schematic representation of the surface oxidation-reduction levels; the result is shown in Fig. 1. The levels were computed by the procedure given in a previous paper.[2]

Comparison of Fig. 1 with similar data for unsupported chromia[2] shows that chromia and chromia-alumina differ markedly with respect to the amount of hydrogen adsorbed on the reduced catalyst at high temperature. Whereas unsupported chromia can take up about one hydrogen atom per surface oxide ion, chromia-alumina has a very low capacity for adsorbing hydrogen; in fact, within the experimental error, it cannot be definitely stated that *any* adsorbed hydrogen is retained by reduced chromia-alumina after evacuation at 500°. This might have been adduced as evidence for stabilization of the Cr^{+3} state by the alumina support (since hydrogen adsorption can be considered as equivalent to chromous oxide formation), except for the fact that the amount of excess oxygen taken up by oxidized chromia-alumina is quite comparable with that taken up by unsupported chromia.[2]

The conditions under which the water evolution during cycling in hydrogen and oxygen at 500° was determined are analogous to those employed for gas adsorption in the circulating system. The total amount of water evolved during a complete cycle at 500° was 260 micromoles water per gram; according to part (A) of Fig. 1, the calculated amount would be $(2 \times 134) + 13 = 281$ micromoles water per gram.

The thermal effects observed during cycling chromia-alumina in hydrogen and oxygen at 500° are similar to those previously described for unsupported chromia.[2] In the case of chromia-alumina, however, it would appear that practically all the water should be formed during the reduction, since there is very little adsorbed hydrogen on the reduced catalyst. It must be concluded, therefore, that the heat effects are not exclusively due to the production of water as postulated by Givaudon and co-workers.[4]

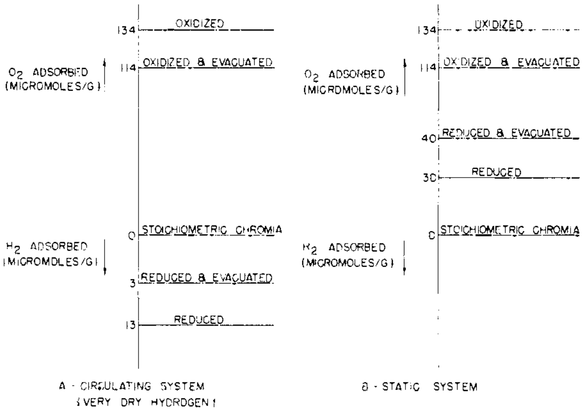

Fig. 1.—Schematic representation of the oxidation-reduction levels of chromia-alumina.

Experiments with unsupported chromia indicated that the excess oxygen present after high temperature oxidation may be used as a rough measure of the specific surface area of the chromia (within, say, a factor of two).[2] To the extent that this procedure is valid, a chromia area of 22 m.^{2}/g. *catalyst* may be calculated for the chromia-alumina (see above). Since only 20% of the catalyst is chromia, the chromia area is $5 \times 22 = 110$ m.^{2}/g. *chromia*, which is three times the value (35 m.^{2}/g.) obtained for a stabilized, unsupported chromia catalyst; that is, the chromia is three times more efficiently distributed in the supported than in the unsupported catalyst. The equivalent chromia particle diameter in the supported catalyst is 106 Å., as compared with 335 Å. for the unsupported chromia.[3]

MARCUS HOOK, PENNSYLVANIA

[CONTRIBUTION NO. 138 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

The Adsorption of Ionic Surfactants and their Gegenions at the Air-Water Interface of Aqueous Solutions

BY C. P. ROE AND P. D. BRASS

RECEIVED MARCH 5, 1954

The adsorption of ionic surfactants and their gegenions in the air-water interface of aqueous solutions has been studied by means of surface tension measurements under conditions which permit a simple and exact interpretation. The significant result disclosed is that the surface excess in a surfactant solution does not vary with the concentration of surfactant in the bulk solution throughout a wide range just below the so-called critical micelle concentration. Composition of the adsorbed layer and thermodynamic properties of the dissolved surfactant are discussed. Radioactive tracer measurements on solutions of a labeled surfactant have been found to confirm the conclusions reached from surface tension measurements. A new technique for the direct tracer study of adsorption on solid surfaces is described and some results are presented.

