CCA-740

541.183.022
Conference Paper

Titration of Monolayers*

E. D. Goddard

Lever Brothers Company, Edgewater, New Jersey, U.S.A.

Received October 22, 1972

The early work on the effect of pH on ionizable materials at aqueous interfaces and the consequent development of the concept of an effective pH in the interface region, which differs from that in aqueous bulk phase, are outlined. Properties as a function of pH of monolayers of a variety of surfactant types, *viz.*, weak and nonelectrolytes (fatty acids, amines, amine oxides, alcohols, ethers), intermediate strength electrolytes (alkyl phosphates), strong electrolytes (alkyl sulfates and alkane sulfonates, both as spread and adsorbed monolayers) and two zwitterionic materials, are presented in some detail. Use is made of the approaches of Schulman and Hughes and of Davies for analysis of the results which are shown generally to be consistent with a shift towards weakness of the monolayer electrolyte because of the charge developed during its ionization; exceptions are the zwitterionic materials. Points of interest are (*a*) the need to invoke acid-soap formation to explain the surface potential— pH data of close-packed fatty acid monolayers; (*b*) a prevalent tendency for most of the anionic or nonionic monolayers to form oxonium ions at very low pH; (*c*) the relatively expanded nature of the uncharged form of monolayers of the highly dipolar amine oxide compared to its ionized form; (*d*) definite indications of »weakness« in both spread and adsorbed films of long chain sulfates and alkane sulfonates. A brief section on the influence of pH on polyelectrolyte monolayers is included.

INTRODUCTION

During the early part of this century considerable attention was given to the question of the distribution of ions near or at a charged interface or body in contact with an aqueous solution of an electrolyte. This led to the development of the theories of Gouy, Chapman, Stern, and others. In this paper we will be concerned largely with the ionic distribution as it affects hydrogen (or hydroxyl) ions near interfaces containing ionizable materials. The most widely investigated materials of this nature have been fatty acids, the properties of which were known to be highly influenced by the pH of their adjacent solutions from the early work on monolayers of Adam[1,2] and others. The first systematic investigation of the phenomenon seems to have been undertaken by Peters[3] who examined the influence of pH and, to some extent, ionic strength of aqueous solutions on their interfacial tension against benzene solutions of various fatty acids and aliphatic amines. It was noticed that the resulting curves of interfacial tension *vs.* pH resembled bulk phase titration curves but with an apparent shift of about 3 pH units in the direction of

---

* Based on a lecture presented at the *III International Summer School on the Chemistry of Solid/Liquid Interfaces*, Rovinj, Yugoslavia, July 1—5, 1972.

increased weakness. This subject was extended by Danielli[4] who, following earlier workers[5], suggested that the pH in the surface layer differed from that in the bulk aqueous phase because of the charge in the surface. This concept has gained general acceptance; by assuming that the degree of lowering of interfacial tension was directly proportional to the fraction of fatty acid ionized in the interface Danielli confirmed that the p*K* of the fatty acid could be shifted in the direction of weakness by as much as 4 units and that this shift was greater the lower the ionic strength of the aqueous solution. Danielli's results closely paralleled those of Schulman *et al.*[6,7] on the surface potential *vs.* pH curves of spread monolayers of fatty acids at the air/aqueous solution interface which again resembled a bulk phase titration curve; they revealed that surface potential is a particularly sensitive measure of ionization. Other approaches for studying the ionization of spread films of fatty acids have involved direct analysis, either chemical[8] or by infra red[9], of samples »skimmed« from the surface of subsolutions of varying pH; they led to results in harmony with the preceding.

In summary, it is now well established that ionizable materials at interfaces display an apparent weakness ascribable to, and determined in magnitude by, the electrical potential ψ generated at the interface by ionization. This has led to general acceptance of the concept of an effective pH in the surface phase, $\mathrm{pH_s}$, which differs from that in the bulk, $\mathrm{pH_b}$, and given by the expression

$$\mathrm{pH_s} = \mathrm{pH_b} + e\psi/2.3\,kT \qquad (1)$$

with a resulting shift in the dissociation constant K given by

$$\mathrm{p}K_\mathrm{s} = \mathrm{p}K_0 - e\psi/2.3\,kT \qquad (2)$$

This concept has been utilized and its applicability demonstrated in other fields, for example, in the titration of proteins[10] and polyelectrolytes[11], and for describing solution properties in the neighborhood of ionized surfactant micelles[12,13] — all cases involving systems in which a substantial electrical potential exists or develops on the »particle« in solution. The choice of the potential, ψ, employed depends on the particular electrical model chosen for interpretation of the data.

It is the intent of this paper to review the work on the ionization of various surfactants at the air/water interface which has been carried out during the last decade or so in the author's laboratory. Reference will, however, be made in several instances to data obtained in various other laboratories in order to present a coherent picture. In this respect it is perhaps appropriate at the outset to acknowledge the pioneering contributions made to the field by J. H. Schulman, already referred to, and by J. T. Davies[14,15] in applying the formalism of electrical double layer treatment to the properties of ionized monolayers.

Equations: In dealing with monolayers spread on aqueous solutions of uni-univalent electrolytes of molarity, c, the ψ term in this paper will generally be the so called »ψ_0« potential, *i. e.*, that in the plane of the charged head groups of the surfactant layer given by Gouy-Davies[15] expression,

$$\psi_0 = -(2\,kT/e)\ \sinh^{-1}\ (134/\mathrm{A}c^{1/2}) \qquad (3)$$

where A′ = area per charge in Å^2.

For monolayer »surface potential« (ΔV), we use the Schulman-Hughes equation[7]

$$\Delta V = (12 \pi \mu / A) + \psi_0 \tag{4}$$

where μ is the »surface moment« in mD of the monolayer material and A its area per molecule.

For the electrical contribution, π_r, to the surface pressure (π) of the monolayer we use the Gouy-Davies[15] expression

$$\pi_r = 6.1\, c^{1/2} \left[\cosh (e \psi_0 / 2\, kT) - 1\right] \tag{5}$$

This contribution, π_r, can be substantial, as is shown in the section on amine oxides.

As an example, for the ionization of a fatty acid, HA, we have

$$HA \rightleftarrows H^+ + A^- \tag{6}$$

$$\psi_0 = -(2\, kT/e)\ \sinh^{-1}\ (134\, \alpha / Ac^{1/2}) \tag{7}$$

where α is the degree of dissociation.

$$pH_b = pK + \log \alpha/(1-\alpha) - e\psi_0/2.3\, kT \tag{8}$$

$$\Delta V = (12\, \pi/A)\ [(1-\alpha)\, \mu_1 + \alpha\, \mu_2] + \psi_0 \tag{9}$$

where μ_1 and μ_2 are the surface moments of the uncharged and charged components of the monolayer. While, as will appear in the text, ΔV is usually a more sensitive indicator than π of the ionization of the monolayer, this is not always so. In these instances the π changes will be discussed in more detail. In general, standard techniques of measuring π-A and ΔV-A isotherms were employed, details of which can be obtained in the references cited.

