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The Adsorption of Sodium Octanoate and Octanoic Acid at the Air/Solution Interface

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Surface tension measurements on solutions of octanoic acid in water at 20°C are recorded. Data are also given on the variation of surface tension of octanoic acid solutions with pH at 20°C at ionic strength 0.01. The effect of temperature on the surface tension of solutions in 0.1 *N* NaOH and HCl was also studied. The temperature effects were used to calculate the heats of adsorption of the unionised and ionised fatty acid, and these heat calculations are used to test theories of the ionic double layer. The effect of temperature on the equation of state of the monolayers is compared with the theory of Davies[1, 2].

INTRODUCTION

A large number of experiments have been reported on the surface tensions of aqueous solutions of fatty acids[11]. Only a few measurements are reported on octanoic acid solutions. Frumkin[3] has measured surface tensions of octanoic acid at 25°C in 0.07 *N* HCl. Forch[12], Korzheniovskii[13] and Tamamushi[14] have given data on solutions in water without added salts. None of these papers is recent.

Octanoic acid is well suited for studies on the changes of adsorption and monolayer characteristics resulting from ionisation in the monolayer. Longer chain fatty acids are too insoluble in acid solutions for conveniently accurate work, whereas the salts of the lower fatty acids give a small surface tension decrease except in high concentration ranges in which theoretical treatment of the data is more difficult. The object of the experiments recorded here was to test theories of the ionic double layer, firstly by comparing the heats of formation of the double layer with those predicted by the Gouy theory as extended by Derjaguin[4] and Verwey and Overbeek[5], and secondly to test the equation of state for ionised monolayers derived by Davies[1, 2] on the basis of the same theories.

EXPERIMENTAL

The octanoic acid used was an Eastman Kodak specimen. This material is claimed to be not less than 98% pure, the residual impurities being mostly homologues of octanoic acid. Analysis of the sample by vapour phase chromatography of the methyl ester confirmed the high purity and revealed no homologues or other

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impurities. Distilled water was taken from a laboratory still and passed over an ion exchange column. This water was then distilled in a well-steamed pyrex still. Good quality distilled water was shown to be necessary for work on fatty acids by Sanders and Spink[6, 7] because of the extreme sensitivity of fatty acid monolayers to calcium ions. Analytical grade sodium chloride contains significant amounts of calcium and other alkaline earths, and was therefore purified by precipitation from saturated solution with HCl gas. This method has been shown to remove alkaline earths[8]. Analytical grade caustic soda and hydrochloric acid were used.

Surface tension measurements were made by the drop volume method, using the corrections of Harkins and Brown[9]. The drops were formed on the ground glass tip of an Agla micrometer syringe. The barrel of the syringe was mounted in a jacket through which water was circulated from the thermostat. The whole assembly, including the micrometer, was enclosed in a metal cylinder immersed in the thermostat. This equipment will be described by Parreira[10]. At high *p*H the saturated atmosphere inside the cylinder was freed of CO_2 by passage of N_2 through caustic soda washers followed by passage through a vapour saturator. The reproducibility and accuracy of the method was best for octanoic acid solutions in the presence of added electrolyte, in which case the reproducibility was better than ± 0.1 dyne/cm. For solutions in water without added strong electrolyte the surface tension showed considerable ageing, and poor reproducibility resulted. No detailed study was made of this ageing effect in water solutions, and the values recorded on Fig. 1 are those of drops one minute after formation. The ageing effects were not found when strong electrolyte was added, and the surface tensions given for these solutions are equilibrium values.

The concentration scales in the figures refer to normalities at 20°C.