Introduction

The behavior of the fatty acid soaps as surface active materials has been studied by a very great number of investigators. Despite the vast amount of work reported in the literature, there appears to be one aspect of the subject which has escaped attention, namely, the relatively simple and yet exact interpretation of surface tension data available when the hydrogen ion and gegenion concentrations are held constant as the detergent ion concentration is varied in a range below but near to the critical micelle concentration. In the present paper this subject is discussed on the basis of data obtained by two independent absolute methods. The treatment is extended to classes of materials other than the fatty acid soaps.

It is well known that the surface tension of an ionic detergent solution is in general a sensitive function of the total electrolyte concentration and hydrogen ion concentration. This is recognized to signify that adsorption of normally surface inert solutes is induced by the presence of a surface active solute. Quantitative study of this effect has yielded data which imply that the adsorbed layers in the cases considered may be regarded as being composed of neutral detergent molecules.

Interpretation of the data has been made by a rigorous and direct application of the adsorption equation of Gibbs, with the aid of a few results on the thermodynamic properties of electrolyte solutions.

Supplementary evidence concerning the adsorption of surface active solutes has been obtained by a tracer study of radioactive potassium palmitate solutions. The results are in agreement with those obtained by other methods.

Experimental

Materials.—The fatty acid soaps used in the experimental part of this work were prepared by neutralizing the corresponding acids with potassium hydroxide. The free fatty acids were of the best quality supplied by the Eastman Kodak Co. and were sold under the following melting point specifications: lauric acid, 42–43°; palmitic acid, 61–62°. No attempt was made to purify these acids, since drops of the corresponding soap solutions formed during surface tension measurements exhibited satisfactory stability and reproducibility.

The sodium dodecyl sulfate used was a specimen supplied through the courtesy of the du Pont Company. It was substantially free of inorganic salt and was satisfactorily pure.

Laurylamine hydrochloride was prepared from Eastman best grade of the free amine by dissolving in benzene and neutralizing with hydrogen chloride according to the method of Ralston and Hoerr.[1]

Radioactive palmitic acid and radioactive sodium acetate, both tagged with C^{14} in the carboxyl group, were used as supplied by Tracerlab, Inc., Cambridge, Mass.

Methods.—Surface tensions were measured by the drop weight method. Drops were formed on a stainless steel tip, and the usual precautions concerning maturing of drops and separation from the tip were observed. The correction factors of Harkins and Brown[2] were applied to all data on drop weights.

The surface excess of radioactive potassium palmitate in aqueous solution was studied making use of a modification of the method described by Aniansson.[3] The quantity measured in the case of a given specimen of solution of known palmitic acid content was the total number of disintegrations per unit time detected by the counter under given reproducible geometric conditions. This number is denoted by k and may be regarded as made up of three components, so that we may write

$$k = k_0 + k_1 + k_2$$

where

k_0 = background count in absence of any specimen per unit time

k_1 = count contributed by the radioactive material in the bulk soln. phase as distinguished from the surface per unit time

k_2 = count contributed by the surface excess per unit time

The background, k_0, was obtained directly by operating the counter without any specimen. The contribution of the bulk solution, k_1, was obtained by comparison with a solution of labeled sodium acetate of known activity relative to the palmitic acid. The count, k_2, contributed by the surface excess was then calculated by difference.

The reduction of the count, k_2, to an absolute concentration in moles per cm.^{2} was achieved by measuring the activity of a spread film containing a known surface concentration of labeled palmitic acid in the field of the counter. The geometric conditions were exactly the same as those employed in the measurement of the soap solutions. The film was spread by placing a known amount of labeled palmitic acid in benzene solution on the surface of a dilute HCl solution contained in one of the specimen dishes used in the counter. After evaporation of the benzene the residue of palmitic acid was melted by heating the substrate to a temperature just above the melting point of the acid and was then cooled to room temperature. The quantity of acid used was in each experiment less than that required to form a monolayer on the surface of the HCl solution and was assumed to be spread uniformly over the entire free surface of the liquid in the specimen dish. The reliability of the latter assumption was tested by using two different amounts of acid in the spread film experiments. The ratio of counts observed was in satisfactory agreement with the ratio of amounts of palmitic acid used.