We now present results on a series of materials which are representative of weak, non, intermediate strength, strong and zwitterionic electrolytes. In addition a short section on horizontally oriented, *viz.*, polymeric, films will be presented.

Fatty Acids

These have been the subject of most intense study by the insoluble monolayer technique. After the work of Schulman and Hughes[7], which had utilized various buffers to cover the pH range, Glazer and Dogan[16] using HCO_3^-/CO_3^{2-} buffer obtained substantially higher ΔV values over most of the pH range. Recognizing the high sensitivity of ionized fatty acids to foreign ions subsequent workers tended to avoid complex buffer systems. Thus Sanders and Spink[17] utilized ammonia solutions, and Betts and Pethica[18] completely unbuffered sodium chloride subsolutions adjusted in pH with small amounts of HCl or NaOH. The results obtained by these latter workers, while agreeing with one another, again led to substantially higher ΔV values than the earlier ones; the ΔV—pH characteristic no longer resembled a titration curve and was represented as essentially linear over the range pH 3 to 9. The work of Goddard and Ackilli[19], which emphasized the extreme sensitivity of the monolayers to minute amounts of contaminant polyvalent cations, especially Ca^{2+}, was shown essentially to confirm the data on unbuffered subsolutions of Betts and Pethica, but demonstrated the existence of a previously undetected critical point at

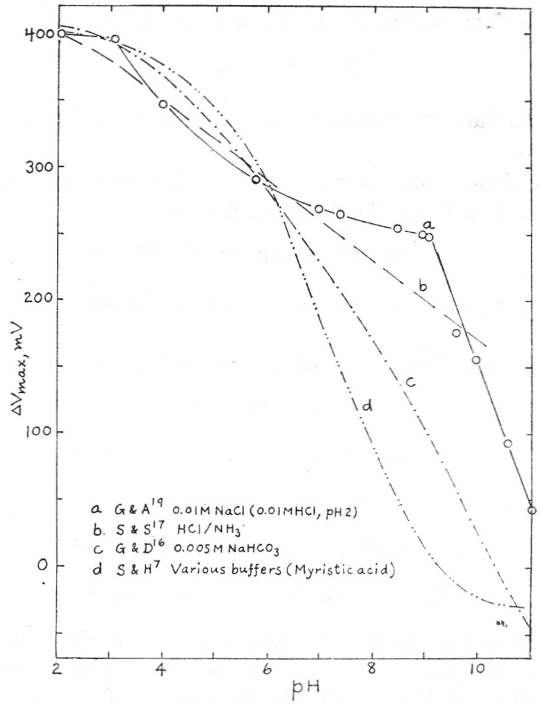


Fig. 1. Variation with pH of ΔV_{max} for close packed films of stearic (and myristic) acid reported by various workers.

ca. pH 9 above which there was a drastic reduction in ΔV values. See Fig. 1. This led the latter authors[19] to consider the possibility that complex, *i. e.*, acid-soap, formation was occurring in these close packed monolayer systems, but unfortunately an electrical analysis of the potential data, using the Gouy equations in their formal range of applicability together with the equation of Schulman and Hughes, did not allow of a choice between the simple and acid-soap dissociation modes. However, the intrinsic pK value derived for the fatty acid in the surface for conditions of low α where the Gouy equations are applicable was close to the accepted bulk phase values of 5 — results which were similar to those of Betts and Pethica.

The π-A characteristics[19] of the stearic acid monolayers were very revealing. Despite increasing ionization, the condensed nature of the film was almost unchanged up to pH 9. According to equation (5) considerable increases in the film pressure from the electrical contribution π_r, of the ionized component were to be anticipated. It was found that the pH had to be increased well beyond 9 before this occurred; the highly expanded films which were obtained at high pH did, however, provide qualitative substantiation of the Davies equation as was confirmed in later work[20]. These two observations concerning ΔV and π behavior in the vicinity of pH 9 seemed to be linked and this led to further investigation of the phenomenon, especially in the light of the well known strong association[21] known to occur between ionized and unionized forms of fatty acids in bulk phase. In continuing the study, the potential work[22] was repeated on unbuffered subsolutions in a CO_2-free envi-

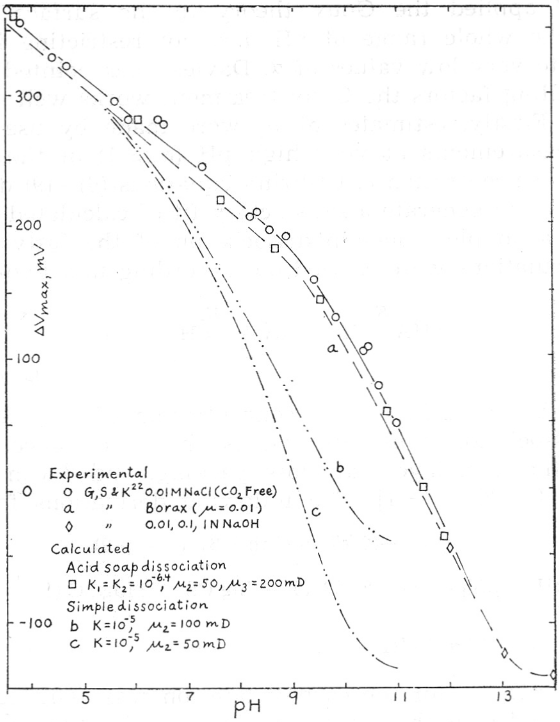


Fig. 2. Experimental ΔV_{max} -pH curves for behenic acid monolayers on 0.01 ionic strength sub-solutions at 26 °C; points for 0.1 and 1.0 M NaOH included. Calculations are for c = 0.01 M.

ronment; it was demonstrated that the critical phenomena occurring around pH 9 were partly, but not wholly, the consequence of buffering by atmospheric CO_2, since a slope change, albeit smaller, in the ΔV—pH characteristics still occurred at the same pH. Data similar to the latter were obtained using carefully purified borax buffer systems (Fig. 2). The hazards of changing even the type of monovalent counterion on the critical phenomena occurring around pH 9 are emphasized in work recently reported by Shah.[23]. To avoid the possibilities of dissolution of the more highly ionized monolayers of stearic acid our work had been continued with the longer chain behenic acid. The ΔV—pH relationships obtained for this C_{22} acid agreed very well with those obtained for the C_{18} acid. Further evidence for the high degree of interaction between the unionized and ionized forms of this fatty acid came from the observation that only above pH *ca.* 10—11 was a significant expansion of the monolayers, as predicted on electrical grounds, observed. It is for this reason, *viz.*, the propensity towards association between ionized and unionized forms, that we prefer not to attempt any quantitative analysis of the degree of ionization of spread monolayers from π-A curves, which route was taken by Payens[24] in his work on alkyl phosphonic acids; it must be emphasized, though, that the tendency towards association is lessened as surface concentration and chain length decrease.