RESULTS

In Fig. 1 are shown the surface tension (γ) results for octanoic acid in water, 0.01 *N* HCl and 0.01 *N* NaCl at 20°C. The values in water are non-equilibrium as stated above. Changing from NaCl to HCl reduces the surface tension as expected, due to the repression of ionisation of the fatty acid. Fig. 2 shows the effect of *p*H on a 2×10^{-3} *M* solution of octanoic acid in solutions of 0.01 ionic strength. The surface tension decrease is largest in acid solution due to the preferred adsorption of the non-ionised form of the acid. This result may be compared with the findings of Peters[15, 16] and Danielli[17] who showed that the oil/water interfacial tensions of oil solutions of long chain acids were higher at low *p*H. In this case the ionised form of acid is better adsorbed at the interface. This is in agreement with the air/water results. The effect of *p*H on the surface tensions of octanoic acid solutions is also seen in Fig. 3. In this figure the effect of temperature on the surface tensions of the acid in 0.1 *N* HCl and 0.1 *N* NaOH is shown over a range of concentrations. When the data of Fig. 3 are plotted on a linear concentration scale it is seen that in 0.1 *N* HCl the surface tension-concentration relation is sigmoid. This is shown in Fig. 4 in which surface pressure (π) is plotted against concentration (π = lowering of γ). This unusual sigmoid curve in HCl solutions was obtained and discussed by Frumkin[3], whose results at 25°C in 0.07 *N* HCl are also shown in Fig. 4. In NaOH solutions the plot of π against concentration is not sigmoid, but shows a crossing of the graphs for 20°C and 40°C., as seen in Fig. 5.

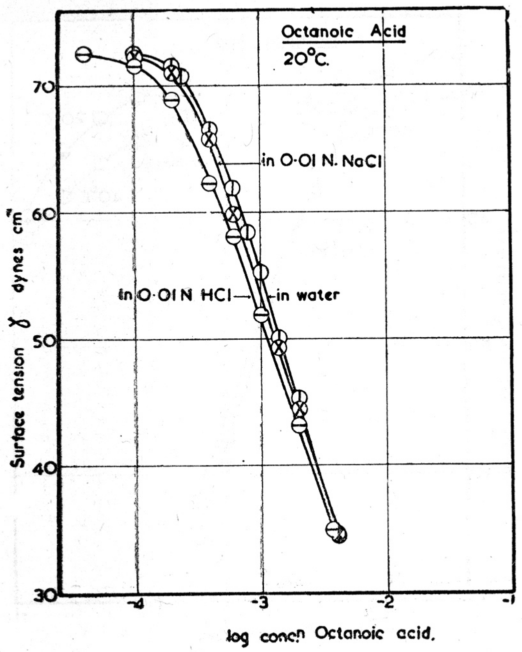

Figure 1. Surface tensions of octanoic acid solutions at 20°C ⦶ in water, ⊗ in 0.01 *N* NaCl, ⊖ in 0.01 *N* HCl.

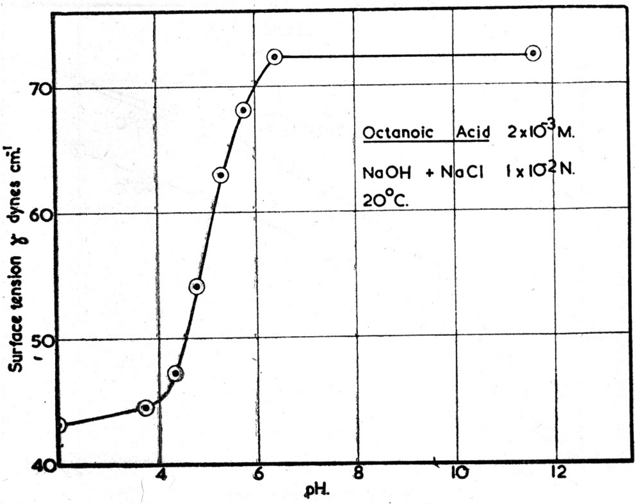

Figure 2. The effect of pH on the surface tensions of octanoic acid at 20°C. Concentration of the octanoic acid 0.002 *M*. In all systems the concentration of NaOH + NaCl was kept constant and equal to 0.01 *N*.

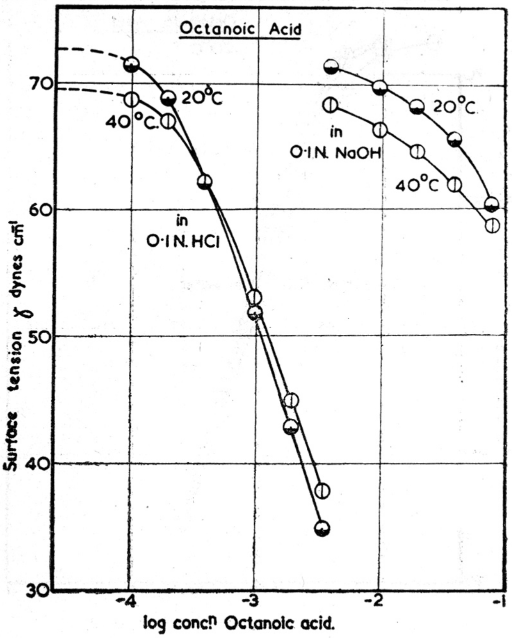

Figure 3. **Surface** tensions of octanoic acid solutions in HCl (0.10 *N*) and NaOH (0.10 *N*) at 20°C and 40°C.