The procedure for measuring adsorption of labeled soap on solid surfaces with the aid of thin films will be described in detail, since it is believed to have some novel features. Films of polystyrene were prepared by spreading a layer of a 0.5% benzene solution of the polymer on a sheet of cellophane tightly stretched over a well leveled plate glass surface. After the solvent had evaporated, the thin polymer film adhered very tightly to the cellophane backing. Circular test pieces of the adhering film and backing were cut out and separated from the plate glass support. The circular sections of polymer film were easily separated from the cellophane backing after soaking for a few minutes in water. The polymer films floated flat on the surface and were stored thus until they were used.

In order to mount a film for study in the counter, a specimen dish was immersed beneath the film while in storage on a water surface and was gently raised under the film until the latter and the dish brimming with water were completely separated from the storage bath. The films had been cut to a size nearly to cover the open surface in the specimen dishes. By means of a hypodermic syringe with a small gage needle the water in the dish was exhausted until the film was spread on the nearly dry bottom of the dish. The amount of water held between the film and the dish was estimated to be negligible. The solution to be studied was slowly introduced from the syringe so as to float the film as the solution spread over the bottom of the dish. Care was taken not to contaminate the upper surface of the film with a radioactive solution, since experience showed that such contamination was difficult to remove.

Experiments showed that polymer films sufficiently thin to show primary interference colors did not interfere with radiation from compounds labeled with carbon 14. No films were used which did not satisfy this criterion.

Results and Discussion

Surface tension *vs.* logarithmic concentration data on aqueous solutions of each of four ionic surface active materials are presented graphically in Figs. 1–4, inclusive. The surface active solutes are potassium palmitate, potassium laurate, dodecylamine hydrochloride and sodium dodecyl sulfate. The distinctive feature of these experiments is that in each series the total gegenion concentration was held constant at 0.1 mole per liter. Care also was taken where necessary to control *p*H so as to prevent hydrolysis.

The graphs in Figs. 1–4 possess a feature to which we wish to draw attention. It is their linearity throughout an extensive interval of soap concentrations just below the critical micelle concentrations. This is interpreted with the aid of the thermodynamic equation of Gibbs. The Gibbs equation may be written, for a system of n components at constant temperature and pressure

$$d\gamma = -RT[\Gamma_1 d \log a_1 + \Gamma_2 d \log a_2 + \ldots + \Gamma_n d \log a_n] \quad (1)$$

---

(1) A. W. Ralston and C. W. Hoerr, This Journal, **68**, 851 (1946).

(2) W. D. Harkins and F. E. Brown, *ibid.*, **41**, 499 (1919).

(3) G. Aniansson, *J. Phys. Colloid Chem.*, **55**, 1286 (1951).

where

γ = surface tension in dynes per cm.
a_1 = molar activity of component no. 1, etc.
Γ_1 = surface excess of component no. 1, etc., in the surface considered in moles/cm.^{2}
R = molar gas constant
T = absolute temperature

We shall discuss the data on potassium laurate (Fig. 1) in detail, but it is clear that the general conclusions will be equally valid for the other three systems. In the potassium laurate solutions the pH value was held at 10.0 with a buffer consisting of a mixture of K_2CO_3 and $KHCO_3$, and the total concentration of potassium ion, *i.e.*, the sum of the buffer salt and the soap, was held constant at 0.1 mole per liter. Thus, the only variable components of the system were the neutralized soap and the anions of the buffer mixture. The variations of the latter were relatively small, and, as will be shown subsequently, the inorganic anions exhibited no surface activity in these solutions. Since the system has now been reduced to one variable component, the Gibbs equation may be written

$$\Gamma = -\frac{1}{RT} \times \frac{\partial \gamma}{\partial \log a} \qquad (2)$$

where Γ and a now refer to the soap. The situation is further simplified by noting that the activity coefficient of the soap does not vary, and hence

$$\Gamma = -\frac{1}{RT} \times \frac{\partial \gamma}{\partial \log c} \qquad (2a)$$

where c = molar concentration of soap.

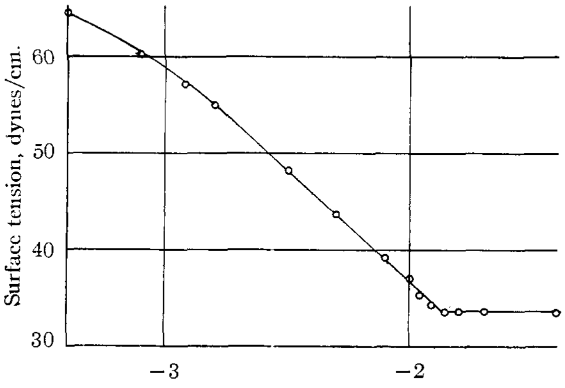

Fig. 1.—Surface tension *vs.* log concn. of potassium laurate solutions; pH 10.0, [K$^+$] = 0.1 mole per liter.