To make an approach towards a (semi)quantitative treatment of the data, and for want of an electrcial model which appears to be any more directly applicable, we[22] applied the Gouy theory to the surface potential results obtained over the whole range of pH, *i. e.* not restricting it as in the case of the C_{18} acid to very low values of α. Davies[15] has pointed out that in view of several cancelling factors the Gouy treatment works well outside its formal working range. Firstly, estimates of μ_2 were made by use of equations (3) and (4) and measurements at very high pH ($\alpha \approx 1$) of the effect on ΔV of varying the salt concentration c. Utilizing equations (6)—(9) demonstrated that it was not possible to generate a satisfactory fit of calculated and observed ΔV through use of a simple, one-step dissociation of the fatty acid. See Fig. 2. Accordingly calculations were carried out according to a two-step dissociation.

$$\underset{2C\,(1-\alpha)}{2\,\mathrm{HA}} \overset{K_1}{\rightleftarrows} \mathrm{H}^+ + \underset{C\beta}{\mathrm{HA.A}^-} \overset{K_2}{\rightleftarrows} \mathrm{H}^+ + \underset{2C\,(\alpha-\beta)}{2\,\mathrm{A}^-} \tag{10}$$

where α and β are defined by the concentration of the various species, K_1 and K_2 are dissociation constants, 2 C is the total concentration of A in moles/liter for the monolayers at close packing, and β can be expressed as $\alpha/[4^{-1}C^{-1}(1-\alpha)^{-1}(K_2/K_1)^{1/2}+1]$. The following derivations follow[22]

$$\psi_0 = -(2\,kT/e)\sinh^{-1} 67\ (\alpha - \beta/2), \tag{11}$$

$$\mathrm{pH} = \mathrm{p}K_1 - e\,\psi_0/2.303\,kT + \log C\beta - 2\log 2C\,(1-\alpha), \tag{12}$$

and

$$\beta = (12\,\pi/A)\,[(1-\alpha)\ \mu_1 + (\alpha-\beta)\,\mu_2 + \beta\,\mu_3] + \psi_0 \tag{13}$$

where μ_1 is 200 mD, μ_2, for the carboxylate ion was assigned values between 50 and 100 mD, and μ_3 is the surface moment per long chain of the acid-soap.

For any arbitrary ratio of K_2/K_1 chosen the value of K_1 was obtained by matching the calculated and experimental ΔV-pH curves in the low pH region where almost all the acid is unionized. By a process of trial and error it was confirmed that, for a match at pH < 9, the value of μ_3 had to be close to that of μ_2. The best overall fit for an assumed depth of surface phase of 10 Å was obtained with $K_1 = K_2 = 10^{-6.4}$, $\mu_2 = 50$, and $\mu_3 = 200$ mD. The results are seen in Fig. 2.

Because of the assumptions, the number of adjustable parameters, and the limitations of the electrical model, the good correspondence between the theoretical and experimental curves cannot, of course, be taken as absolute confirmation of the acid-soap dissociation in the surface. However, the evidence adduced does provide a fair measure of support for such dissociation.

It is of interest to point out that, even above pH 12, ΔV continued to decrease. Although these conditions necessitated a change in subsolution ionic strength they do imply that in close-packed monolayers of fatty acid, ionization may not be complete even at pH 14. Similar trends have been reported elsewhere[20].

Fatty Alcohols and Ethers

It is well known that monolayers of these materials are little affected by subsolution pH. The ΔV-pH measurements of Schulman and Hughes[7] on octadecanol and octadecyl methyl ether, however, reveal two interesting features: *(a)* a fall-off in ΔV values of the alcohol at very high pH (*ca.* 12) indicative of the behavior of an extremely weak acid; *(b)* an upswing of ΔV

at very low pH (*ca.* 1), of both the alcohol and the ether, and, in fact, of fatty acid, and ascribed in all cases to oxonium ion formation. We shall return to this phenomenon later.

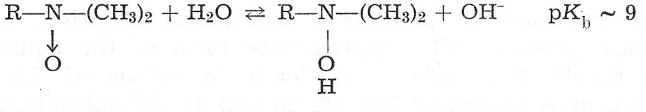
Fatty Amines

Fatty alkyl primary amines have been examined, following the early work of Peters, both by Glazer and Dogan[16] (C_{18}) and by Betts and Pethica[18] (C_{19}) over a wide pH range. The ΔV-pH characteristics obtained again resemble a titration curve, once more with indications of apparent weakness when compared to bulk pK values of amines. Both sets of data indicate high positive values around 700 mV (ionized form) at low pH which fall off at high pH (unionized form), although it is clear that the two sets of data differ considerably in detail. Moreover, the Betts and Pethica data reveal a considerable dependence on the monovalent counterion present (Na^+ *vs.* NH_4^+). These authors utilized equations (7) and (9) in differential form to estimate the pK value of the C_{19} amine from the ΔV-pH data. Their estimated pK extrapolated to a value of 10.1 in the limit of $\alpha = 0$. This somewhat high value could be lowered by *ca.* 0.5 units if a suitable dipole correction were introduced but there was no indication of constancy of pK with α.

It seems to the present author that more work on the pH dependence of the properties of amine monolayers is required. Examination of the π-A/pH data of Betts and Pethica suggests the degree of expansion of the monolayers at low pH is not consistent [see equation (5)] with that of a fully charged monolayer. This is reinforced by data of our own[25] on the C_{20} amine at pH 3, which reveal monolayers relatively condensed as compared with a longer chain C_{22} quaternary ammonium monolayer, as is illustrated in the next section. This may again reflect the presence of an ion/dipole association (amine/amine hydrochloride complexes have been reported in bulk phase[26]) or possible sensitivity to very small amounts of contaminant anions, although Betts and Pethica did take the precaution of carrying out some of their work in a protected atmosphere. Comparison of their data with those of Harkins[27] on the C_{18} homolog, octadecyl amine, which gave rise to highly expanded monolayers at low pH, does, however, suggest a rather critical dependence of the π-A characteristic of primary amines on chain length.

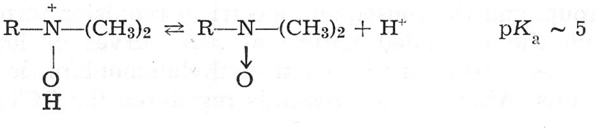
Amine Oxides

Amine oxides represent a relatively new class of surfactant whose surface characteristics have received little attention. They are very weak bases. A typical amine oxide, *viz.*, alkyl dimethyl amine oxide, ionizes[28] according to



$$\mathrm{R{-}\underset{\substack{\downarrow\\ O}}{N}{-}(CH_3)_2 + H_2O \rightleftarrows R{-}\underset{\substack{|\\ O\\ H}}{\overset{+}{N}}{-}(CH_3)_2 + OH^-} \qquad pK_b \sim 9 \qquad (14)$$

Alternatively, the ionic or protonated form may be considered a weak acid dissociating according to



$$\mathrm{R{-}\underset{\substack{|\\ O\\ H}}{\overset{+}{N}}{-}(CH_3)_2 \rightleftarrows R{-}\underset{\substack{\downarrow\\ O}}{N}{-}(CH_3)_2 + H^+} \qquad pK_a \sim 5 \qquad (14a)$$

In our studies[29], monolayers of the docosyl analog, DCDAO, were examined as a function of subsolution pH.

