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ADSORPTION OF ORGANIC COMPOUNDS AT ELECTRODES

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I. INTRODUCTION

The adsorption of organic compounds on the electrode surface can be studied by measuring the interfacial tension, γ, the electrode charge, q, and the differential capacity of the double layer, C, as well as the quantities in some way associated with γ, q or C, e.g. the dependence of contact angle and hardness, or of the boundary friction at the electrode surface, on the potential.

On the basis of the quantitative theory of the polarographic maxima of the second kind[1-3], conclusions on the adsorption of organic compounds can be drawn from the data on the inhibition by organic molecules of the tangential motions of a dropping mercury electrode.

Moreover, the adsorption of organic compounds at the electrode–solution interface can be studied directly by determining the decrease in the concentration of the substance adsorbed in a dilute solution, e.g. by the method of radio tracers developed by Blomgren and Bockris[4,160] or the spectrophotometric method of Conway *et al.*[5].

Information concerning the adsorption of organic compounds at the electrode surface can also be obtained indirectly from kinetic data, since any change in the structure of the electric double layer has an appreciable effect upon the rate of electrochemical processes, if these are not diffusion-controlled[6-8,161].

However, since the principal data on the effect of the electric field on the adsorption of organic compounds were obtained by the electrocapillary method and from measurements of differential capacity, only these two methods will be considered here in detail.

II. THE EFFECT OF ADSORPTION OF ORGANIC SUBSTANCES ON THE INTERFACIAL TENSION

1. *The Gibbs Adsorption Isotherm*

From Gibbs' adsorption equation

$$\mathrm{d}\gamma = -\sum_i \Gamma_i \,\mathrm{d}\mu_i = -RT\sum_i \Gamma_i \,\mathrm{d}\ln a_i \tag{1}$$

where Γ_i, μ_i and a_i represent the Gibbs surface excess per cm^2, the chemical potential and the activity of the *i*th component of the solution, respectively, it follows that the substances decreasing the interfacial tension are positively adsorbed at the interface of the phases. Henceforth, if no statement is made to the contrary, the location of the metal–electrolyte interface will be determined by the condition $\Gamma_{\mathrm{H_2O}}=0$. This condition determines the surface excesses of the other components of the solution unambiguously.

2. *Effect of the Presence of Organic Compounds in Solution upon the Interfacial Tension*

Isolated measurements of the interfacial tension in the presence of organic compounds were made as early as the end of the last century[9, 10], but systematic data on the effect of organic compounds on the electrocapillary curves were first obtained by GOUY[11]. He showed that in the presence of organic substances the electrocapillary curve always lies below the curve obtained with the solution of the supporting electrolyte. The decrease in the interfacial tension reaches its maximum in the vicinity of the potential of zero charge (p.z.c.) of the solution of the supporting inorganic electrolyte and becomes smaller with a pronounced rise in the negative or positive surface charge. In many cases, at sufficiently negative or positive potentials, no decrease in the interfacial tension due to the organic additions is observed at all, and the electrocapillary curve obtained in the prescence of an organic substance merges with that measured in the supporting solution.

Another rather common feature of electrocapillary curves in the presence of organic compounds is the shift in the electrocapillary maximum. The latter corresponds, according to Lippman's equation

$$q = -\frac{\mathrm{d}\gamma}{\mathrm{d}E} \tag{2}$$

(where E is the electrode potential* referred to the p.z.c.) to the coordinates in γ and E of the point for which $q=0$.

Electrocapillary curves observed in the presence of organic compounds show great diversity of form. Some characteristic shapes are shown in *Figure 1.* Of special interest is the sharp change in slope observed with the solutions of many neutral aliphatic compounds (*Figure 1a*), which in some cases assumes the character of a break.

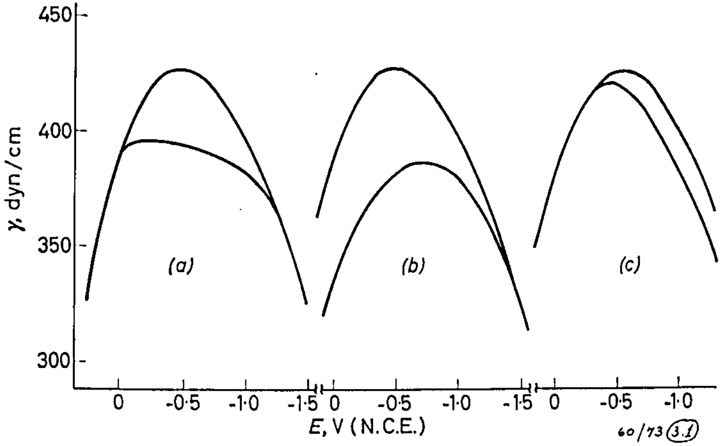

Figure 1. Electrocapillary curves: (*a*) 1N Na_2SO_4 *and* 1N $Na_2SO_4+0{\cdot}1$M $C_5H_{11}OH$*;* (*b*) 1N Na_2SO_4 *and* 1N Na_2SO_4+1M *pyrogallol;* (*c*) 1N H_2SO_4 *and* 1N $H_2SO_4+0{\cdot}1$N $[(C_2H_5)_4N]OH$

A comparison of electrocapillary curves measured in solutions of organic substances forming an homologous series shows that the decrease in interfacial tension and, consequently, adsorption at identical concentrations rise with an increase in chain length. According to Kaganovich, Gerovich and Osotova[162], in the case of adsorption on mercury of normal fatty acids (from acetic to caproic) from 1N Na_2SO_4 solutions, the Traube rule is observed. At small coverages the Traube coefficient is ~3·6. In accordance with the Gibbs equation, 1, the decrease in γ becomes greater with increasing concentration of the organic compound[12] (*Figure 2a*).

An increase in the concentration of the supporting electrolyte in the presence of an organic substance was shown by Gouy[11b] to result in a decrease in the interfacial tension. But in the case of a capillary inactive electrolyte, Na_2SO_4, this decrease in γ is caused by an increase of μ_{org}, the chemical potential of the organic substance ('salting out'

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* The symbol E is used in this Chapter for this definition of the potential and is a special value of the term $\Delta\phi$, the metal solution p.d. used in other Chapters.

effect), rather than by adsorption of the inorganic ions[12a]. In fact, if μ_{org} = const, as is, for example, the case with solutions saturated with respect to the organic substance but containing varying amounts of Na_2SO_4, the interfacial tension at the p.z.c. appears to be approximately constant, as shown in *Table 1*.