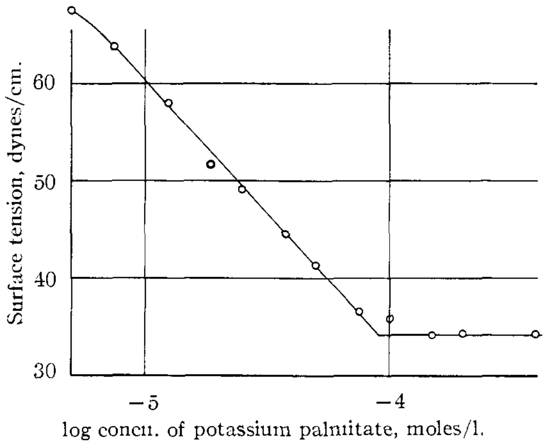

Fig. 2.—Surface tension *vs.* log concn. of potassium palmitate solutions; pH 12.3, [K$^+$] = 0.1 mole per liter.

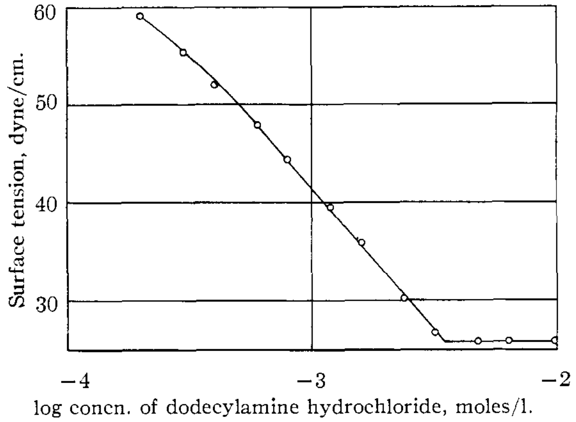

Fig. 3.—Surface tension *vs.* log concn. of dodecylamine hydrochloride solutions; pH 2.0, [Cl$^-$] = 0.1 mole per liter.

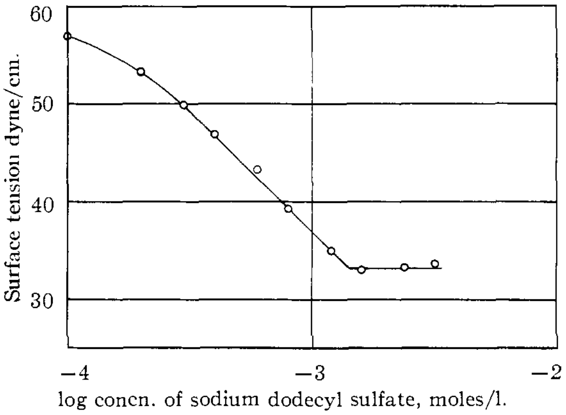

Fig. 4.—Surface tension *vs.* log concn. of sodium dodecyl sulfate solutions; pH 6.5, [Na$^+$] = 0.1 mole per liter.

The curve in Fig. 1 may now be discussed by direct reference to equation 2a. Throughout an interval on the c-axis extending from $c = 0$ to $c = 0.0137$ mole per liter, the slope of the curve is a direct and unequivocal measure of the surface excess of soap, or of the amount of soap adsorbed per unit area, in the air–water interface. At sufficiently low values of c the vanishing slope implies that adsorption is negligible. As c increases, the gradually increasing negative value of the slope implies an increasing degree of adsorption. However, the interesting feature disclosed by the data in Fig. 1 is that a region of constant slope is reached at a soap concentration of approximately 0.0016 mole per liter and extends to a concentration of 0.0137 mole per liter. This implies that in the concentration interval $0.0016 \geqq c \geqq 0.0137$ mole per liter, a constant value of adsorption at the air–water interface is exhibited by potassium laurate solutions in which pH and gegenion concentrations are held constant as indicated. When the surface has become thus saturated with adsorbed soap, further increase of the bulk soap concentration in the solution, although it causes a steady decrease of surface tension, produces no change in the magnitude of the surface excess. This state of affairs persists until the soap concentration approaches the value known as the critical micelle concentration.