The π-A and ΔV-A plots for DCDAO films spread on 0.01 ionic strength subsolutions of various pH are presented in Fig. 3. In the range of area below 75 Å²/molecule the isotherms divide into two groups — a more expanded alkali group and a less expanded acid group. The most expanded curve was observed at pH 11 and the least at pH 3. In all cases transition in the π-A curve is detectable between 50 to 60 Å²/molecule. A maximum occurred around pH 5.6 in the ΔV value at closest packing which was 735 mV.

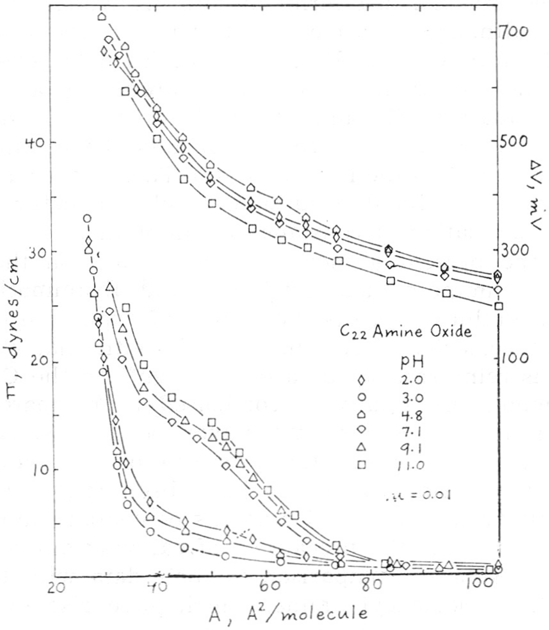


Fig. 3. Effect of pH on Π-A and Δ V-A of docosyldimethylamine oxide at 25° C. Subsolutions are of 0.01 ionic strength (NaOH or HCl/NaCl).

The effect of acidity at low pH is illustrated in Fig. 4 for substrates of HCl of varying ionic strength. Highest surface pressures were observed with the 0.01 M HCl and highest surface potential with 0.001 M HCl.

An unusual feature of the π-A curves is that, over most of the area range, DCDAO yields less expanded films in the ionized form, for which the Gouy-Davies equation (5) predicts a substantial electrical contribution, π_r, to the surface pressure. The approximate form of the equation, *viz.*, $\pi_r = 2\,kT/A - 6.1\,c^{1/2}$ (for $Ac^{1/2} < 38$), leads to values of 7.5, 9.5, 15.5 and 19.5 dynes/cm at A values of 100, 80, 50 and 40 Å²/molecule and c = 0.01 M. While the π values of an ionized monolayer represent the same sum of kinetic, cohesive and electrical terms[15], the influence of a formal positive charge on the head group, and the consequent electrical repulsion term, is usually readily evident from the expanded nature of π-A curves of ionized films. Fig. 4 shows the π-A curve of docosyltrimethylammonium ion (DCTAB) as an example of this. Whereas the pressures registered for DCTAB are, for reasons

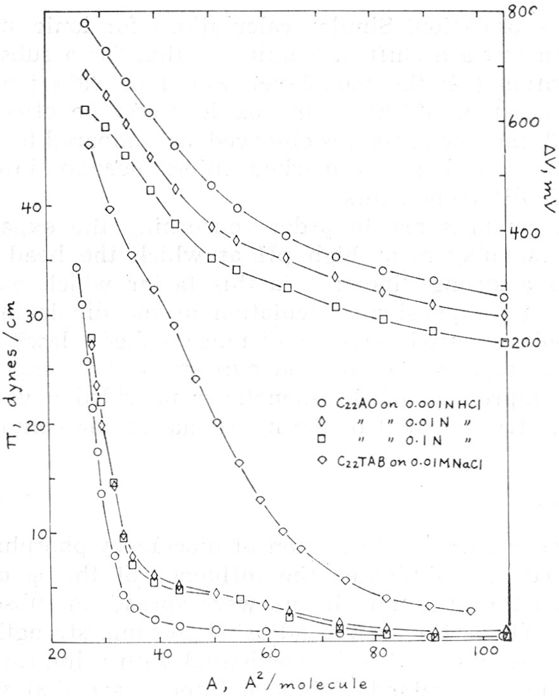


Fig. 4. Effect of HCl concentration on Π-A and Δ V-A isotherms of docosyldimethylamine oxide at 25° C. Isotherm (Π-A) for docosyltrimethylammonium ion included.

of monolayer cohesion, less than the π_r values listed above they considerably exceed those of the closely related DCDAOH$^+$.

There are two likely causes of the diminished repulsive forces in the latter case. The first is hydrogen bonding between the head groups either directly or through intervening water molecules. The quaternary ammonium group in ionized amine oxides is unusual in possessing a hydroxyl group. The strong electron attracting, positively charged nitrogen substantially augments the polarization of this OH group.

The second factor concerns completeness of ionization of the head group. If the pK_a value of DDAOH$^+$ is 5[28], then the ratio of DCDAO to DCDAOH$^+$ at pH 3 is 0.01, at pH 2, 0.001, and at pH 1, 0.0001, *i. e.*, substantially complete ionization in all cases. However, much of the monolayer information does not support this. Although $(\Delta\Delta V)_A$ values for the monolayers at pH 2 and pH 1 (respective ionic strengths 0.01 and 0.1) approximate 59 mV over most of the area range and thus conform to predictions of the Gouy-Davies[15] electrical model, this is not the case in comparing the pH 3 and pH 2 curves (ionic strengths 0.001 and 0.01) especially at higher areas. Similar indications of incomplete ionization come from a detailed study of the effect of pH and ionic strength on the π-A curves[29] which point to incomplete ionization in the area range below the transition point for all subsolutions except pH 1, 0.1 M HCl subsolution. This is predictable from the following: for ionic strength 0.01 and an area/charge of 75 Å^2, the calculated ψ_0 potential (Gouy) is 180 mV, corresponding to an upward shift in pH of 3 units in the surface phase and clearly sufficient to effect substantial deionization of the monolayer on a pH 2 subsolution. Similar calculations for ionic strength 0.1 subsolution lead to an upward shift of 2 units, so that for a subsolution of pH 1 according to equation (14) the monolayer would be 99% ionized. At higher areas, whereas ionization of the amine oxide might be effectively complete at both pH 1 and 2, the low pressures observed, as compared to those of DCTAB monolayers, point even here to marked intermolecular interaction in the case of the $DCDAOH^+$ monolayers.

Some closing remarks are in order concerning the expanded nature of the amine oxide monolayers at high pH at which the head groups, though unionized, possess a strong dipole: it is this factor which we believe is the primary cause of the expansion. Calculation of the dipole interaction forces based on a »dipole squared, inverse distance cubed« law[30] and a vertical orientation[31] of the dipoles, led to good agreement with experimental values of the work of compression of the monolayer provided a value, $\varepsilon = 10$, was taken for the dielectric constant of the interfacial region containing the amine oxide dipoles.