Table 1

Interfacial Tension in Presence of Organic Materials as a Function of Electrolyte Concentration

Organic additive	0·01N	Na_2SO_4 0·1N dyn cm^{-1}	1·0N
n-amyl alcohol (0·1M)	402·0	—	395·5
iso-amyl alcohol (sat)	388·3	388·3	388·7

On the other hand, surface-active ions of the supporting electrolyte not only change the chemical potential of the organic substance in the solution but also affect the structure of the electric double layer, increasing or decreasing the adsorption of organic molecules. Thus, in the presence of I$^-$ anions, which decrease the mutual repulsion between the adsorbed cations of $[(C_3H_7)_4N]^+$, the adsorption of the latter cations increases[11b, 12a]. At the same time, the specific adsorption of

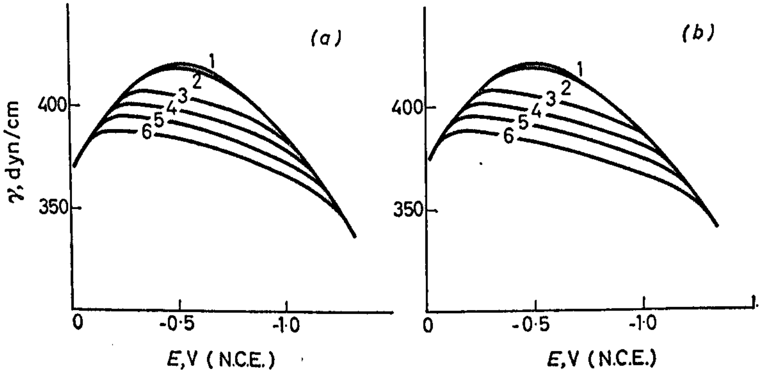

Figure 2. Electrocapillary curves observed in 1N NaCl *with additions of* *t*—$C_5H_{11}OH$ (FRUMKIN[12b])

1 0; 2 0·01M; 3 0·05M; 4 0·1M; 5 0·2M; 6 0·4M

(a) experimental data; (b) calculated

Br^- and I^- anions decreases the adsorption of ethyl alcohol, phenol and of the salicylate anion[13].

3. *Frumkin's Theory of Adsorption of Compounds as a Function of Potential*

A quantitative theory of the adsorption of organic compounds at the electrode–solution interface, which accounts for the shape of the electrocapillary curves, was developed by FRUMKIN[12b] in 1926. According to him, the work expended in the process of adsorption depends on the presence of the electric double layer at the metal–electrolyte interface, and the contribution due to electric forces per unit area on complete coverage can be expressed as the sum of two terms

$$W_s = \tfrac{1}{2}(C_0 - C')E^2 + C'E_N E \qquad (3)$$

where C_0 and C' are the capacities of the double layer at the surface coverages by the organic substance $\theta = 0$ and $\theta = 1$, respectively; E is the electrode potential relative to the p.z.c. at $\theta = 0$ and E_N the shift in the p.z.c. during the transition from $\theta = 0$ to $\theta = 1$. A better approximation is obtained if we substitute in equation 3 $\Delta\gamma_e$ to $\frac{1}{2}C_0E^2$, where $\Delta\gamma_e$ = the lowering of γ caused by the electric double layer in the absence of the substance adsorbed at a given value of E. The first term in equation 3 can be associated with the change in the energy of the double layer condenser due to a decrease in the dielectric constant and to an increase in the double layer thickness, occurring when the organic molecules enter the double layer, whereas the second term can be associated with the dipole moment of the molecules adsorbed, which are substituted for the water molecules in the process of adsorption in the surface layer.

The significance of equation 3 can be made clear if one considers the work expended in introducing a dielectric with a lower dielectric constant into a flat condenser taken as a model of the electric double layer. In this case, E denotes the potential difference between the plates of the condenser of capacity C_0, the charge/cm^2 is C_0E, and the electric energy stored/cm^2, $\frac{1}{2}C_0E^2$. The potential of the negative plate can be arbitrarily equated to zero. With the quantity E held constant, a substance is introduced into the space between the condenser plates (with the area 1 cm^2) and this reduces the value of the capacity at complete coverage of the whole area to C'. Let us denote the amount of substance introduced per cm^2 by Γ and the amount needed for the coverage of 1 cm^2 by Γ_m. Then, the area on which the capacity will be reduced to C' will be equal to ΓS, where $S = 1/\Gamma_m$.

Suppose now that the substitution of a new dielectric will not only result in the capacity reduction but, in the absence of free charges on the condenser plates, will also set up a potential difference, E_N, between the latter, due, for instance, to the presence of oriented dipoles in the layer introduced. The electric energy stored in this dielectric, in the absence of an external field, is $\frac{1}{2}C'E_N^2$ per cm^2. After the substitution of the dielectric, the charge on the condenser per cm^2 will be equal to $C_0E(1-\Gamma S)+C'(E-E_N)\Gamma S$, and consequently, at the potential E, the amount of electricity

$$C_0E-[C_0E(1-\Gamma S)+C'(E-E_N)\Gamma S] = [C_0E-C'(E-E_N)]\Gamma S$$

will be released. After the substitution of the dielectric, the electrical energy of the condenser will be equal to

$$\tfrac{1}{2}C_0E^2(1-\Gamma S)+\tfrac{1}{2}C'^2\Gamma S$$

Hence it follows that upon substitution of the dielectric the work expended to increase the electric energy of the system is equal to

$$\tfrac{1}{2}C_0E^2(1-\Gamma S)+\tfrac{1}{2}C'^2\Gamma S+[C_0E-C'(E-E_N)]E\Gamma S-\tfrac{1}{2}C_0E^2-\tfrac{1}{2}C'E_N^2\Gamma S$$
$$= [\tfrac{1}{2}(C_0-C')E^2+C'E_NE\tfrac{1}{2}-C'E_N^2]\Gamma S$$

If the work expended per cm^2 at a definite value of E is denoted by $\bar{W}_E$, it is evident that

$$\bar{W}_E-\bar{W}_0 = [\tfrac{1}{2}(C_0-C')E^2+C'E_NE]\Gamma S \qquad (4)$$

At a large enough value of $|E|$ and $C_0>C'$ the value of $\bar{W}_E-\bar{W}_0$ is always positive, which accounts for the decrease in the adsorption of organic substances with increasing potential from that of zero charge. Despite the fact that at a constant potential the decrease in the capacity results in that in the amount of energy stored in the capacitor, the work expended in introducing the substance lowering the capacity increases with a rising $|E|$ on account of the expenditure of energy necessary to set free part of the charge. According to equation 4, the work expended per mole due to the presence of the electric field, in agreement with equation 3, is equal to

$$[\tfrac{1}{2}(C_0-C')E^2+C'E_NE]S = W_sS$$

By applying this deduction to the adsorption of an organic substance, we find that since the electrostatic contribution to the adsorption work per mole of organic substance is equal to W_sS, where S is now the area occupied by 1 mole of adsorbed substance, the effect of the electric field on adsorption can be expressed in terms of an increase in the bulk concentration of the organic substance needed to attain a definite surface excess upon the transition from the zero value of the potential difference, i.e. from the electrocapillary maximum, to the p.d. E, in the ratio exp $[(W_sS)/RT]$, i.e.

$$\ln \frac{c_E}{c_0} = \frac{W_sS}{RT} \tag{5}$$

Here c_E/c_0 is the ratio of the concentrations of the adsorbed substance which are in equilibrium with the same adsorbed amount at the potential difference E and at the potential of zero charge* at $\Gamma=0$, respectively.

The deduction presented here can be generalized for the case of a variable capacity condenser, but this will not be done, since the result needed can be readily obtained for the general case from the thermodynamic theory of electrocapillarity.

In fact, the basic equation of electrocapillarity is of the form

$$\mathrm{d}\gamma = -q\,\mathrm{d}E - RT\sum_i \Gamma_i\,\mathrm{d}\ln a_i \tag{6}$$

where E, as in equation 2, denotes the metal–electrolyte potential difference referred to the point of zero charge in the absence of the organic substance.