At potassium laurate concentrations which exceed 0.0137 mole per liter Fig. 1 shows that the slope of the γ *vs.* log c curve vanishes altogether. This is recognized to imply that a constant equilibrium value of molecularly dispersed soap has been reached or exceeded, but it does not imply that adsorption in the air–water interface changes or drops to zero. The ability of the solution to dissolve additional soap is regarded as resulting in the appearance of a new solute species, namely, soap micelles. It is beyond the scope of this paper to discuss the properties of micellar soap solutions, but a few comments on the transition from molecularly dispersed solutions to micellar solutions are pertinent. We have chosen in the figures to represent this transition as being discontinuous in the sense that below the so-called critical micelle concentration the solutions are completely free of micelles and that above this concentration any increase in the gross soap concentration results only in the production of micelles. For many purposes this may be an adequate picture, and our data are not sufficiently detailed or precise to demonstrate the need of refinement. It is recognized, however, that the data do not exclude the more likely possibility that dissolved soap is in thermodynamic equilibrium with micelles at all concentrations both above and below the so-called critical micelle concentration, and that, strictly speaking, the latter term is a misnomer.

This completes our detailed discussion of the data presented in Fig. 1, the salient feature of which is to recognize the existence of an extensive concentration interval below the critical micelle concentration throughout which constant adsorption at the air–water interface is exhibited. This effect is disclosed as a result of holding the gegenion concentration constant as the soap concentration is varied.

It is clear that Figs. 2, 3, 4, may be discussed in exactly the same manner. The numerical values of surface excess and critical micelle concentration (c.m.c.) are summarized in Table I.

Table I

Fig. no.	Surfactant	*p*H	C.m.c. (moles/l.)	$10^{10}\ \Gamma$ (moles/cm.^{2})
1	$C_{11}H_{23}COOK$	10.0	1.37×10^{-2}	4.24
2	$C_{15}H_{31}COOK$	12.3	0.90×10^{-4}	4.62
3	$C_{12}H_{25}NH_2HCl$	2.0	3.50×10^{-3}	5.20
4	$C_{12}H_{25}SO_4Na$	6.5	1.45×10^{-3}	4.40

The adsorption of gegenions in the air–water interface of an ionic surfactant solution was studied by means of surface tension measurements. It is known that the aqueous solution of an ionic surfactant frequently shows a strong dependence of surface tension on the content of relatively surface inert electrolytes. From this it is inferred, by reference to equation 1, that in a surfactant solution an otherwise surface inert electrolyte may become surface active. Induced surface activity of this sort has been studied in such a way as to throw light on the thermodynamic properties of the soap in solution and hence to allow an inference concerning the composition of the adsorbed layer.

We shall first discuss the adsorption of hydrogen ions and of potassium ions at the surface of a potassium laurate solution. Two series of experiments were necessary for this purpose. In the first series the hydrogen ion concentration was varied, while the soap concentration and total potassium ion concentration were held constant at 0.001 and 0.1 mole per liter, respectively. The data obtained are presented in Table II. Control of *p*H was achieved by varying the ratio of carbonate to bicarbonate in the buffer mixture of potassium salts. No cations other than K^+ and no anions other than carbonate and bicarbonate were introduced. *p*H values were measured with the glass electrode.

Table II

Surface Tension of Potassium Laurate Solutions

Total lauric acid = 0.001 mole/l.; total K^+ = 0.1 mole/l.

*p*H	$[CO_3^=]$, mole/l.	$[HCO_3^-]$, mole/l.	γ
10.5	0.045	0.01	57.0
9.95	.035	.03	57.7
9.65	.025	.05	57.6
9.35	.015	.07	57.1
9.0	.005	.09	57.3

The only terms in equation 1 which need to be considered are those corresponding to the hydrogen ion and the anions of the buffer mixture. Since there is no dependence of surface tension on *p*H or on the carbonate–bicarbonate ratio in the interval studied, it may be inferred that within this interval there is no adsorption of hydrogen ions or of the anions of the buffer mixture. That is, there is no hydrolysis of the adsorbed soap.

In the second series of experiments the potassium laurate concentration was held at 4.0×10^{-3} moles per liter, the *p*H was held constant near 10, and the total salt concentration was varied. Data on potassium laurate solutions are presented in Fig. 5. Interpretation requires further discussion of the Gibbs equation.