Alkyl Phosphates

In unpublished work[32] the ionization of dioctadecylphosphate was studied. In order to reduce or »eliminate« the influence of the ψ potential on the course of the ionization, the monolayers were spread on subsolutions of high ionic strength (H_2SO_4 or Na acetate adjusted to ionic strength 4 with NaCl). The monolayers were observed to be condensed with a limiting area ~ 40 Å²/ /mol in the pH range examined. Points of interest are that visual inspection of the ΔV *vs.* pH plot (Fig. 5) suggests a p*K* value of *ca.* 4, whereas the bulk values indicate a much stronger acid and, secondly, that the values at low pH, at which ionic strength would be expected to have little influence, are very similar to those reported by Parreira[33]. Both the present data and those of Parreira show a sharp upswing in the ΔV values at close packing at very

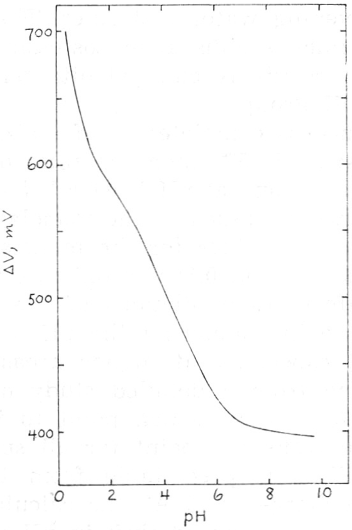


Fig. 5. Variation with pH of ΔV for close packed films of dioctadecyl phosphate on subsolutions of ionic strength 4, at 20° C.

low pH[7]. Because of a double long chain in the molecules their π-A/pH characteristics were rather insensitive to ionization. Parreira carried out an analysis of his ΔV-pH data according to the Betts and Pethica method[18] and obtained extrapolated $pK_{\alpha \rightarrow 0}$ values close to 2, which agrees well with the bulk phase value of phosphoric acid. A suitable dipole correction removed the dependence of pK upon α up to a value of α of 0.06 but not beyond. The early data[32] on the very concentrated salt solutions serve to demonstrate that even under conditions of very high ionic strength it is not possible to neglect the effect of the developing ψ on ionization. An electrical analysis of these old data was not attempted in view of the obvious strain imposed on the Gouy-Chapman model by the conditions of very high ionic strength.

Long Chain Sulfonates and Sulfates

In view of their stability to chemical hydrolysis we[34] elected to use a long chain sulfonate (actually an alkyl benzene sulfonate) rather than a long chain sulfate for our pH studies on a typical »strong acid« monolayer salt. Surface pressure and surface potential/area curves for nonadecylbenzene sulfonate are presented in Fig. 6. It is of interest that in this case the π-A data reveal considerable changes occur at pH $\sim$ 4, and that at pH 2 and 3 the monolayer is noticeably more expanded than at the higher pH's. A similar effect has been reported by Dreher[35], and by other workers[36,37] for monolayers of alkyl sulfates. Pethica and Few[36] ascribe the effect to an H-bonded structure involving hydronium ions, while Dreher ascribes it to deionization of the film. An interesting feature which the data of Fig. 6 display is relative insensitivity

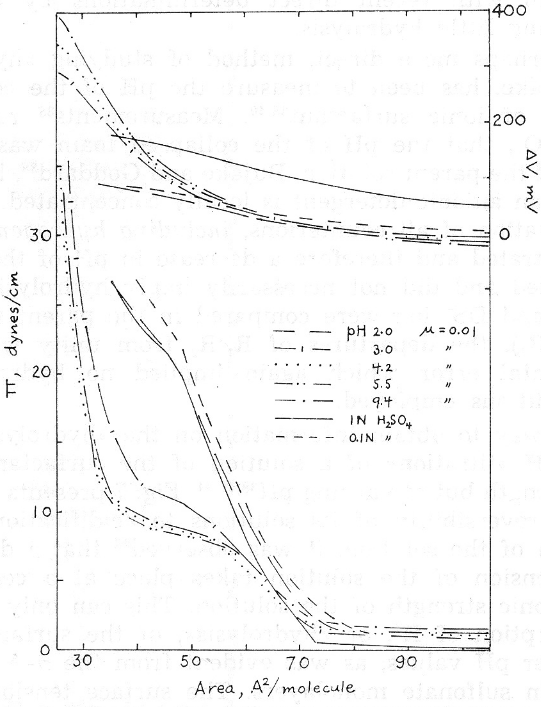


Fig. 6. Effect of pH on Π-A and Δ V-A isotherms of nonadecylbenzene sulfonate at 25 °C. Subsolutions are 0.01 ionic strength (NaOH of HCl/NaCl) except for 0.1 N H_2SO_4 and 1 N H_2SO_4.

of ΔV in the pH range where the π-A characteristics change but a marked elevation of potential at very low pH. Despite the fact that the latter conditions necessitated an increase in subsolution ionic strength, it is likely that the same phenomenon is involved as invoked earlier by Schulman[7] for fatty acids, alcohols and ethers, *i. e.*, oxonium ion formation, and which we also observed for the alkyl phosphates.

The pH effects above raise the question of the actual acid strength of alkyl sulfonates and sulfates, especially in the surface. This question of surface hydrolysis, *i. e.*, preferential adsorption of H^+ or its chemical combination with the head group, has been under discussion for many years, and has been approached from a different starting point, *viz.*, dependence of the surface properties of adsorbed monolayers on pH. For a 1 : 1 surfactant electrolyte Na^+S^-, the Gibbs adsorption equation can be written

$$-\mathrm{d}\gamma = \mathrm{x}kT\Gamma_{\mathrm{S}^-}\,\mathrm{d}\ln m_{\mathrm{NaS}}\, f_{\mathrm{Na}^+,\,\mathrm{S}^-}, \qquad (15)$$

where γ is the interfacial tension, Γ the surface excess and the rest of the terms have their usual significance, In the equation, x equals 1 or 2 for complete or zero hydrolysis[38], respectively. Attempts to measure directly the amount of adsorption and thus establish the correct form of the equation have involved in the main two methods, *viz.*, the radiotracer technique and a substantial extension of the interface by foaming followed by collapsing the foam and determining the surfactant concentrations. Foaming experiments[38] on sodium dodecyl sulfate (NaDS) and dodecane sulfonate ($NaDSO_3$) showed good agreement with the »2« form of the equation, and are in excellent agreement (NaDS) with recent direct determinations by the radio tracer method[39], indicating little hydrolysis.

A second, perhaps more direct, method of studying »hydrolysis« or the extent of H^+ uptake, has been to measure the pH of the collapsed foam of foamed solutions of ionic surfactant[38,40]. Measurements[38] revealed for both NaDS and $NaDSO_3$, that the pH of the collapsed foam was in fact slightly lower than that of the parent solution. Bujake and Goddard[38], however, stressed the point that if an anionic detergent is locally concentrated, *e. g.*, by adsorption, the concentration of all counterions, *including hydrogen ion,* would also be locally concentrated and therefore a decrease in pH of the collapsed foam was to be expected and did not necessarily imply hydrolysis. In fact, when the ratios of H^+ and DS^- ion were compared in the parent solution (R_1) and collapsed foam (R_2), the departures of R_1/R_2 from unity were found to be within experimental error which again implied no hydrolysis under the near-neutral conditions employed.