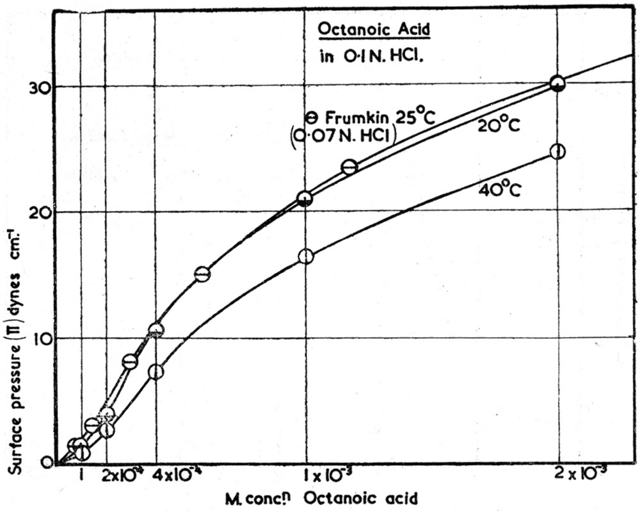

Figure 4. Surface pressures of octanoic acid solutions in HCl. ◒ in 0.1 *N* HCl at 20°C, ⦶ in 0.1 *N* HCl at 40°, ⊖ Frumkin's data[3] in 0.07 *N* HCl at 25°.

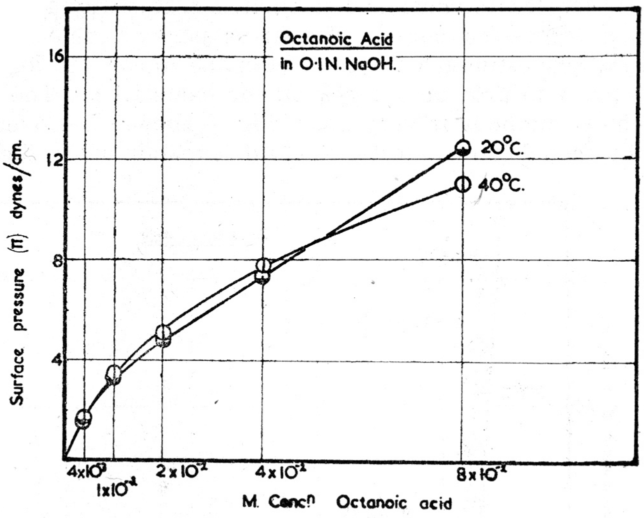

Figure 5. Surface pressures of octanoic acid solutions in 0.1 *N* NaOH at 20⁰ and 40⁰C.

DISCUSSION

The surface tension results may be used to calculate the surface density of the adsorbed films. For octanoic acid solutions in 0.1 *N* HCl the Gibbs adsorption equation may be used directly in the simple form