It is clear that surviving terms in equation 1 are due to soap, gegenions, and water. Let us designate activity of laurate ions by a_1, activity of potassium ions by a_2, activity of water by a_3 and let ϕ_1, ϕ_2, ϕ_3 be the corresponding activity coefficients. Then if c_1, c_2, c_3 are the corresponding concentrations, equation 1 becomes

$$-\frac{d\gamma}{RT} = \Gamma_1(d \log \phi_1 + d \log c_1) + \Gamma_2(d \log \phi_2 + d \log c_2) + \Gamma_3 d \log a_3 \quad (3)$$

It is reasonable to assume that variations in log a_3 may be neglected and since c_1 is held constant, d log c_1 vanishes. Furthermore electrical neutrality in the adsorbed layer requires that $\Gamma_1 = \Gamma_2$, since we have demonstrated that no hydrogen ions are adsorbed. Then the slope of the curve shown in Fig. 5 is to be identified with the left member of the following equation

$$-\left(\frac{\partial \gamma}{\partial \log c_2}\right)_{c_1 = \text{const.}} = RT\Gamma_1\left[1 + \frac{\partial \log \phi_2}{\partial \log c_2} + \frac{\partial \log \phi_1}{\partial \log c_2}\right]_{c_1} \quad (3a)$$

The magnitude of the third term in the square bracket is of interest, and we make use of our experimental data in order to obtain it. First of all, it is necessary to evaluate the second term, namely, $\partial \log \phi_2/\partial \log c_2$. This has been done by two different procedures, first, by means of the thermodynamic data to be found in the literature and, second, by means of a calculation based on the theory of Debye and Hückel, with the aid of ionic diameters obtained from crystal structure.

Similar data have also been obtained and analyzed with solutions of dodecylamine hydrochloride and sodium dodecyl sulfate. These are summarized in Table III, in which the following notation is used

c_1 = detergent concn. in moles/l.
Γ_1 = surface excess of detergent in moles/cm.² as read from linear portions of Figs. 1, 3 and 4
S_0 = $(\partial\gamma/\partial \log_{10}c_2)_{c_2=0.1}$ in dynes/cm. as read from Fig. 5
c_2 = gegenion concn. in moles/l.
S_1 = $(\partial \log \phi_2/\partial \log_{10}c_2)_{c_2=0.1}$ calcd. from thermodynamic data
S_{12} = value of this derivative calcd. from theory of Debye and Hückel
S_2 = $(\partial \log \phi_1/\partial \log_{10}c_2)_{c_2=0.1}$ obtained by use of S_1
S_{22} = value of this derivative obtained by use of S_{12}

TABLE III

Detergent	10^3 c_1	10^{10} Γ_1	S_0	S_1	S_{12}	S_2	S_{22}
$C_{11}H_{23}COOK$	4.0	4.06	16.4	−0.22	−0.043	−0.07	−0.25
$C_{12}H_{25}NH_3Cl$	1.0	5.09	19.0	− .095	− .047	− .24	− .29
$C_{12}H_{25}SO_4Na$	0.35	4.32	18.7	− .084	− .062	− .15	− .18

The agreement between S_1 and S_{12} is for present purposes fairly satisfactory in the dodecylamine hydrochloride and sodium dodecyl sulfate solutions, in which the ballast salts are KCl and NaCl, respectively. This implies that in these cases the mean solute activity obtained from thermodynamic measurements is approximately equivalent to the activity of either of individual ionic components of the ballast salt, and it is clear from the last two columns of Table III that it does not make much difference whether one uses S_1 or S_{12} in equation 3a. In the potassium laurate solutions where a buffer mixture of K_2CO_3 and $KHCO_3$ was used as ballast, there is no agreement between S_1 and S_{12}. This is taken to imply that the mean activity of the solute corresponding to S_1 is not equivalent to the individual activity of the cation, and that in dealing with the latter one must have recourse to the calculated value, corresponding to S_{12}. We shall base our discussion on this conclusion and shall assume that the values in the S_{12} and S_{22} columns are the appropriate ones to use.