Yet another way to obtain information on the »hydrolysis« is via direct surface tension-pH »titration« of a solution of the surfactant maintained at constant ionic strength but of varying pH[38,40,41]. Fig. 7 presents data for $NaDSO_3$ which show the reversibility of its solutions to acidification. Depending on the ionic strength of the solution, it was observed[38] that a definite reduction of the surface tension of the solution takes place at a certain pH, which depends on the ionic strength of the solution. This can only mean that some preferential adsorption of H^+, or »hydrolysis«, of the surfactant takes place at these and lower pH values, as was evident from the π-A results obtained for the long chain sulfonate monolayers. The surface tension data allow an estimate of the degree of hydrolysis by use of the Gibbs equation.

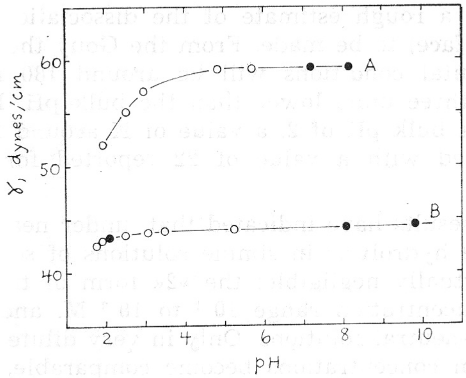


Fig. 7. Surface tension *vs.* pH for 10^{-3} M sodium dodecane sulfonate at 25° C. Curve A, 10^{-2} ionic strength; curve B, 10^{-1} (●, solutions taken to lowest pH followed by NaOH addition).

Activity coefficients are assumed to be unity, and the equation is written

$$-d\gamma/kT = \Gamma_{H^+} d\ln C_{H^+} + \Gamma_{Na^+} d\ln C_{Na^+} + \Gamma_{S^-} d\ln C_{S^-} + \Gamma_{HS} d\ln C_{HS}. \quad (16)$$

We consider a change in pH at constant ionic strength and at constant surfactant concentration. No formation of HS is assumed in the first case, and we set $dC_{H^+} = -dC_{Na^+}$. The last two terms of equation (16) disappear leading to the relation[40]

$$d\gamma/(2.303kT\, d\,\text{pH}) = \Gamma_{H^+}(1 + C_{H^+}/C_{Na^+}) - \Gamma_{S^-}(C_{H^+}/C_{Na^+}) \quad (17)$$

Calculations were made for the conditions of curve A, Fig. 7, *i. e.*, 10^{-3} M $NaLSO_3$, 10^{-2} M added electrolyte, and an assumed (constant) value of $1/\Gamma_{S^+}$ of 50 Å²/molecule. These indicate that when the pH is changed from 4 to 2, the $\Gamma_{H^+}/\Gamma_{S^-}$ ratio increases from 0.08 to near unity.

In the second case, formation of unionized acid is assumed according to the equilibrium,

$$[H^+]\,[S^-] = K\,[HS].$$

Because of the high acid strength of these long-chain acids, the relation $dC_{H^-} = -dC_{Na^+}$ still holds to a good approximation, and equation (16) can be written.

$$-d\gamma/kT = \Gamma_{H^+} d\ln C_{H^+} - \Gamma_{Na^+}(C_{H^+}/C_{Na^+})\, d\ln C_{H^+} + \Gamma_{S^-} d\ln C_{S^-} + \Gamma_{HS}(d\ln C_{H^+} + d\ln C_{S^-}). \quad (18)$$

With the further assumption of $dC_{S^-} = 0$, $\Gamma_{H^+} = \Gamma_{Na^+}\left(\frac{C_{H^+}}{C_{Na^+}}\right)$, and the same value of Γ_{S^-}, calculations based on the final equation

$$-d\gamma/kT = \Gamma_{HS} d\ln C_{H^+}. \quad (19)$$

indicate that Γ_{HS}/Γ_{S^-} increases from a value of 0.08 at pH 4 to 0.4 at pH 2 for the conditions of curve A.

Such data allow a rough estimate of the dissociation constant K of HS (if present in the surface) to be made. From the Gouy theory the ψ_0 potential under our experimental conditions will be around 180 mV and hence the »surface« pH about three units lower than the bulk pH. From the computed value of Γ_{HS}/Γ_{S^-} at a bulk pH of 2, a value of K around 20 is then obtained. This can be compared with a value of 22 reported for *p*-toluenesulphonic acid[42].

To sum up, the results have indicated that, under near-neutral conditions, the extent of surface hydrolysis in simple solutions of sodium lauryl sulfates and sulfonates is virtually negligible; the »2« form of the Gibbs equation is applicable in the concentration range 10^{-2} to 10^{-3} M, and probably down to about 10^{-4} M in near-neutral solutions. Only in very dilute solutions where the hydrogen and sodium concentrations become comparable, such as were used in some of the early radiotracer work, or in solutions artificially adjusted in pH to achieve this condition, would this situation change. The surface tension study, however, has indicated, for alkyl sulfonates, and confirmed, for alkyl sulfates, that under conditions of low pH, manifestations of preferential adsorption of H^+ over Na^+ become evident. This lends general support to the results obtained by the insoluble monolayer technique.

The results do not allow of an unequivocal choice between the various explanations of surface weakness of these electrolytes which comprise preferential adsorption of hydrogen ions, formation of unionized acid in the surface, ion pair formation, or other alternatives, although the data presented do seem to provide fairly strong evidence for deionization.

Zwitterionic Materials

Although materials of formal biological interest are not discussed, we will deal in this section with two materials[34], a sulfobetaine and a sulfoamine, which may be considered, from the ionic viewpoint, as the analog, respectively, of a lecithin (strong base, strong acid head group), and a cephalin (weak base, strong acid head group) although they differ in having the terminal group of the zwitterion negative rather than positive as is the case in the phosphatidyl materials. For work on the effect of pH on the properties of the latter materials the reader is referred to the literature[43,44].

(a) Sulfobetaine. — The material chosen for study, docosylammoniopropanesulfonate, $C_{20}H_{41}N^+(CH_3)_2(CH_2)_3SO_3^-$, forms liquid expanded monolayers[34]. See Fig. 8. In this respect it is similar to films of many lecithins. Because of internal compensation of the ionic components of the head groups, monolayers of zwitterionic materials are largely insensitive to changes in the ionic composition of the subsolution, including pH, although there is no agreement as to the exact configuration of the head groups in the interface (*viz.*, horizontal *vs.* vertical array of the ionic dipoles). It is noteworthy, however, that changes, albeit small, in both the π-A and ΔV-A characteristics are evident at very low pH ($\sim$ 1). See Fig. 8. That such changes occur at a much lower pH than with a simple long chain sulfonate is understandable since in the latter case, as discussed, the surface pH is noticeably lower than in the bulk phase, whilst in the present case little shift in surface pH *versus* that in bulk would be expected in view of the effectively zero ψ_0 potential of these monolayers.