Hence it follows for a dilute solution of the organic substance at constant activity of the indifferent electrolyte

$$\mathrm{d}\gamma = -q\,\mathrm{d}E - RT\Gamma\,\mathrm{d}\ln c \tag{6a}$$

whence

$$\frac{1}{RT}\left(\frac{\partial q}{\partial \ln \mathrm{c}}\right)_E = \left(\frac{\partial \Gamma}{\partial E}\right)_c \tag{7}$$

Equation 7 was first deduced by Gouy[11c] in 1916. It follows from it that

$$\left(\frac{\partial \ln c}{\partial E}\right)_\Gamma = -\left(\frac{\partial \ln c}{\partial \Gamma}\right)_E\left(\frac{\partial \Gamma}{\partial E}\right)_c = -\frac{1}{RT}\left(\frac{\partial q}{\partial \Gamma}\right)_E \tag{8}$$

This equation is of principal interest for the problem under consideration since, by making certain assumptions about the value of

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* In the case when the orientation of the substance adsorbed at the metal–electrolyte interface may vary, the decrease in the standard free energy of adsorption under the influence of the electric field of the double layer can result in the orientation of adsorbed molecules on a strongly charged surface being essentially different from that on an uncharged surface[21]. This consideration is of importance in understanding the conditions of reduction of organic substances at sufficiently negative potential values[14, 161].

$(\partial q/\partial \Gamma)_E$, the dependence of the adsorbability of the substance on the electric field of the double layer can be determined.

The simplest assumption is expressed by

$$q = q_0(1-\theta)+q'\theta \tag{9}$$

where θ = coverage of the surface with the adsorbed substance and q_0 and q' = the values of q at $\theta=0$ and $\theta=1$, respectively. Equation 9 is valid when the covered and the uncovered parts of the surface can be considered as two condensers connected in parallel. As will be shown below, this concept can be regarded only as an approximation. According to equation 2

$$q_0 = \frac{\partial(\Delta\gamma_e)}{\partial E} \tag{10}$$

If the initial double layer capacity can be equated to a constant C_0, $\Delta\gamma_e=\frac{1}{2}C_0E^2$. For the majority of calculations, however, this approximation proves to be too rough. On the contrary, since the capacity of the covered part of the surface is much smaller than that of the uncovered one, it can be considered to be approximately equal to a constant C'. The difference between C' and the initial capacity may be due both to a change in the effective dielectric constant of the double layer condenser and to that in the thickness of the double layer caused by the adsorption of the organic substance.

The following expression is obtained for q':

$$q' = C'(E-E_N) \tag{11}$$

where E_N is the potential of the point of zero charge on the covered part of the surface. The shift in the point of zero charge in the case of the adsorption of an organic substance is usually associated with the change in the electric moment of the surface layer upon the substitution of the dipoles of the organic substance for the oriented water dipoles[11c, 12a]. This problem has been discussed in more detail by FRUMKIN[15a] with regard to the change in the potential difference at the air-solution interface on adsorption of organic substances* (cf. [16, 17]).

The orientation of dipoles undoubtedly plays in the case of the adsorption of organic substances an essential part in the change of the

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* It should be noted that, while the change in the capacity is connected with the penetration of the molecules of the organic substance inside the electric double layer, the oriented dipoles of the polar groups of adsorbed organic compounds are bound to influence the quantity E_N when they are located outside the ionic double layer as well, since the potential differences in the layers connected in series are additive.

p.z.c., but it has to be kept in mind that this change may be due to other causes as well, e.g. to a change in the potential distribution in the electronic cloud at the metal surface. The use of equation 11 is not connected with any suppositions about the nature of the quantity E_N, but the assumption that E_N may be regarded as a constant independent of Γ and E is an approximation the validity of which can be proved only from experimental data. It is essential for the practical application of the relationships obtained that the inaccuracies in the calculation of q' are often relatively of no great importance, since the change in q for adsorption of many organic compounds is determined in the first place by the term $q_0(1-\theta)$.

The last assumption to be made in connection with equation 9 concerns the quantity θ. If the assumption that the coverage is proportional to the adsorbed amount is taken as the first approximation, $\theta = \Gamma/\Gamma_m = \Gamma S$, where Γ_m is the maximum adsorbed amount per 1 cm^2 and S the area covered by 1 mole of adsorbed substance.

On the basis of the above and from equations 10 and 11, equation 9 can be written in the form

$$q = \frac{\partial(\Delta\gamma_e)}{\partial E}(1-\Gamma S) + C'(E-E_N)\Gamma S \tag{12}$$

It follows from equations 12 and 8 that

$$\left(\frac{\partial \ln c}{\partial E}\right)_\Gamma = \frac{1}{RT}\left[\frac{\partial(\Delta\gamma_e)}{\partial E} - C'(E-E_N)\right]S$$

$$\ln\frac{c_E}{c_0} = \frac{1}{RT}[\Delta\gamma_e - \tfrac{1}{2}C'E^2 + C'E_N E]S \tag{13}$$

Equation 13 corresponds to equation 5, if $\Delta\gamma_e$ is equated to $\frac{1}{2}C_0E^2$ i.e if the capacity at $\theta=0$ is considered to be a constant. For the potential E_m, corresponding to the maximum of the adsorption, it follows from equation 5 that

$$E_m = -\frac{C'E_N}{C_0-C'} \tag{14}$$

In order to find, on the basis of equation 13, the dependence of the adsorption on the electrode potential, it is necessary to know the equation of the adsorption isotherm. A convenient expression was deduced by FRUMKIN[15b] by combining an equation of the state of the surface layer allowing for both surface coverage and interaction between the adsorbed particles

$$\frac{\Delta\gamma}{RT\Gamma_m} = -\ln(1-\theta) - a\theta^2 \tag{15}$$

and the adsorption equation of Gibbs, 1. $\Delta\gamma$ is the lowering of the interfacial tension by the organic substance, that is the surface pressure of the substance adsorbed, and a a quantity characterizing the interaction between the adsorbed particles. The equation of the adsorption isotherm thus obtained is

$$Bc = \frac{\theta}{1-\theta} \exp(-2a\theta) \tag{16}$$

where B is the constant determining the adsorption equilibrium at small coverages. At $a=0$, equation 16 is transformed into the Langmuir isotherm

$$Bc = \frac{\theta}{1-\theta} \tag{16a}$$

Therefore, equation 16 may be considered as representing Langmuir's adsorption isotherm, assuming that the work of adsorption changes linearly with the coverage. A similar equation was deduced later as an approximate expression for the adsorption isotherm for a regular localized monolayer by FOWLER and GUGGENHEIM[18]. A positive value of a in equation 16 corresponds to attraction, a negative to repulsion between adsorbed particles.

PARSONS[163] criticized the use of Langmuir's adsorption isotherm when considering the adsorption from solutions as deduced for the case of localized adsorption. He proposed the theory of adsorption of organic molecules on the basis of the equation of state of HELFAND, FRISH and LEBOWITZ[164] which expresses the two-dimensional pressure of a system of rigid spheres, corrected for the long-range interaction between adsorbed molecules in the same way as it was done by Frumkin. However, the lowering of the interfacial tension by the adsorbed layer should be treated as the two-dimensional analogue of the osmotic pressure of a concentrated solution rather than as that of the pressure of a compressed gas. This analogy leads in the case of the ideal behaviour of the solute, both in the bulk of the solution and in the surface layer, assuming that the molecules of the solvent and of the solute occupy the same areas, to the equation of state

$$\Delta\gamma = -RT\Gamma_m \ln(1-\theta)$$

and therefore to Langmuir's adsorption isotherm[15b,165a]. The same result is obtained from the statistical theory of ideal solutions[166,167]. This justifies the use of equation 15 as a semi-empirical basis for the treatment of the adsorption from solutions. For a more detailed discussion of this question cf.[165a-c].