$$d\,\pi = RT\,\Gamma'\,d\ln c \qquad (1)$$

where R is the gas constant, T the absolute temperature, Γ' is the surface concentration in moles/cm.², and c is the bulk concentration of octanoic acid. The concentration may be used for activity in the dilute solutions used in this work. The invariance of Γ' with surface thickness is discussed by Guggenheim[18]. Equation (1) is applicable for non-ionised adsorbents in dilute solution. It has been shown[19, 20] that equation (1) may also be used for ionised detergents in the presence of excess neutral electrolyte. In the experiments given here for NaOH solutions the octanoic acid was dissolved in NaOH sufficient to give 0.1 *N* sodium ion concentration when the solution was made up to the required volume. In this way the sodium ion concentration is made constant but the *p*H changed with concentration of octanoic acid. The change in *p*H at 20⁰C was from 12.81 in the absence of octanoic acid to 12.72 for 4×10^{-2} *N* octanoic acid and to 12.20 at 8×10^{-2} *N* octanoic acid. Up to 4×10^{-2} *N* octanoic acid, therefore, changes in *p*H may certainly be neglected. In view of the negligible effect of *p*H on γ above *p*H ~ 7 (Fig. 2) changes in *p*H up to 8×10^{-2} *N* octanoic acid may also be neglected. With sodium ion concentration constant and *p*H nearly enough constant, the arguments given by one of us (B. A. P.)[19] lead to the conclusion that the surface density of the ionised octanoic acid may be calculated from the surface tension data with the 1 *RT* form of the Gibbs adsorption isotherm as given in equation (1). The molecular densities of the ionised and non-ionised octanoic acid calculated in this way are given in Fig. 6 as conventional force-area curves. The areas per molecule were calculated from the graphically estimated slopes of both the linear and logarithmic plots of Figs. 3, 4, and 5 to provide a check on the calculations. The agreement in the two graphical methods is very good. Fig. 6 shows that over most of the area range the monolayers of octanoic acid 'expand' when the temperature and pH are increased. This is a normal result. At areas below 50 Å^2/long chain, the π-A curves of the ionised fatty acid may cross the curve for the non-ionised acid.

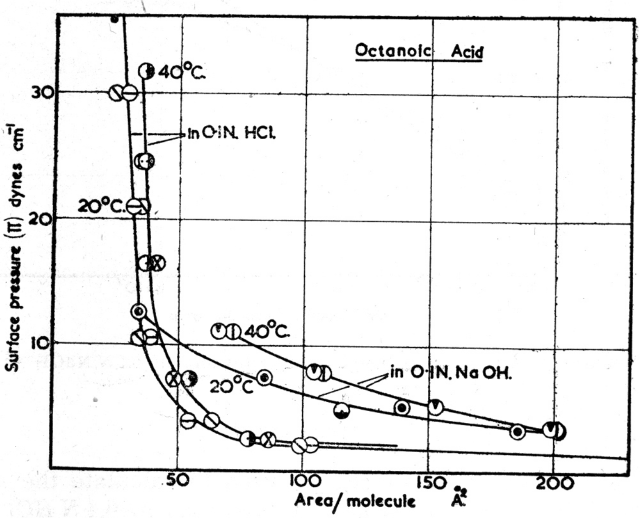

Figure 6. Force-area curves for octanoic acid solutions in 0.1 N HCl and 0.1 N NaOH at 20° and 40°C as calculated from equation (1).

The force-area curves of Fig. 6 allow a direct test of the equation of state for ionised films proposed by Davies[1, 2]. This equation of state is based on the theory of Derjaguin[4] and Verwey & Overbeek[5]. The increase in surface pressure ($\Delta\,\pi$) resulting from the ionisation of a monolayer is equated with the Helmholtz free energy of formation per unit area ($-\Delta\,F$) of the electrical double layer. For systems involving only uni-univalent electrolytes we have

$$\Delta\,\pi = -\Delta\,F = \frac{8\,n\,k\,T}{\varkappa}\left[\cos\mathrm{h}\ \frac{e\,\psi}{2\,k\,T} - 1\right] \tag{2}$$

where n is the number of ions of either sign/cc. of the bulk solution, k is the Boltzmann constant, $\varkappa$ is the Debye-Hückel characteristic reciprocal distance, e is the proton charge and ψ the Gouy double layer potential which is given by

$$\psi = \pm\,\frac{2\,k\,T}{e}\,\sin\mathrm{h}^{-1}\ \frac{\sigma}{2}\sqrt{\frac{2\,\pi}{\varepsilon\,n\,k\,T}} \tag{3}$$

where σ is the surface charge density and ε is the dielectric constant of the solution.