It is to be expected that S_{22} would be larger in absolute magnitude than S_{12}, since increasing electrolyte concentration in detergent solutions is known to exert a large depressing effect on the critical micelle concentration. Hence, the relative values of S_{22} and S_{12} appear to be reasonable in each case. Since the absolute values of S_{12} are known to be approximately correct, it appears safe to draw the inference that the detailed behavior of these solutions with respect to each component may be fully accounted for by thermodynamic equation of Gibbs. The reasonableness of the results appears to justify the assumptions which were made in order to reduce equation 3 to the form 3a. Thus, the adsorbed layer is found to exhibit no surface hydrolysis and no state of electrostatic unbalance.

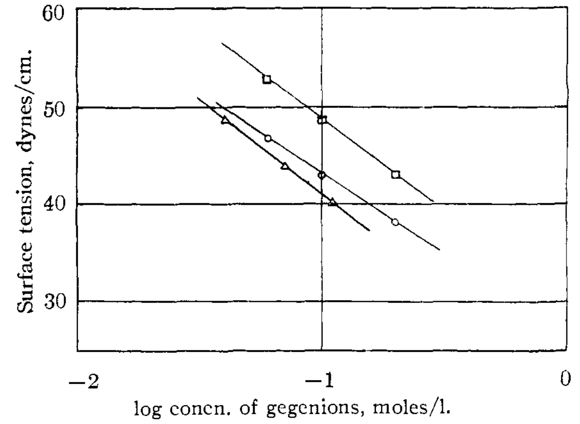

Fig. 5.—Surface tension *vs.* log gegenion concn. in detergent solutions: ○, K^+, in potassium laurate solutions [laurate$^-$] = 0.004 *M*; Δ, Cl^- in dodecylamine hydrochloride solutions [dodecylammonium$^+$] = 0.001 *M*; □, Na^+ in sodium dodecyl sulfate solutions [dodecyl sulfate$^-$] = 0.00035 *M*.

Radioactive tracer measurements on solutions of labeled potassium palmitate were undertaken in order to secure an independent check on the overall reliability of the conclusions drawn from surface tension measurements.

Radioactive palmitic acid was dissolved in 0.1 *N* KOH solution and this soap solution was diluted with 0.1 *N* KOH as required for the counting experiments. Thus, a series of solutions was prepared in which the only variable was the concentration of labeled palmitic acid. Count data were obtained on these solutions and were analyzed for values of the surface excess of soap according to the method outlined in the section on experimental details. The results are listed in Table IV, in which the symbol Γ_t is used to denote the surface excess of soap estimated from tracer measurements.

TABLE IV

ADSORPTION OF RADIOACTIVE POTASSIUM PALMITATE AT AIR–WATER INTERFACE

$k_0 = 40$; $K^+ = 0.1$ mole per liter

10^5c (moles/l.)	k	k_1	k_2	$10^{10}\Gamma_t$ (moles/cm.²)
1.17	88	8	40	2.5
2.34	99	15	44	2.8
4.68	136	31	65	4.2
7.02	149	46	63	4.0
9.4	168	61	67	4.3
11.7	180	76	64	4.1
14.0	200	91	69	4.4
17.3	215	113	62	4.0
19.7	232	129	63	4.0
23.4	254	153	61	3.9

Comparison of Tables I and IV indicates that the two methods of estimating the maximum value of the surface excess are in excellent agreement.

There appears to be a discrepancy between the two methods with regard to the soap content of potassium palmitate solutions at which saturation of the surface is reached. This is not regarded as a serious matter, since it can probably be accounted for by the presence of a small amount of impurity in the radioactive palmitic acid.

It remains to present data on the adsorption of labeled potassium palmitate on thin films of polystyrene. The technique of making these measurements is described in a previous section. Data are presented in Table V; c = concentration of potassium palmitate.

TABLE V

10^5c (moles/l.)	$10^{10}\Gamma$ (moles/cm.^{2})
1.17	0.6
2.34	1.0
4.68	1.7
7.02	2.6
9.36	3.6
11.7	4.0
17.3	4.2
23.4	3.8

It is of interest that in this case, too, saturation of the interface occurs at a concentration of soap considerably below the critical micelle concentration.

Acknowledgment.—The authors desire to acknowledge the technical assistance of Mr. Frank Grosseibl, who made most of the surface tension measurements reported in the foregoing paper.