The effect of the electric field on the adsorption of the organic substance according to equation 13 can be expressed by a change in the quantity B

$$B = B_0 \exp - \left[\frac{\Delta\gamma_e + C'E\left(E_N - \frac{E}{2}\right)}{A} \right] \tag{17}$$

where B_0 is the value of B at $E=0$ and $A = RT\Gamma_m$, Γ_m representing the limiting value of the adsorption.

By using equations 16 and 17, it is possible to calculate the dependence of the coverage θ on the electrode potential and then, by means of the equation of state 15, to find the value of the decrease in the interfacial tension due to the adsorption of organic molecules on the electrode surface. Such calculations for the case of adsorption of t-amyl alcohol from 1N NaCl solutions were made by Frumkin[12b] and showed fair agreement between the calculated and experimental electrocapillary curves (*Figure 2*).

4. *Improvement in Theory by taking into account Decrease of Area per Adsorbed Molecule*

A more detailed analysis, however, showed that the break in the experimental curves at positive surface charges is more pronounced than is predicted from the theory. This result can be explained by the decrease in the area per adsorbed molecule of amyl alcohol occurring with an increase in the coverage.

Suppose as a first approximation that S decreases linearly with Γ (*Figure 3*), and, consequently, with the quantity $\theta_s = \Gamma/\Gamma_m$ which, under these conditions, no longer represents the coverage. In this case, it can be readily shown that the equation of the straight line $S-\Gamma$ is of the form

$$S = \frac{k}{\Gamma_m} - \frac{k-1}{\Gamma_m^2}\Gamma \tag{18}$$

where $k = S_{\theta=0}/S_{\theta=1}$. Since $\theta = \Gamma S$

$$\theta = \Gamma S = k\theta_s - (k-1)\theta_s^2 \tag{18a}$$

By introducing equation 18a into 9, we obtain

$$q = q_0(1-k\theta_s) + q' k\theta_s + (k-1)(q_0 - q')\theta_s^2 \tag{19}$$

From equations 8 and 19 we obtain after some transformations

$$B_0 c \exp\left[-k\frac{W_s}{A}\right] = \frac{\theta_s}{1-\theta_s} \exp\left\{-2\theta_s\left[a_0 + \frac{W_s}{A}(k-1)\right]\right\} \tag{20}$$

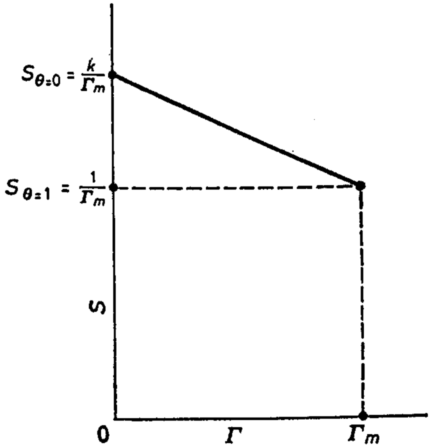

Figure 3. Schematic dependence of area/mole adsorbed molecules on adsorption value

In other words, the decrease in S with a rise in Γ results not only in a decrease by k times the constant A but also in an increase with the potential in the effective value of the attraction constant a in equation 16. It follows from the analysis of equations 16 and 17 that the latter corresponds to a more pronounced change in the coverage with the potential, which is manifested in sharper breaks in the electrocapillary curves. As shown by Frumkin[12b], a change in S with the coverage of only 9 per cent ($k = 1{\cdot}09$) results in a much better agreement between the calculated and experimentally observed electrocapillary curves of 1N NaCl solutions with different additions of t-$C_5H_{11}OH$. The deduction of equation 20 is, however, not quite rigorous, since the assumption about the constancy of B_0 and a_0, if there is a dependence of S on Γ, may be considered only as a rough approximation.

5. *Butler's Theory of Adsorption of Compounds as a Function of Potential*

A somewhat different quantitative theory of the effect of the adsorption on the shape of the electrocapillary curves was advanced by Butler[19]. According to him, the electric contribution to the work of adsorption per volume element of the surface layer is equal to

$$W = [\tfrac{1}{2}(p_A - p_B)X^2 + (\mu_A - \mu_B)X]\delta V \qquad (21)$$

where p_A and p_B are the polarizabilities of water and of the organic substance, μ_A and μ_B their permanent dipole moments, respectively, referred to unit volume, and G is the strength of the electric field.

Equation 21 is similar to equation 3 in Frumkin's theory, the difference being that the former deals with bulk properties of dielectrics, which certainly cannot be used when considering the behaviour of the substance in the double layer, whereas the latter makes use of properties of the double layer* which can be found from experiment. In other respects the treatment of the effect of the electric field on the adsorption of organic substances is also different in these two theories. According to Butler

$$\Gamma = \Gamma_0 \exp\left[-\frac{W}{kT}\right] \tag{22}$$

where Γ_0 is the adsorption of the organic substance in the absence of the electric field of the double layer. Assuming G to be proportional to E and combining all the constants, equations 21 and 22 lead to

$$\Gamma = \Gamma_0 \exp\left[-(\alpha E^2+\beta E)\right] \tag{23}$$

Butler assumes further that, for a solution of given composition, Γ is proportional to the decrease in the interfacial tension, $\Delta\gamma$, and hence

$$\Delta\gamma = \Delta\gamma_0 \exp\left[-(\alpha E^2+\beta E)\right] \tag{24}$$

or

$$\Delta\gamma = \Delta\gamma_m \exp\left[-\alpha(E-E_m)^2\right] \tag{25}$$

where $\Delta\gamma_m=\Delta\gamma_0 \exp(\beta^2/4\alpha^2)$ is the maximum decrease in the interfacial tension, and $E_m = -(\beta/2\alpha)$ the potential at which it is observed.

By means of equation 25 it was possible to explain, to a first approximation, the shape of the electrocapillary curves obtained by Gouy[11] and by BUTLER and OCKRENT[20a] in solutions containing additions of different organic compounds. Butler's assumption, however, that the decrease in the interfacial tension is proportional to the amount of the organic substance adsorbed, i.e. that $-\mathrm{d}\gamma=k'\,\mathrm{d}\Gamma$, according to equation 1 is equivalent to the assumption of the correctness of Freundlich's isotherm

$$\Gamma = k_1 c^{RT/k'} = k_1 c^n \tag{26}$$

or, in the particular case of $k'=RT$, to that about the applicability of Henry's law to the adsorption of organic molecules

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* In fact, it can readily be shown that, if the change in the capacity is determined by that in the polarizability of the medium between the sheets of the double layer and the change in the position of the p.z.c. by the dipole moments of the oriented molecules of the substance adsorbed and of the solvent, then equations 3 and 21 formally coincide.

$$\Gamma = k_1 c \tag{27}$$

Moreover, equation 22 is compatible with thermodynamics only in the region of Henry's law.

This condition limits the applicability of Butler's theory to only small values of Γ. Subsequently, in order to describe the effect of combined adsorption of two organic substances on the shape of the electrocapillary curve, BUTLER and OCKRENT[20b] developed a theory using Shishkowsky's equation, with a correction similar to that of Frumkin's for the attraction between the adsorbed molecules. The use of this theory allowed a quantitative determination of the effect of the combined adsorption of caffein and phenol on the shape of the electrocapillary curves[20c]. However, the data obtained for the mixtures of sodium cinnamate and sodium-*o*-toluate were at variance with the theory, the experimental value of $\Delta\gamma$ being smaller than the calculated one. This discrepancy was attributed by the authors to the effect of adsorbed ions impeding the further adsorption of ions with the same sign of charge.