For a fully ionised monolayer (such as octanoic acid at $pH > 12$) σ is given directly by the surface density of the long chain ions if no ion-pairing occurs. The absence of ion-pairing is assumed in Davies' equation of state. The dielectric constant (ε) in equation (3) is usually taken as that for water. The tests hitherto given for the Davies equation of state[1, 2] depend essentially on making a reasonable assumption of the equation of state for an uncharged film, and adding to this a term for the free energy of the double layer. With the data on octanoic acid, however, the π-A curves for the ionised and non-ionised film enable $\Delta\pi$ to be obtained directly for comparison with $\Delta\pi$ obtained from equations (2) and (3). This is a more satisfactory procedure for testing the theory. The comparison of theory and experiment is shown on Fig. 7. At molecular areas greater than 80 Å²/molecule the experimental and theoretical values of $\Delta\pi$ show the same trend, with poor agreement at 20°C and better agreement at 40°C. At areas below 80 Å²/molecule the entire trend of the experimental curves is radically different from the theoretically expected values. At areas below 70 Å², Davies[1] proposed that the cohesion surface pressure in charged films at the air/water interface is independent of area, and is different for cationic and anionic monolayers. The rapid divergence of $\Delta\pi$ from the theoretical below 80 Å²/molecule could at first sight, therefore, be due to a difference in cohesion in ionised and non-ionised species. To see whether this assumption could give a better agreement for $\Delta\pi$ between experiment and theory the octanoic acid data at high and low pH have been compared directly with the extended equations of state for the air-water interface given by Davies. Firstly, for an uncharged film at the air/water interface Davies proposes (following Guastalla[21]) for higher areas only at 20°C

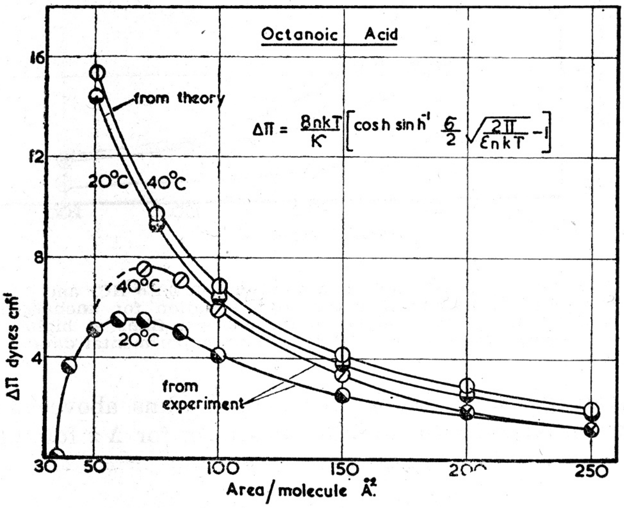

Figure 7. Comparison of the equation of state from the theory (Davies) and experiments for the octanoic acid at 20⁰ and 40⁰C.

$$\left(\pi + \frac{400\,N}{A^{3/2}}\right)(A - A_0) = k\,T \qquad (4)$$

where N is the number of CH_2 groups in the chain, and A_0 is a co-area taken to be 20 Å². In point of fact equation (4) fits the force-area curve for octanoic acid on 0.1 N HCl very well over the whole area range (see Fig. 8). The equation of state given by Davies for ionised films above 70 Å²/molecule is based en equation (4) with the addition of a term for $\Delta\pi$ for the double layer, that is

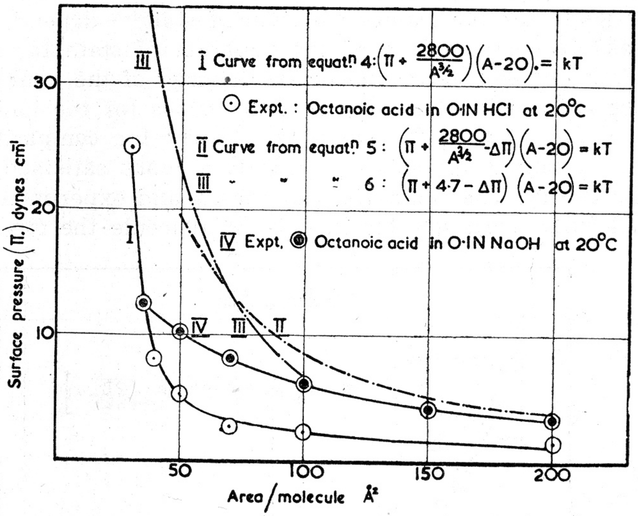

Figure 8. Force-area curves for octanoic acid solutions in 0.1 N HCl and 0.1 N NaOH at 20^0 as compared with theoretical equations. I curve from equation for uncharged films (Guastalla and Davies), II and III curves from equation for charged films at higher and lower areas, respectively (Davies). Circles denote experimental data.