PASSAIC, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

The Ionization Constant of Metanilic Acid from 0 to 50° by Means of E.M.F. Measurements

BY RAYMOND D. McCOY AND D. F. SWINEHART

RECEIVED APRIL 19, 1954

The ionization constant of metanilic acid has been determined from 0 to 50° by the use of cells without liquid junction. The equation $-\log K = 1327.59/T + 0.002813197T - 1.55334$ expresses the experimental data as a function of temperature in the above temperature range with a standard deviation of 0.00054 in $-\log K$ for eleven experimental points. An exceedingly small value of ΔS^0 for the ionization reaction, -0.57 e.u. at 25°, is found.

Introduction

The ionization constant of metanilic acid has been measured by several investigators. Of these investigations all but one[1] are results of conductivity measurements and were interpreted without taking interionic attractions into account. The resulting values are as follows:

Investigator	$K \times 10^4$	t, °C.
Ostwald[2]	1.85	25
White and Jones[3]	0.90	0
	1.33	12
	1.99	25
	2.62	35
Boyle[4]	2.11	25
Zollinger, Büchler and Wittwer[1]	2.24	25

It has been shown by Carr and Shutt[5] from measurements of the change of dielectric constant with *p*H of sulfanilic acid solutions that sulfanilic acid is a zwitterion. Considering that metanilic is even weaker than sulfanilic acid, it is reasonable to suppose the former acid also exists in solution as a zwitterion. Hence the ionization constant is for the reaction

$$^+H_3NC_6H_4SO_3^- = H_2NC_6H_4SO_3^- + H^+$$

It is the object of this investigation to present accurate values of the ionization constant of metanilic acid determined over the temperature range 0 to 50° by the measurement of the electromotive force of cells without liquid junction following the general method developed by Harned and co-workers.[6]

The cells were of the type Pt, H_2/HMet(m_1), NaMet(m_2), NaCl(m_3)/AgCl–Ag, where HMet and NaMet are metanilic acid and its sodium salt and m_1, m_2 and m_3 are molalities. By elimination of $m_{H^+}\gamma_{H^+}$ from the cell potential equation

$$E = E^0 - \frac{2.3026RT}{F} \log m_{H^+}m_{Cl^-}\gamma_{H^+}\gamma_{Cl^-} \qquad (1)$$

and the thermodynamic ionization constant expression

$$K = \frac{m_{H^+}m_{Met^-}\gamma_{H^+}\gamma_{Met^-}}{m_{HMet}\gamma_{HMet}} \qquad (2)$$

there results the following relation

$$\frac{(E - E^0)F}{2.3026RT} + \log \frac{m_{HMet}m_{Cl^-}}{m_{Met^-}} = -\log K - \log \frac{\gamma_{HMet}\gamma_{Cl^-}}{\gamma_{Met^-}} \qquad (3)$$

The ionization constant was calculated from equation 3 using a method similar to that developed by Hamer[7] and identical with that of MacLaren and Swinehart[8] used in the determination of the ionization constant of sulfanilic acid.

The values of the molal electrode potentials, E^0, of the silver–silver chloride electrode have been determined by Harned and Ehlers[9] and recalculated by Swinehart.[10] The values of the function $2.3026RT/F$ in absolute volts have also been calculated by Swinehart[10] using the constants of Bearden and Watts.[11]

Experimental

The materials and reagents were purified and analyzed in a similar manner to that indicated by MacLaren and Swinehart.[8] It may be noted, however, that in their experiments, stock solutions of sulfanilic acid showed a yellow color upon standing for a week or more. This coloration was attributed to a trace of oxygen remaining in the solution. How-

---

(1) H. Zollinger, W. Büchler and C. Wittwer, *Helv. Chim. Acta*, **36**, 1711 (1953).

(2) W. Ostwald, *Z. physik. Chem.*, **3**, 406 (1889).

(3) G. F. White and H. C. Jones, *Am. Chem. J.*, **44**, 159 (1910).

(4) M. Boyle, *J. Chem. Soc.*, **115**, 1505 (1919).

(5) W. Carr and W. J. Shutt, *Trans. Faraday Soc.*, **35**, 579 (1939).

(6) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950.

(7) W. J. Hamer, THIS JOURNAL, **56**, 860 (1934).

(8) R. O. MacLaren and D. F. Swinehart, *ibid.*, **73**, 1822 (1951).

(9) H. S. Harned and R. W. Ehlers, *ibid.*, **55**, 2179 (1933).

(10) D. F. Swinehart, *ibid.*, **74**, 1100 (1952).

(11) J. A. Bearden and H. M. Watts, *Phys. Rev.*, **81**, 73 (1951).