6. *Shift of Potential of Zero Charge owing to Adsorption*

The shift in the p.z.c. during the adsorption of organic molecules on the mercury surface was associated both by Frumkin[16] and Butler partly with their permanent dipole moment. Thus, when these adsorbed dipoles are oriented, an adsorption potential corresponding to the shift in p.z.c. is built up at the mercury–solution interface—a fact noted already by Gouy[11b]. Frumkin[17] compared the shifts in the p.z.c. caused by the adsorption of various organic compounds at the mercury–solution interface with adsorption potentials at the air–solution interface. This comparison showed, in the case of aliphatic oxygen compounds, that the adsorption potentials of these substances at both the interfaces are identical in sign and similar in magnitude (cf. [21]). The values observed were qualitatively interpreted on the basis of the assumption that the adsorption of organic substances involves the substitution of molecules of these substances for the dipoles of water, oriented with their negative oxygen end outwards, i.e. in the direction of air or mercury. The organic molecules are oriented with their hydrocarbon chain in the direction of the interface and the orientation of the C—O bond gives rise to a positive potential difference between the outer phase and the bulk of the solution[15a].

In the case of aromatic compounds, however, the comparison of adsorption potentials, ΔE, at the mercury–solution and air–solution interfaces leads to considerable discrepancies in magnitude, and sometimes even in sign, of ΔE. Thus, for example, in the case of *ortho*- and *para*-cresols, the ΔE at the mercury–solution interface are $-0{\cdot}20$ and $-0{\cdot}29$ V, respectively (the p.z.c. is shifted in the direction of negative E values), whereas at the air–solution interface the adsorption of these compounds increases the potential difference by $+0{\cdot}01$ and $+0{\cdot}26$ V, respectively.

7. *Influence of π Bonding on Adsorption of Aromatic Compounds*

The comparison of the electrocapillary behaviour of aromatic and corresponding hydroaromatic hydrocarbons (benzene cyclohexane, naphthalene decahydronaphthalene) carried out by GEROVICH[22, 23] showed that the shift in p.z.c. in the negative direction and the adsorption of aromatic compounds on a positively charged mercury surface are due to the interaction between the π-electrons of the aromatic nuclei and the mercury surface which is facilitated by the flat orientation of the benzene ring at the mercury–solution interface (cf.[21]). Another result of this flat orientation is the establishment of different conditions for the interaction of the polar group with the mercury surface, as compared with the adsorption of aliphatic compounds.

It was shown by GEROVICH and RYBALCHENKO[23] that the adsorption of organic compounds at large positive surface charges (which does not occur in the case of neutral molecules having no π-electrons) increases with an increase in the number of double bonds (*Table 2*).

The surface activity of hydrocarbons with a similar structure increases ca. 21·5 times with the addition of each benzene ring[22]. As shown by GEROVICH and POLJANOVSKAJA[24], when acid solutions of aniline, with the latter present in the form of $C_6H_5NH_3^+$ ions, are substituted for neutral ones, the adsorption of the organic compound at positive surface charges decreases but does not disappear. This result shows the predominance of the interaction between the positively charged surface and the π-electrons of the aromatic nucleus over the electrostatic repulsion between the organic cations and the surface. A similar conclusion was reached by BLOMGREN and BOCKRIS[25] who studied the adsorption on mercury of a series of aromatic amines, aniline, *o*-toluidine, 2,3- and 2,6-dimethylaniline, pyridine and quinoline from 0·1N HCl solution. According to these authors, the substances are adsorbed predominantly as RNH_3^+ ions, lying flat on the electrode surface. The amount adsorbed varies little with the potential over a range of about 1 V, the adsorption on the positive branch being principally determined by π-electronic interaction and that on the negative branch by coulombic forces.

Table 2

Dependence of Adsorption on Number of Double Bonds

Organic compound	*Concentration*	$\Delta\gamma$ *at* $E = +0{\cdot}5$ V (ref. to p.z.v.)	*Supporting electrolyte*
cyclohexane	1 M	0·0	0·2 N NH_4NO_3 in CH_3OH
cyclohexene	1 M	1·1	
1, 3-cyclohexadiene	1 M	2·5	
benzene	1 M	4·5	

The adsorption isotherm of Blomgren and Bockris is of the form

$$\ln\left(\frac{\theta}{1-\theta}\,\frac{55{\cdot}5}{c_A f_p^s}\right) = -\frac{1}{RT}\left(\Delta\bar{G}_A^0 + \frac{Ne_0^2\theta^{1/2}}{\pi^{1/2}\,\epsilon_s} - \frac{3}{4\pi^3}\,\frac{Nh\nu}{\epsilon_0}\theta^3\right) \qquad (28)$$

where c_A and f_p^s are bulk concentration and activity coefficient of the substance adsorbed, $\Delta\bar{G}_A^0$ the difference in standard electrochemical free energies of adsorption of adsorbate and water at $\theta = 0$, ϵ_s = static dielectric constant of water in the adsorbed layer, ϵ_0 = electronic dielectric constant of the solvent and ν = a characteristic frequency of the electronic oscillators in the adsorbate molecules. The second term in the right-hand side of equation 28 accounts for the coulombic and the third for the dispersive forces between the aminium ions adsorbed. The interaction is predominantly repulsive; the dispersive type manifests itself only at higher θ values.

FRUMKIN *et al.*[26] and Conway and Barradas[21] considered also those adsorption effects which are observed in the absence of π-electrons; in the case of the uncharged mercury surface these effects are in many respects similar to the phenomena observed with adsorption at the air–solution interface. In the absence of π-electrons, the adsorption of organic cations (cyclohexyl ammonium) on a positively charged Hg surface can occur only as a result of interaction with the specifically adsorbed anions[2b].

8. *Other Examples of Adsorption on Mercury*

The electrocapillary method has been widely used for the investigation of adsorption on mercury of various organic compounds. FRUMKIN, GORODETSKAYA and CHUGUNOV[27] studied the formation on mercury of multilayers during the adsorption of caproic acid and phenol from their saturated solutions; these are not formed under similar conditions at the solution–air interface. This method was also used

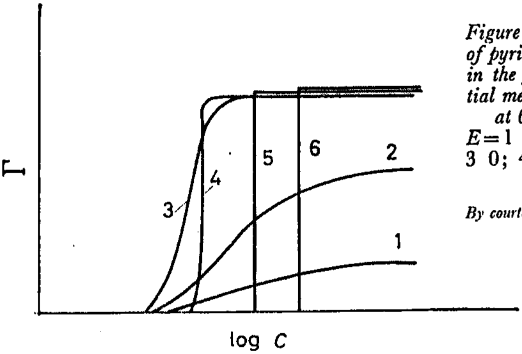

Figure 4. Adsorption isotherms of pyridine from alkaline solutions in the function of electrode potential measured relative to the p.z.c. at $\theta = 0$ (from GIERST[35]*).*
E=1 +0·4 V; 2 +0·2 V; 3 0; 4 −0·2 V; 5 −0·4 V; 6 −0·6V

By courtesy of Electrochemical Society

for quantitative determination of the adsorption on mercury of butyl alcohol[3]; determination of effective dipole moments of oxalic, acetic, propionic, n-butyric, tartaric, citric, maleic and fumaric acids[28]; study of the adsorption on mercury of alkaloids[29] and wetting agents[30] of heterocyclic and aromatic ammonium ions in solutions of sulphuric[31] and hydrochloridic acid and KCl[22]; the adsorption of dibenzylsulphoxide[32] and of aliphatic aminoethers[33] and the behaviour of mixtures of organic compounds[20b, c, 34].