$$\left(\pi + \frac{400\,N}{A^{3/2}} - \Delta\pi\right)(A - A_0) = k\,T \tag{5}$$

The divergence between theoretical and experimental values of $\Delta\pi$ shown in Fig. 7 at 20^0C above 70 Å²/molecule is therefore unrelated to differences in cohesion pressure in the ionised and non-ionised film. Below 70 Å², Davies proposes an equation of state for ionised films not based on equation (4), but on a cohesion pressure which is independent of area and dependent on the sign of the film. This equation may be written

$$(\pi + \beta N - \Delta\pi)\,(A - A_0) = kT \tag{6}$$

where π is given by equations (2) and (3) and β is constant equal to 0.67 for anionic monolayers. This equation does not fit the force-area curve of octanoic acid on 0.1 N NaOH, as shown on Fig. 8. It may be concluded that equations (2) and (3) do not quantitatively predict the free energy of the electrical double layer produced as a result of the ionisation of octanoic acid monolayers. Qualitative agreement is found for high area monolayers, the agreement being best at 40^0C. The disagreement with theory, which is most pronounced at low temperature, may be due to specific ion binding, neglect of solvation and other factors ignored in the derivation of equations (2) and (3). A further consideration concerns the equating by Davies of the free energy of formation of the double layer with the change in surface pressure due to ionisation, as in equation (2). In general, changes in surface pressures do not equal changes in Helmholtz free energy[22, 27]. Within the framework of the Verwey-Overbeek theory[5], $\Delta \pi$ may be equated to $-\Delta F$ as proved by Payens[24]. It does not follow that $\Delta \pi$ and $-\Delta F$ for the double layer may be equated in general.

A further test of the theory of Derjaguin[4] and Verwey & Overbeek[5] as applied to octanoic acid monolayers may also be made from the experimental data given here. The heats of adsorption of the ionised and non-ionised fatty acid may be calculated from a thermodynamic treatment given earlier[25, 26]. For the concentrations of octanoic acid and added electrolytes used in the present experiments the equilibrium integral heats of adsorption (ΔH) for both ionised and non-ionised fatty acid are given by

$$\left(\frac{\mathrm{d} \ln c}{\mathrm{d} T}\right)_{\pi} = \frac{H_B - H_S}{R T^2} = -\frac{\Delta H}{R T^2} \qquad (7)$$

using the notation of reference[25]. H_B and H_S are the partial molar heat contents of the adsorbing species in bulk and surface respectively. For the initial portions of the π-c plots, $\pi = \alpha c$, where α is the Traube constant. In this region

$$\frac{\mathrm{d} \ln \alpha}{\mathrm{d} T} = -\frac{\Delta H^0}{R T^2} \qquad (8)$$

where ΔH^0 is a standard integral heat of adsorption equal to ΔH when $\pi \rightarrow 0$. Using equations (7) and (8) the integral heats of adsorption of octanoic acid from 0.1 N HCl and 0.1 N NaOH have been calculated directly from the experimental results and are shown on Fig. 9 as a function of π for

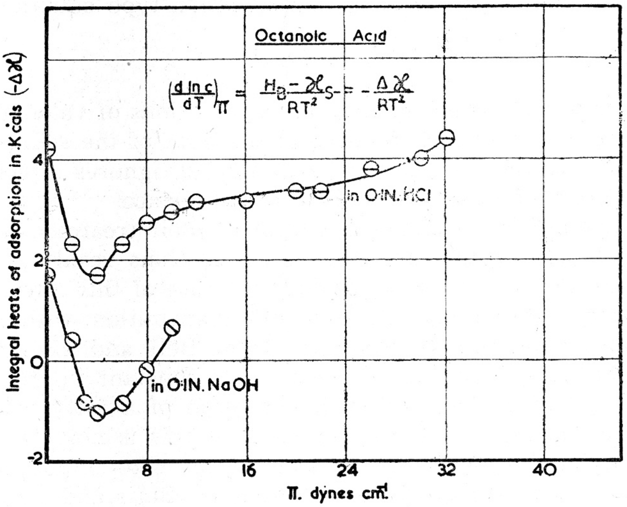

Figure 9. Integral heats of adsorption of octanoic acid in 0.1 N HCl and 0.1 N NaOH.

the interval 20°C — 40°C. By use of the force-area curves of Fig. 6, these heats may be rearranged as a function of area/molecule, using the mean area for any π between 20°C and 40°C. This rearangement of the integral heats of adsorption is shown on Fig. 10. These heats of adsorption on an area scale may now be used to test the validity of the Verwey-Overbeek theory for the Helmholtz free energy of the ionic double layer in the following way .

