamma_{\rm NH}$ found in the different buffer solutions is fairly large, the scattering in the derived values of $\Delta(\log_{10} f_{\rm K}c_{\rm K} + \log_{10} f_{\rm Z})$ is much less, and the values obtained appear reasonable. Only a minor influence of the buffer compounds on the activity changes in the solution is found.

The value of the sulphonate adsorption is appreciably higher than that previously reported ⁷ for sodium undecyl sulphonate. This is probably due to the

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use of a different cation; an analogous effect has been found with secondary alkyl sulphates.¹⁰

buffer composition			pH	•	[K+] mequiv./l.	Δγ dyne/cm	$\Gamma_{ m NH}$ mole/cm ² ×10 ¹⁰	$\begin{array}{c} \Delta(\log_{10}f_{\rm K}c_{\rm K}^+\\ +\log_{10}f_{\rm Z})\end{array}$
no buffer			-		$\binom{45}{80}$	5.0	4.25	+0.210
H ₃ BO ₃ : K ₂ B ₄ O ₇ :	74∙0 m 1∙5	mole/l.	7·48 7·48		45 80 }	5.3	4.34	+0.218
H_3BO_3 : $K_2B_4O_7$:	58·4 5·4	,, ,,	8∙08 8∙08		45 80	4.9	4.02	+0.218
H_3BO_3 : $K_2B_4O_7$:	14·8 16·3	»» »	8·80 8·80		45 80	5.0	4.12	+0.217
$K_2B_4O_7$: KOH:	14·8 10·3	" "	9·30 9·30		45 80	5∙0	4.25	+0.210

Table 1.—Evaluation of $\Delta(\log_{10} f_K c_K + \log_{10} f_Z)$ from surface tension data on buffered K-undecylsulphonate solutions

 $\Gamma_{\rm NH}$ = adsorption of undecylsulphonate ions, as obtained from measurements with varying sulphonate concentration and constant [K+], and $\Delta \gamma$ = change in surface tension on changing [K+] from 45 mequiv./l. to 80 mequiv./l. at constant sulphonate concentration.

Since our method requires only that $\Gamma_{\rm K} = \Gamma_{\rm NH}$, but no accurate investigation into the value of $\Gamma_{\rm NH}$ itself, the purification of the sulphonate solutions was somewhat less rigorous as that applied previously.⁷ This, too, may have influenced the values of $\Gamma_{\rm NH}$ given in table 1.

MEASUREMENTS ON LAURATE SOLUTIONS

The interfacial tension data on buffered potassium laurate solutions are collected in table 2.

IAD	<u> </u>	111121011101						
buffer composition				FTZ +1	C _T — mequiv./1.	interfacial tension against		
			pH	mequiv./l.		air dyne/cm	n-dodecane dyne/cm	
K ₂ B ₄ O7 KOH	7 14·8 mmole/l. 10·3 "		9.33	45 }	4·70 3·66	47∙3 50∙85	18·97 21·75	
				80 }	5·80 3·50	40·45 47·35	13·09 18·77	
H3BO3 K2B4O7	14∙8 16∙3	,, ,,	8.72	45 }	4·60 2·85	39·9 46·85	13·98 19·25	
				80 }	4·25 2·51	37·4 45·1	11·77 18·08	
H3BO3 K2B4O7	58·4 5·4	" "	8 ∙07	45 }	2·87 1·41	36·75 47·3	12·32 20·63	
				80 }	2·14 1·23	37·55 45·8	12·56 19·45	
H3BO3 K2B4O7	74∙0 1∙5	,, ,,	7.47	45 }	1·19 0·71	38·1 46·45	13·76 20·8	
				80 }	1·13 0·68	35·8 44·0	12·33 18·77	

TABLE 2.—INTERFACIAL TENSION DATA ON POTASSIUM LAURATE SOLUTIONS

In all cases, KCl was added until the required cation concentration had bee obtained. Two independent sets of measurements were made on the adsorption of laurate against air. The adsorptions calculated from both sets of data agre within the expected error of measurement (see below).