The adsorption of heterocyclic bases (pyridine and its derivatives) was investigated by GIERST[35] and by Conway and Barradas[21]. Of special interest in the data obtained by Gierst is that he observed an alteration in the form of the adsorption isotherm of pyridine with a change in the electrode potential (*Figure 4*). The transition from a monotonous curve to a jumpwise increase in the coverage with a rise in the concentration when the potential is shifted to more negative values is in a qualitative agreement with equation 16 and indicates an increase in the apparent attraction between the adsorbed molecules.

From electrocapillary measurements, Conway and Barradas[21] calculated the adsorption isotherms of pyridine and its derivatives and those for aniline in 1N KCl and HCl solutions, the standard free energies of adsorption, $\Delta \bar{G}^0_A$, of these compounds being determined on the basis of the isotherms. In neutral solutions (1N KCl) the values of the limiting adsorption, Γ_m, for the substances investigated correspond to an orientation of adsorbed dipoles perpendicular to the surface; this sets in at values of θ lesser the more the organic molecule is deficient in π-electrons. In accordance with the calculation of the electrostatic interaction of the dipoles, the value of $|\Delta \bar{G}_A|$ decreases linearly with $\theta^{3/2}$ in this case, and the π-electronic interaction with the electrode surface can be neglected in the perpendicular configuration.

The equation of state of the adsorbed layer is of the form[21]

$$\ln\left(\frac{\theta}{1-\theta}\frac{55\cdot5}{c}\right) = -\frac{\Delta\bar{G}_A^0}{RT}-\frac{P\theta^{3/2}-Q\theta^3}{RT} \qquad (29)$$

where P and Q are constants depending on the dipole moment, the area occupied by the adsorbed molecule and on some other characteristics of the particles adsorbed as well as on the dielectric constant of the surface layer. The term with $\theta^{3/2}$ takes account of the electrostatic repulsion between the parallel oriented dipoles, and the term with θ^3 represents the van der Waals attraction.

In acid solutions (1N HCl), where aniline as well as pyridine and its derivatives are present in the form of cations, the values of Γ_m correspond to a flat orientation of adsorbed particles, which is favourable for the π-electronic interaction with the metal surface. In this case, a linear decrease in the absolute value of the free energy of adsorption in dependence on $\theta^{1/2}$ is observed at small θ whereas, at large coverages, $|\Delta\bar{G}_A|$ increases as a result of the van der Waals interaction between the adsorbed particles which is proportional to θ^3.

Conway and Barradas discuss the relationship between the adsorption at the Hg–water and air–water interfaces. They come to the conclusion that there is a small increase of $|\Delta\bar{G}_A^0|$ upon transition from the air–water to the uncharged Hg–water interface which is partly accounted for by the π-electron interaction with the metal surface. The major contribution to $|\Delta\bar{G}_A^0|$ is determined at both interfaces by the squeezing out of the organic molecule from the bulk of the electrolyte to the interface. This conclusion is in agreement with the results obtained by Frumkin, Kaganovich and Bit-Popova[26].

On the basis of electrocapillary measurements, BLOMGREN, BOCKRIS and JESCH[36] made a detailed study of the adsorption of butyl, phenyl and naphthyl compounds containing —OH, —CHO, —COOH, —CN, —SH, >S, >CO, $—NH_3^+$ and $—SO_3^-$ groups, with 0·1N HCl used as the electrolyte. Adsorption isotherms were calculated for all the compounds studied, the values of Γ_m and $\Delta\bar{G}_A^0$ being determined on their basis. As follows from the values of Γ_m obtained, the butyl derivatives are adsorbed in such a way that, at $\theta=1$, their dipoles are perpendicular to the surface, whereas the phenyl and naphthyl derivatives are oriented in the adsorption layer parallel to the surface.

It was found that at the p.z.c. at $\theta=0\cdot25$ the standard free energies of adsorption for the derivatives of a particular radical depend to a first approximation linearly on their standard free energies of dissolution, $\Delta\bar{G}_s^0$. By extrapolating the values of $\Delta\bar{G}_A^0$ to $\Delta\bar{G}_s^0=0$ and subtracting the difference between the standard chemical potentials of water at the surface and in the bulk of the solution calculated under certain assumptions, Bockris *et al.*[36] obtained the values of 'intrinsic' standard free energies of adsorption, $(\Delta \bar{G}_A^0)_{\text{intr}}$, which characterize the interaction of mercury with the corresponding organic radicals regardless of the substituent groups. The values of $(\Delta \bar{G}_A^0)_{\text{intr}}$ increase considerably, by 6 kcal mole^{-1}, upon transition from butyl to naphthyl radicals, an effect which is due to the π-electronic interaction of naphthyl (and phenyl) with mercury.

It is of interest to note that, with many of the compounds studied, the values of $\Delta \bar{G}_A^0$, calculated from the adsorption isotherms on the negative branch change linearly with the coverage θ, which is in agreement with equation 16 in the case of a constant, positive or negative, value[12b] of a. At $\theta > 0{\cdot}8$–$0{\cdot}9$, when the area per adsorbed molecule begins to decrease markedly, a rises and the dependence of $\Delta \bar{G}_A^0$ on θ becomes more pronounced. On the positive branch a repulsion between the adsorbed molecules is observed in the case of phenol. The transition from attraction to repulsion occurs at less positive potentials the smaller the coverage.

The problem of the effect of different substituent groups and of the type of hydrocarbon radical on the adsorbability of organic compounds at the mercury–solution interface will not be further discussed here, since the principal aim of this review is to consider the part played by the electric field in the processes of adsorption of organic compounds. It may be mentioned though that one of the authors used an alternative method of approach to the problem indicated which, in a number of cases, appears to yield somewhat different results, viz. the comparison of the decrease in the interfacial tension and of the adsorption potentials at the mercury–solution and solution–air interfaces[17, 22, 26, 37–39].

9. *Adsorption of Tetra-alkylammonium Salts*

From electrocapillary measurements carried out with solutions of tetra-alkylammonium iodides, Devanathan and Fernando[40] calculated the adsorption of $[(CH_3)_4N]^+$, $[(C_2H_5)_4N]^+$ and $[(C_3H_7)_4N]^+$ as well as of I^- ions as a function of the mercury electrode charge and of the concentration of the salt. It was shown somewhat unexpectedly that the adsorption of $[(CH_3)_4N]^+$ and of I^- was independent of the concentration of $[(CH_3)_4N]I$, although both these ions are specifically adsorbed on the mercury surface. The authors explain this result by the mutual effect of $[(CH_3)_4N]^+$ and I^- ions which form anionic and cationic bridges in the double layer. This explanation appears doubtful, however. Another unexpected result is that the adsorption of the $[(CH_3)_4N]^+$ ion on a negatively charged surface is smaller than that of the K^+ cation.