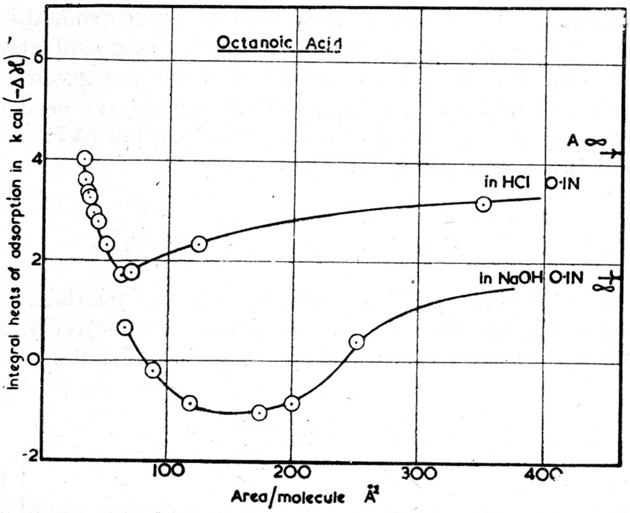

Figure 10. Integral heats of adsorption of octanoic acid in 0.1 N HCl and 0.1 N NaOH plotted as a function of area/molecule.

Underlying the derivation of equations (2) and (3) is the assumption that in region of the interface the concentration of ions of either sign may be related simply to the electrical potential by a Boltzmann-type equation of the form

$$n^{\pm} = n_0^{\pm} \, e^{\frac{z e \psi'}{k T}} \tag{9}$$

where $n^{\pm}$ refers to ionic concentration of + or — ions of valency z in a region near the surface at potential ψ' relative to the bulk of the solution; $n_0^{\pm}$ refers to the bulk concentration of the ions. Equation (9) ignores effects such as the change of solvation of ions near a dielectric interface.

Bell and Levine[27] have included a term in their treatment of free energy of the double layer for the free energy of the ions resulting from solvent interactions, but do not appear to consider the case of this interaction varying near the interface. Assuming a Boltzmann distribution with solvent interactions constant, equation (9) reappears from Bell and Levine's treatment. In the event of ion-solvent interactions being constant up to the interface, the energies of ionic interactions (*e. g.* ionisation of a fatty acid) should be constant through the double layer region. That this is not the case has been noted for a long chain phosphonic acid at the oil/water interface by Payens[24] and for stearic acid at the air/water interface by Betts and Pethica[26]. In both these cases, the intrinsic ionisation constants for these acids were apparently different in the interface as compared with the ionisation constants in the bulk, although it must be pointed out that the arguments both of Payens and Betts and Pethica involve a circularity if equation (9) is invalid. The heats of adsorption of octanoic acid given in Figs. 9 and 10, like the π measurements of Figure 7 are obtained on the basis of classical thermodynamics and may be used for testing the Verwey and Overbeek theory without involving any circularity. If the heats of dilution of the octanoic acid and sodium octanoate in the bulk solutions are taken as zero (which is justifiable at the low concentrations used), the differences between the equilibrium integral heats of adsorption for ionised and non-ionised octanoic acid shown on Fig. 10 will by Hess' Law be equal to the difference between the heats of ionisation of the octanoic acid in the surface and bulk phases respectively. These differences in heats of ionisation, denoted by $\Delta\Delta H_i$, are shown on Fig. 11. To compare these $\Delta\Delta H_i$ with those expected from the Verwey-Overbeek theory, we may note that from the assumptions of the theory the $\Delta\Delta H_i$ should be equal to the electrostatic part of the heat of formation of the double layer. This quantity may be calculated from the electrostatic part of the Helmholtz free energy of formation of the double layer ΔF_e, where