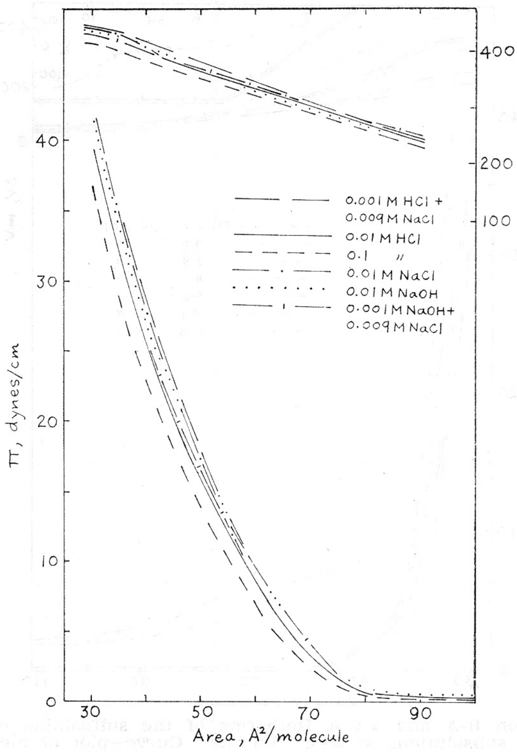


Fig. 8. Effect of pH on the Π-A and Δ V-A isotherms of the sulfobetaine at 25^0 C. Subsolutions are of 0.01 ionic strength except for the 0.1 M HCl.

(b) Sulfoamine. — The material chosen, 2-(*N*-methyl, *N*-2-hydroxydocosyl) aminoethane sulfonate-$C_{20}H_{41} \cdot CH(OH)CH_2N(CH_3)(CH_2)_2SO_3Na$, possesses a strong terminal acidic group (SO_3^-) and an ionizable tertiary nitrogen group. At neutral pH, its monolayers[34], presumably in zwitterionic form ,are also rather insensitive to changes in the ionic composition of the subsolution. On the other hand, at high pH when the amine group becomes progressively unionized, a marked expansion of the monolayer occurs and specific counter-cation effects are observed. Fig. 9 shows the influence of pH. At pH values in the range 2 to 8 of the 0.01 ionic strength subsolutions there is only slight variation in the π-A isotherms at least in the pressure range up to about 7 dynes/cm. At pH 9.2 a definite, though small, contraction of the monolayer occurred. This precedes a large expansion at pH 10.3 and an even larger one at pH 11.3.

For purposes of comparison, the results of Standish and Pethica[44] on 1,2-dipalmitoyl phosphatidyl ethanolamine (PE) are appropriate. Under subsolution conditions of 0.01 ionic strength they obtained rather condensed monolayers over the range pH 4—9.8 and detected a pronounced expansion at high pH (11.9) as we did with the sulfoamine[34]. The ΔV data for the latter material show there is a steady reduction of ΔV with increased pH similar to that obtained by Standish and Pethica for their PE monolayers.

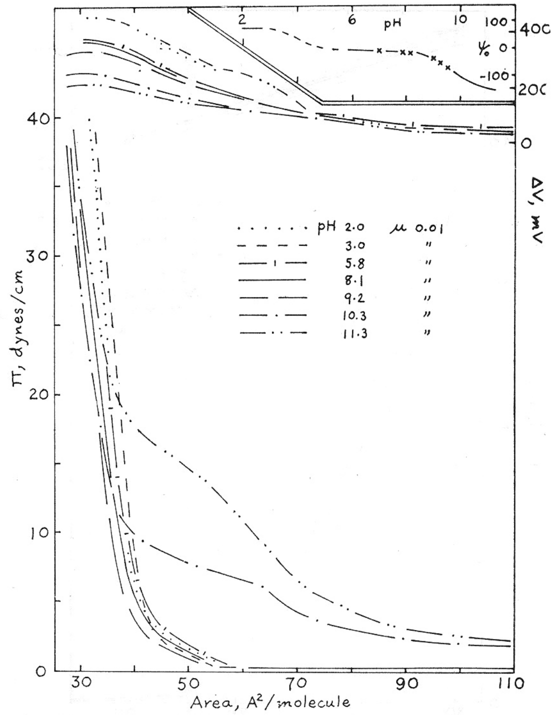


Fig. 9. Effect of pH on Π-A and ΔV-A isotherms of the sulfoamine on 0.01 ionic strength (NaCl + HCl or NaOH) subsolutions at 25° C. Inset: Curve—plot of measured values of ΔV (40 $Å^2$) *vs.* pH; x — calculated values of ψ^0 (40 $Å^2$) *vs.* pH.

The change of ΔV/A characteristics of the sulfoamine above neutral pH, and the attendant monolayer expansion at high pH are clearly connected with the deionization of the amine group. The change of ΔV with pH allows estimation of an ionization constant. To illustrate the ΔV/pH variation we have plotted ΔV values at an area of 40 $Å^2$/molecule as a function of pH. See the inset in Fig. 9. The plateau region at neutral pH resembles that found by Standish and Pethica[44] for dipalmitoyl PE monolayers. To estimate pK values they proposed that the plateau section of the ΔV-pH curve corresponds to the condition of $\psi_0 = 0$ and zero net charge at the monolayer. We applied this approach to estimate the pK_a values of the amine group. Application of the approach is less appropriate at low pH since in this region it is not clear that the change in ΔV corresponds (solely) to deionization of the sulfonate group, particularly since there is no corresponding expansion effect of the monolayers. We make use of the method described previously in the section on fatty acids to estimate values of ψ_0 as a function of »a«. In this case addition of base causes increasing deionization of the nitrogen, thus causing a net negative charge of the head group. The fraction of molecules which possess this negative charge is referred to as »a« in equations (7) to (9).

The value of ΔV at the plateau was taken as 340 mV and the calculations were restricted to values of a below 0.05 in order (a) to meet better the conditions under which the Gouy theory is applicable and (b) to stay within the range where the dipole contribution to ΔV would not be expected to change seriously from that of the zwitterion. The points so obtained were plotted as values of ($pH_b - pK_a$) as a function of ψ_0. Superimposing the ordinate $\psi_0 = 0$ of this graph on the ordinate $\Delta V = 340$ of the ΔV *vs.* pH graph and shifting laterally to get the best fit, we estimated a value for pK_a of 10. See Fig. 9. This value is reasonably close to the bulk value for trimethylamine. Any »surface weakness« of the amine resulting from the positive contribution of the charged amine groups to the ψ_0 potential is offset by a negative contribution from the neighboring sulfonate group, the net effect being incorporated into the above treatment.