10. *Theory of Bockris, Devanathan and Müller*

According to Bockris, Devanathan and Müller[168], the principal factor determining the dependence of the adsorption process of organic compounds at the mercury–electrolyte interface on the electrode charge is the competition of organic molecules with water. The water molecules located at random near the uncharged mercury surface are oriented by the action of the field, which hinders the adsorption of organic substances. To a first approximation, these authors arrive at the following relation:

$$\frac{\theta_{org}}{1-\theta_{org}} = \frac{c_{org}}{c_w} \exp\left[-\frac{\Delta G^0_{ads}}{RT}\right] \exp\left[-\frac{n\mu X}{kT} \tanh\left(\frac{\mu X}{kT}\right)\right] \tag{29}$$

where θ_{org} is the surface coverage with the adsorbed substance, c_{org} and c_w the concentrations of organic substance and of water, respectively, μ is the dipole moment of water, n the number of water molecules displaced by a molecule of organic substance from the surface (it being assumed in the calculation that $n=2$), X the strength of the electric field in the centre of the adsorbed water dipole and ΔG^0_{ads} the change in the standard free energy in the course of adsorption on an uncharged surface. The latter is determined as the difference between the change in the free energy upon transition of a molecule of the adsorbed substance from the bulk of the solution to the uncovered mercury surface and that occurring upon transition on n molecules of water from the surface to the bulk. By taking into consideration the energy of the lateral interaction of the adsorbed dipoles, the authors arrive at a more accurate expression for the dependence of adsorption on the charge, which is in qualitative agreement with the experiments.

There is no doubt about the necessity of stressing the fact that in the consideration of the dependence of adsorption on the nature of the adsorbate, the competition with the adsorption of water should be taken into account*, but the proposed method of calculating the dependence of adsorption on the charge is incomplete. The dependence of the free energy of the adsorbed water layer on the charge

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* Otherwise it would be impossible to explain the weaker adsorption of some organic substances at the solution–mercury interface as compared with the solution–air interface. Frumkin, Kuznetsov and Kaganovich[169] showed that the adsorptivity of perfluoroacids of the fatty series C_2–C_4 decreases 15–50 times upon transition from the interface with air to that with mercury. To take into consideration the water displacement in the case of adsorption of organic substances is also necessary for making Langmuir's isotherm applicable to adsorption on the surface of solutions. Solvent competition was by Butler[19].

is determined not only by the orientation of the water molecules, but by their polarizability as well. When considering the process of adsorption at a constant charge, as is done by Bockris, Devanathan and Müller (and not at a constant potential as in the present survey), it is necessary to take into account the increase in the electrical energy of the double layer upon the substitution of water by the organic substance.

According to Bockris, Devanathan and Müller, the potential difference due to the orientation of water dipoles does not exceed 0·1 V, whereas the polar group of the organic compound should have no effect upon the potential distribution, as it is beyond the limits of the double layer (see footnote, p. 156). It is not clear, however, how under such conditions the adsorption of organic substances could cause shifts in the point of zero charge of up to 0·5 V.

11. *Adsorption from Non-aqueous Solutions*

A number of authors have made electrocapillary measurements in non-aqueous solvents[37, 41–49]. The first of this kind were carried out by Frumkin[41] with methyl and ethyl alcohols, acetone and pyridine. The interfacial tension at the maximum of the electrocapillary curve ($\gamma_{E=0}$) is in this case considerably smaller than in aqueous solutions (*Table 3*).

Table 3

Interfacial Tension at Potential of Zero Change as a Function of Organic Solvent

Solvent	*Solute*	$\gamma_{E=0}$
water	0·1N $NaHSO_4$	426·7
methanol	0·1N NH_4NO_3	392·2
ethanol	0·2N NH_4NO_3	386·1
acetone	0·9N $LiNO_3$	387·5
pyridine	1·0N NH_4CNS	360·7

A characteristic feature of the electrocapillary curves in non-aqueous solvents with small additions of water is the adsorption of water molecules under strong negative polarization, resulting in a decrease in the interfacial tension compared to that of the solution in the pure organic solvent[41]. This effect, which was confirmed by the measurements of Ockrent[42] with solutions in CH_3OH, C_2H_5OH, n-C_3H_7OH and n-C_4H_9OH, is a result of the larger capacity of the double layer when filled with water molecules as against that in the presence of alcohol molecules. A quantitative study of the substitution of one solvent in the double layer for another, with regard to the dependence of the effect on the electrode potential and on the bulk proportion of the solvents, was made by PARSONS and DEVANATHAN[45] for HCl solutions in CH_3OH–H_2O mixtures and by Maizlish, Tverdovsky and Frumkin[37] for saturated NaCl and NH_4Cl solutions in mixtures of water with ethyl alcohol. These papers appear to be the only ones in which adsorption at the mercury–solution interface was calculated by the exact equation of Gibbs and not by the approximate one, i.e. with an allowance for the experimental values of the activities. In both systems studied, the composition of the solution surface layer at the interface with uncharged mercury proved to be very similar to that at the interface with air over the concentration range. The values of $\Gamma_{C_2H_5OH}$, assuming $\Gamma_{H_2O} = 0$, and those of Γ_{H_2O}, assuming $\Gamma_{C_2H_5OH} = 0$, were given[37]. At potentials more negative than $-1{\cdot}4$ V (relative to Ag–AgCl in the solutions studied), Γ_{H_2O} becomes positive at all concentrations of alcohol.

12. *Reduction of Interfacial Energy at Solid Electrodes upon Organic Adsorption*

All electrocapillary curves presented here have been obtained with the mercury electrode*. This is due to the fact that the interfacial tension on solid metals cannot be measured directly. However, from some properties of the solid metal–solution interface conclusions can be drawn about the change in the interfacial tension under the influence of the electric field or of some organic additions and, consequently, adsorption phenomena on solid metals can also be studied. One of such properties is the wetting of metals by a solution, characterized by the value of the contact angle η. As shown by several workers[52–56], the dependence of the contact angle on the electrode potential in those inorganic electrolytes and solutions of surface-active substance which lower η (*Figure 5*) resembles an electrocapillary curve, and the maximum of the η–E curve lies close to the p.z.c. The similarity between the dependence of η on E and the electrocapillary

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* The electrocapillary curves for a thallium amalgam in the presence of isoamyl alcohol, pyrogallol and thiourea were determined by FRUMKIN and GORODETSKAYA[50], those for liquid gallium in the presence of isoamyl alcohol, phenol and pyrogallol by MURTAZAEV and GORODETSKAYA[51] and recently by FRUMKIN and POLYANOVSKAYA[161]. The decrease in the interfacial tension caused by adsorption of organic substances appears to be much smaller in the case of gallium than in that of mercury. The different behaviour of gallium might be connected with the fact that the free energy of wetting liquid gallium with water amounts to ca. 170–190 erg/cm², which appreciably exceeds the value for mercury, 125 erg/cm².

curves was confirmed by Tverdovsky and Frumkin[46] for the mercury–NH_4NO_3 solution interface in mixtures of water with ethyl alcohol. Such measurements of the contact angle in the presence of surface-active substances are of interest also in that they not only give information about the adsorption at the mercury–solution interface but also indicate the existence of adsorption in a thin but multimolecular layer of the solution, which is formed at the interface between mercury and the gas bubble. Some quantitative discrepancies between the results obtained in the papers quoted and the data of SMOLDERS[57] require further investigation.