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values of $\Gamma_z + \Gamma_{HZ}$

The value of $\Gamma_Z + \Gamma_{HZ}$ can be obtained immediately from the data given in table 2 by application of eqn. (6).

VALUES OF Γ_z

On constructing graphs of γ against log $C_{\rm T}$ from the data given in table 2, the value of $\Delta \gamma_{\rm K}$ can be found by measuring the difference in ordinate of the lines in these graphs that give γ at equal pH and different salt content at an arbitrary value of $C_{\rm T}$. If the lines were not strictly parallel, the average of the values of $\Delta \gamma_{\rm K}$ obtained at the highest and at the lowest value of $C_{\rm T}$ measured was used.

Since $\Gamma_Z + \Gamma_{HZ}$ and $\Delta (\log_{10} f_K c_K + \log_{10} f_Z)$ are known, Γ_Z can be calculated from

$$-\Delta\gamma_{\rm K}/2.3 \ RT + 0.021(\Gamma_{\rm Z} + \Gamma_{\rm HZ}) = \Gamma_{\rm Z} \{ (\Delta \log_{10} f_{\rm K} c_{\rm K} + \Delta \log_{10} f_{\rm Z}) + 0.021 \}.$$
(7A)

The factor -0.021 represents the change in $\log_{10} f_Z$ on changing the cation content from 45 to 80 mequiv./l. as estimated from data on KCl.⁹

values of Γ_{HZ}

The value of $\Gamma_{\rm HZ}$ can be calculated both from the foregoing data and by applying eqn. (9). The value $\Delta \gamma_{\rm H}$ is determined from graphs of γ against $C_{\rm T}$ by measuring the change in ordinate between the lines in these graphs that give γ at equal salt content but different $p_{\rm H}$, at the same value of $C_{\rm T}$.

In no case were the γ -log C_T graphs at different pH strictly parallel. However, the value of $\Delta \gamma_H$ is fairly large (5-10 dynes/cm), so that a slight convergence of the lines in question does not influence the results appreciably. The results are collected in table 3.

DISCUSSION

In our previous measurements,⁷ the spread in the values of Γ as obtained from interfacial tension measurements, either by varying the surfactant ion concentration or by varying cation concentration, averaged ± 5 %. If all assumptions made in this paper are correct, we would expect, therefore, a spread of ± 5 % in the values of $\Gamma_Z + \Gamma_{HZ}$, and of Γ_{HZ} from eqn. (9). It follows from statistical analysis that the expected spread of the value of Γ_Z , that is obtained by combination of three determinations with a spread of ± 5 % each, will be ± 9 %.

In general, the accuracy of the data obtained seems in agreement with these estimations. It follows from table 3 that the value of Γ_{HZ} as calculated by means of eqn. (9) is always intermediate between the values for Γ_{HZ} found by applying eqn. (6) and (7) at the limit of the relevant pH change. If our experimental accuracy was much less than that estimated above, such agreement would be very coincidental. Therefore, our results appear to confirm the correctness of the theory given in this paper. Likewise, two independent sets of experiments at the air/water interface gave values of Γ_{Z} agreeing within 10 % at every pH investigated, and values of Γ_{HZ} (eqn. (9)) agreed within 4 %. The value of Γ_{HZ} from eqn. (6) and (7), becomes less certain at high pH values, since then this value is calculated as the difference between two larger quantities. In our case, a difference of 0.3×10^{-10} mole/cm² was found at pH 9.3 between the two sets of measurements.

Recently, the simultaneous adsorption of calcium and sodium ions at the surface of surfactant solutions was measured using a similar method.¹¹ Here,