Films of Horizontally Oriented, Polymeric Materials

This field is referred to only briefly. Early work on protein films by Glazer and Dogan[16], and by Harrap[45], revealed that the extent of ionization may be followed by observation of the ΔV-pH characteristics which again bore a similarity to a bulk phase titration. Harrap also observed that the surface pressure of the protein insulin was at a minimum at the iso-electric point, as was to be expected on electrical grounds. Synthetic polyelectrolyte monolayers have been widely studied, and the reader is refferred, for example, to the extensive studies of the Japanese school of H. Hotta and T. Isemura in the 1950's and of the more recent work of the Belgian school of J. Jaffé and J. M. Ruysschaert. It is of interest that in their most recent publications[46,47] these latter authors conclude that ΔV-pH curves are more readily analyzable than π-pH curves in terms of the degree of ionic dissociation and used methods of analysis very similar to those presented in this article. Interesting effects on the influence of stereoregularity of the polyelectrolytes on these surface properties were uncovered.

REFERENCES

1. N. K. Adam, *Proc. Roy. Soc.* (London) **A 101** (1922) 516.
2. N. K. Adam, *The Physics and Chemistry of Surfaces,* Oxford, 3rd Edit., 1941.
3. R. A. Peters, *Proc. Roy. Soc* (London) **A 133** (1931) 140.
4. J. F. Danielli, *Proc. Roy. Soc.* (London) **B 122** (1937) 155.
5. K. Linderstrom-Lang, *C. R. Lab. Carlsberg* **15** (1924) No. 7.
6. J. H. Schulman and E. K. Rideal, *Proc. Roy. Soc.* (London) **A 130** (1931) 284.
7. J. H. Schulman and A. Hughes, *Proc. Roy. Soc.* (London) **A 138** (1932) 430.
8. E. Havinga, *Rec. trav. chim.* **71** (1952) 72.
9. J. Bagg, M. D. Haber, and H. B. Gregor, *J. Colloid Interface Sci* **22** (1966) 138.
10. J. F. Danielli, *Biochem. J.* **35** (1941) 470.
11. A. Katchalsky, N. Shavit,, and H. Eisenberg, *J. Polymer Sci.* 13 (1954) 69.
12. G. S. Hartley and J. W. Roe, *Trans. Faraday Soc.* **36** (1940) 101.
13. P. Mukerjee and K. Banerjee, *J. Physical Chem.* **68** (1964) 3567.
14. J. T. Davies, *Proc. Roy. Soc.* (London) **A 208** (1951) 224.
15. J. T. Davies and E. K. Rideal, *Interfacial Phenomena,* Academic Press, New York, 1961.
16. J. Glazer and M. Z. Dogan, *Trans. Faraday Soc.* **49** (1953) 448.
17. J. V. Sanders and J. A. Spink, *Nature* **175** (1955) 644.
18. J. J. Betts and B. A. Pethica, *Trans. Faraday Soc.* **52** (1956) 1581.
19. E. D. Goddard and J. A. Ackilli, *J. Colloid Sci.* **18** (1963) 585.
20. E. D. Goddard, O. Kao, and H. C. Kung, *J. Colloid Interface Sci.* **24** (1967) 297.
21. H. C. Kung and E. D. Goddard, *J. Colloid Interface Sci.* **29** (1969) 242.

22. E. D. Goddard, S. R. Smith, and O. Kao, *J. Colloid Interface Sci.* **21** (1966) 320.
23. D. O. Shah, *J. Colloid Interface Sci.* **32** (1970) 570.
24. Th. A. J. Payens, *Thesis,* University of Utrecht, 1955.
25. E. D. Goddard, O. Kao, and H. C. Kung, *J. Colloid Interface Sci.* **27** (1968) 616.
26. H. C. Kung and E. D. Goddard, *Kolloid Z. & Z. Polymere* **232** (1969) 812.
27. W. D. Harkins and R. T. Florence, *J. Chem. Phys.* **6** (1938) 847.
28. P. Nylen, *Z. anorg. allgem. Chem.* **246** (1941) 227.
29. E. D. Goddard and H. C. Kung, *J. Colloid Interface Sci,* in press.
30. M. C. Phillips, D. A. Cadenhead, R. J. Good, and H. F. King, *J. Colloid Interface Sci.* **37** (1971) 437.
31. J. S. Mitchell, *Trans. Faraday Soc.* **31** (1935) 980.
32. E. D. Goddard and A. E. Alexander, Unpublished work (1949)
33. H. C. Parreira, *J. Colloid Interface Sci.* **20** (1965) 742.
34. E. D. Goddard and H. C. Kung, *J. Colloid Interface Sci.* **37** (1971) 585.
35. K. D. Dreher and J. E. Wilson, *J. Colloid Interface Sci.* **32** (1970) 248.
36. B. A. Pethica and A. V. Few, *Discussions Faraday Soc.* **18** (1954) 258.
37. J. N. Phillips and E. K. Rideal, *Proc. Roy. Soc.* (London) **A 232** (1955) 159.
38. J. E. Bujake and E. D. Goddard, *Trans. Faraday Soc.* **61** (1965) 190.
39. M. Muramatsu, Private communication.
40. J. W. James, and B. A. Pethica, *3rd Int. Congr. Surface Activity,* Butterworths, London **2** (1961) 227.
41. W. Kling and H. Lange, *2nd Int. Congr. Surface Activity,* Butterworths, London **1** (1957) 310.
42. R. H. Dinius and G. R. Chopin, *J. Phys. Chem.* **66** (1962) 268.
43. P. J. Anderson and B. A. Pethica, *2nd Int. Conf. Biochem. Problems of Lipids,* Ghent, 1955, 24.
44. M. M. Standish and B. A. Pethica, *Trans. Faraday Soc.* **64** (1968) 1113.
45. B. S. Harrap, *Proc. Int. Wool Textile Res. Conf.*, Australia, 1955, B 98.
46. J. Jaffé, J. M. Ruysschaert, and G. Bricman, *J. Polymer Sci.* **8** A 2 (1970) 817.
47. J. Caspers, J. M. Ruysschaert, and J. Jaffé, *J. Polymer Sci.* **C** No. 34 (1971) 73.

IZVOD

Titracija u monoslojevima

E. D. Goddard

U revijskom prikazu pokazani su fenomeni u monoslojevima na površini vodena otopina/zrak. Sistematski su prikazana svojstva monoslojeva, koji nastaju od triju tipova površinsko aktivnih tvari: slabih ili nelektrolita (masne kiseline, amini, amin-oksidi, alkoholi, eteri), elektrolita srednje jačine (alkil-fosfati) i jakih elektrolita (alkil-sulfati, alkan-sulfonati), Pokazano je da su amfoterni ioni (zwitterioni) poput sulfobetaina i sulfoamina (što su analozi bioloških surfaktanata lecitina i cefalina) materije s posebno interesantnim svojstvima. Obrađen je pojam površinskog pH koji se zbog postojanja površinskog naboja, znatno razlikuje od vrijednosti u masi supstratne otopine. Pokazano je da je mjerenje površinskog potencijala naročito pogodna i osjetljiva tehnika za proučavanje svojstava monoslojeva.

LEVER BROTHERS CO.
EDGEWATER, N. J., U. S. A.

Primljeno 22. listopada 1972.