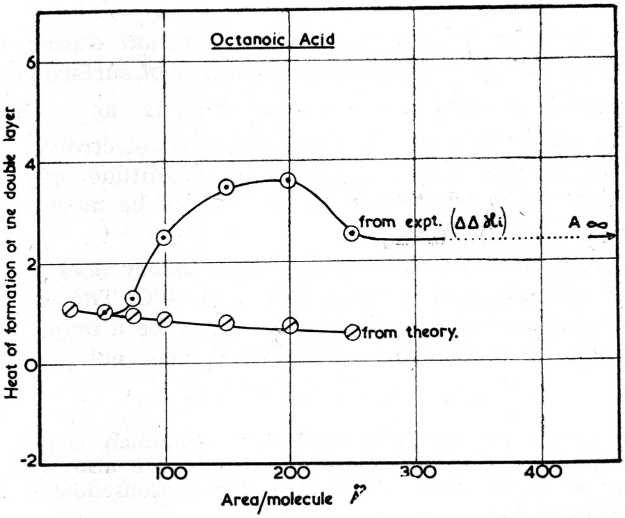

Figure 11. Heats of the formation of the double layer for octanoic acid as calculated from the Verwey-Overbeek theory and as revealed from experiments.

$$\Delta F = \Delta F_{chem} + \Delta F_e$$

$$= -\sigma\psi_0 + \int_0^\sigma \psi \, d\sigma \qquad (10)$$

ΔF_{chem} is the »chemical« part of the free energy of double layer formation. As shown by Verwey and Overbeek[5] ΔF_e may be expressed

$$\frac{1}{2}\sigma\psi_0 < \Delta F_e < \sigma\psi_0 \qquad (11)$$

Thus ΔF_e is equal to $-\Delta F$ at low ψ_0, and equal to $-x\,\Delta F$, at higher ψ_0 where $x > 1$.

On Figure (11) is shown ΔH_e^m, the electrostatic part of the heat of formation of the double layer per mole of octanoic acid. ΔH_e^m is obtained from ΔH_e (the electrostatic part of the heat of formation of the double layer per unit area) which is calculated from the change of ΔF_e with temperature as given by equations (2), (3) and (10). Thus

$$\left(\delta \frac{\Delta F_e}{T} \Big/ \delta \frac{1}{T}\right)_v = \Delta E_e \tag{12}$$

where ΔE_e is the electrostatic part of the energy of formation of the double layer per unit area, and

$$\Delta H_e = \Delta E_e + \Delta \pi \tag{13}$$

assuming that the pressure and volume are constant during the formation of the double layer. ΔH_e is calculated for a number of surface charge densities, and then converted to ΔH_e^m as shown on Fig. 11 as a function of the area/molecule at the surface of 0.1 N uni-univalent electrolyte. The ΔH_e^m is of the same sign as the $\Delta\Delta H_i$ but agrees in magnitude only at low areas/molecule. At high areas, where the surface should be more ideal, the $\Delta\Delta H_i$ are several times larger than ΔH_e^m.

It thus appears that the Verwey-Overbeek theory does not apply to the double layer of octanoic acid between 20°C and 40°C. The variation of heats of hydration of ions near dielectric interfaces may be a major reason for this lack of agreement — particularly as the $\Delta\Delta H_i$ does not go to zero at high areas/molecule.

We wish to record our thanks to Prof. J. H. Schulman, O. B. E. for his active interest in this problem, and for many discussions. We also wish to thank the Governing Body of Trinity Hall, Cambridge, for a Consolidated Zinc Research Grant for one of us (E. M.).

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IZVOD

Adsorpcija natrijeva oktanoata i oktan-karbonske kiseline na međupovršini zrak/otopina.

E. Matijević i B. A. Pethica

Prikazani su rezultati mjerenja površinske napetosti otopina oktan-karbonske kiseline u vodi kod 20⁰C. Dani su i podaci za promjenu površinske napetosti otopina oktan-karbonske kiseline s promjenom *p*H kod 20⁰C i ionske jakosti 0.01. Studiran je utjecaj temperature na površinsku napetost otopina u 0.1 *N* NaOH i HCl. Vrijednosti za napetosti površine, dobivene za različite koncentracije i kod različitih temperatura, upotrebljene su za izračunavanje toplina adsorpcije neionizirane i ionizirane masne kiseline. Ova izračunavanja iskorištena su za verifikaciju teorija dvostrukog ionskog sloja. Utjecaj temperature na jednadžbu stanja monosloja uspoređen je s Daviesovom teorijom.

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