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TABLE 3 .--- ADSORPTION OF LAURATE IONS AND LAURIC ACID AT VARIOUS INTERFACES

interface	pH	K+ mequiv/.1.		$\Gamma_Z \mod cm^2 \times 10^{10}$	$\Gamma_{\rm HZ}$ mole/ ${ m cm}^2$ $ imes 10^{10}$	$\Delta \gamma_{K}$ dyne/cm	$\Gamma_{\rm HZ}$ (form (9)) mole/ cm ² × 10 ¹⁰	Δ _{γH} dyne/cm
air	9.33 }	. 45 80	5·75 5·75	3.55	2.2	-3.9		
	8.72-9.33	45 80					2·3 2·2	— 7·8 — 7·4
	8.72 }	45 80	6∙0 6∙0	3.35	2 ·65	-3.7		
	8.07-8.72}	45 80					2·75 2·7	-10.0 - 9.85
	8.07 }	45 80	6·1 6·1	3.15	2.95	-3.5		
	7.47-8.07	45 80					3·6 3·3	-12.0 -11.1
	7.47 }	45 80	6∙7 6•7	2.8	3.9	-3·0		
n-dodecane	9.33	45 80	4∙55 4∙65	3.15	1.45	-3.55		
	8.72-9.33 }	45 80					1·5 1·45	- 5.25 - 4.75
	8.72 }	45 80	4·5 4·9	2.75	1.95	-3.1		
	8.07-8.72 }	45 80					1·95 1·95	— 7·1 — 7·1
	8.07 }	45 80	4·8 5·1	2.7	2.25	-3·0		
	7.47-8.07 }	45 80					2·7 2·5	- 8.9 - 8.3
	7.47 }	45 80	5·5 5·3	2.3	3.1	-2.4		

the consistency of the results obtained was much worse than is the case in the present measurements. This difference is due to the chemical binding of the adsorbed H⁺ ions, which makes the surface composition in the present case much less dependent upon the bulk ratio of the cations as when the cation adsorptions are determined by electrostatic forces only. To a large extent, our measurements at the air/water and at the dodecane/water interface give analogous results. The laurate ion adsorption slowly increases with pH. At the same time, the lauric acid adsorption decreases somewhat more strongly, resulting in a slow decrease of the total soap adsorption, $\Gamma_Z + \Gamma_{HZ}$.

The lauric acid adsorption is found to decrease slightly on increasing [K⁺] from 45 mequiv./l. to 80 mequiv./l. It follows from our method of calculations that this decrease is connected with the change in laurate ion adsorption with pH. Since no simultaneous decrease of the value of $\Gamma_Z + \Gamma_{HZ}$ with [K⁺] ion concentration is found, it appears that the degree of surface ionization $\alpha = \Gamma_Z/(\Gamma_Z + \Gamma_{HZ})$ increases slightly with the ionic strength of the solution.

It was investigated whether the general shape of the Γ_Z against pH and Γ_{HZ} against pH curves could be calculated by means of the Stern theory of the electrical double layer.¹² The slight increase in ionization on increasing the ionic strength is in conformity with the expectations from this theory.

On the other hand, the change of Γ_{HZ} with "pH is less than would be expected; this might be explained by assuming specific interaction forces between the laurate

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ions and the lauric acid present at the interface. In view of the similarity of the Γ_{HZ} against pH curves at the air/water and at the dodecane/water interface, these interaction forces must be exerted by the hydrophilic parts of the molecules.

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- ¹ Laing, Proc. Roy. Soc. A, 1925, 109, 28.
- ² Raison, Rev. Franc. Corps Gras, 1959, 6, 207.
- ³ Michel, J. Chim. Physique, 1957, 54, 206.
- 4 Loos, Verh. Kon. Vlaamse Acad. Wetensch., Kl. Wetensch., 1950, 12, no. 34.
- ⁵ Guggenheim, *Thermodynamics* (Amsterdam, 1950), p. 39.
- ⁶ Brönstedt, J. Amer. Chem. Soc., 1922, 44, 877.
- 7 Van Voorst Vader, Trans. Faraday Soc., 1960, 56, 1067.
- ⁸ Weissberger, Physical Methods of Organic Chemistry (New York, 1949), 1, p. 373.
- ⁹ Hornibrook, Janz and Gordon, J. Amer. Chem. Soc., 1943, 65, 218.
- ¹⁰ Aickin, J. Soc. Dyers Col., 1944, 60, 36.
- ¹¹ Van Voorst Vader, Proc. 3rd Int. Congr. Surface Activity (Cologne, 1960), vol. B, p. 276.
- 12 Stern, Z. Elektrochem., 1924, 30, 508.