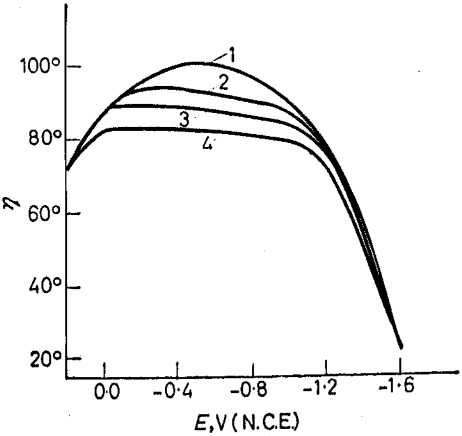

Figure 5. Dependence of contact angle, η, *on mercury electrode potential in* 1N *solution of* Na_2SO_4 *with additions of* n$-C_7H_{15}OH$: 1 0; 2 $1{\cdot}75.10^{-3}$M; 3 $3{\cdot}5.10^{-3}$M; 4 7.10^{-3}M (KABANOV and IVANISHCHENKO[55])

Another property characterizing the value of the interfacial tension at the electrode–solution interface is the hardness of the electrode. According to the theory developed by REHBINDER[58, 59], every action upon a solid body resulting in a decrease in interfacial tension on the inner surfaces of microcracks formed in the process of disintegration, brings about a decrease in the hardness of the body and in its ability to withstand brittle rupture or plastic deformation. Therefore, the dependence of hardness on the electrode potential is similar to the usual electrocapillary curve, the highest value of hardness or mechanical strength, H, corresponding[59–62] to the p.z.c. *Figure 6* shows the dependence of the hardness of metallic thallium on the potential in 1N Na_2SO_4 and in the presence of iso-amyl alcohol[59], and the corresponding electrocapillary curves, measured on a 41·5 per cent thallium amalgam[50]. It illustrates the electrocapillary effect of the decrease in hardness, both under the action of the charge of the electric double layer and as a result of the adsorption of a surface-active substance.

The results of several workers[63-65] have indicated that the dependence of the boundary friction on potential in the presence of organic molecules and ions is, to a first approximation, also represented by a parabolic curve, the minimum of the friction coefficient corresponding to the electrocapillary maximum. Methods based on measurement of hardness and of boundary friction have been compared[66, 67].

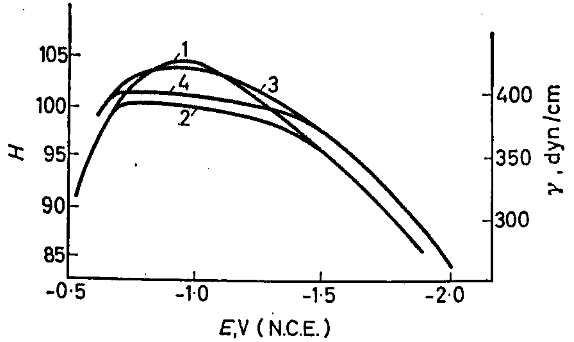

Figure 6. Dependence of hardness of thallium (in arbitrary units) on potential in solutions: 1 1N Na_2SO_4; 2 1N $Na_2SO_4 + 0{\cdot}185M$ iso-$C_5H_{11}OH$ (WENSTRÖM *and* REHBINDER[59]); *electrocapillary curves of* 41·5 *per cent thallium amalgam in solutions:* 3 1N Na_2SO_4; 4 1N $Na_2SO_4 + 0{\cdot}175M$ iso-$C_5H_{11}OH$ (FRUMKIN *and* GORODETSKAYA[50])

Considerable progress has been made lately in the direct determination of adsorption of organic compounds on metals (ethylene on platinum[170], benzene, naphthalene, phenanthrene, cyclohexane[171] and thiourea[160] on gold), due to the use of the method first proposed by JOLIOT[172] and developed by Blomgren and Bockris[4]. This method is based on the measurement of the intensity of radiation penetrating through a metal foil electrode, one side of which is in contact with the solution containing the adsorbate labelled with ^{14}C (or ^{35}S). By means of this method it is possible to determine the dependence of adsorption on potential and on concentration. The adsorption of thiourea on gold as well as on mercury decreases with the potential shifting in the direction of more negative values. This observed dependence of the adsorption on the potential was compared with the results of a model calculation. We cannot agree, however, with the method of this calculation, despite the fact that its results appear to be in approximate agreement with experimental data.

The adsorption of aromatic compounds on gold from N H_2SO_4 passes through a maximum at a potential close to 0·5 V (N.H.E.). The adsorption isotherm of naphthalene is in agreement with the relation

$$Bc = \frac{\theta}{(1-\theta)^5}$$

deduced for adsorption on a homogeneous surface, assuming that the molecule of $C_{10}H_8$, being horizontally oriented, displaces 5 water molecules. The adsorption of aromatic compounds on gold is much more pronounced than that of aliphatic compounds (cyclohexane, fatty acids), which could not be detected by the above method. Higher adsorptivity of aromatic compounds is accounted for by the π-electronic interaction. From the determination of the dependence of adsorption of naphthalene on the concentration of the supporting electrolyte GREEN and DAHMS[171] draw the conclusion that the zero point of gold lies close to 0·3 (N.H.E.) and explain the decrease in adsorption when the potential moves away from the value equal to 0·5 V by the desorbing action of the electric field of the double layer. It is not clear, however, if it is possible to neglect the influence of adsorbed hydrogen and oxygen in the determination of the dependence of adsorption of organic substances on gold upon the potential, as is done by these authors. This question is considered elsewhere[173].

III. THE EFFECT OF THE ADSORPTION OF ORGANIC SUBSTANCES ON THE CAPACITY OF THE ELECTRIC DOUBLE LAYER

1. *Measurement of Adsorption from Capacitance Data*

The differential capacity of the electric double layer is extremely sensitive to adsorption of organic molecules on the electrode surface. This explains why the correct values of the double layer capacity were obtained[69] only in 1935, although attempts to measure the capacity directly had been made[70] since 1870. In fact, as shown by PROSKURNIN and FRUMKIN[69], too low results for the double layer capacity obtained earlier[71-75] were due to the contamination of the electrode surfaces by traces of organic compounds. Only when conditions of extreme cleanliness—careful removal of organic contaminations from all reagents used, absence of rubber tubing and stoppers, as well as of lubricants between ground surfaces—are realized, do directly measured values of differential capacity coincide with those obtained from electrocapillary curves by means of Lippman's equation

$$C = \frac{dq}{dE} = -\frac{d^2\gamma}{dE^2} \tag{2a}$$

From the shape of the electrocapillary curves obtained in the presence of organic substances (*Figure 1a*), and taking into consideration equation 2a, one would expect on the C—E curves a region of low-capacity values limited on both sides by adsorption–desorption peaks, corresponding to sharp changes in the surface charge within a narrow potential range. At large surface charges, both positive and negative, the C—E curves determined in the presence and in the absence of organic substances should be expected to approach one another. The differential capacity curves of the shape mentioned were first obtained by Proskurnin and Frumkin[69] in Na_2SO_4 solution saturated with n-octyl alcohol (*Figure 7*). Similar C—E curves were observed by KSENOFONTOV, PROSKURNIN and GORODETSKAYA[76] with solutions of ethyl and n-butyl alcohols and of phenol*.

The values of the double layer capacity were determined[69,76] by comparison with a reference capacity. This method was also used to study[79,80] the structure of thin films formed by palmitic, oleic and myristic acid and by cetyl alcohol at the mercury–solution interface. The comparison consists in measuring at a constant a.c. strength, $\tilde{\Delta} i$, of frequency ω the potential difference at the cell, ΔE_x and at the reference capacity, ΔE_1, the capacity of the double layer to be determined being equated with the value

$$C_{\text{obs}} = C_1 \frac{\Delta E_1}{\Delta E_x} = C_1 \frac{\tilde{\Delta} i \dfrac{1}{C_1 \omega}}{\tilde{\Delta} i \sqrt{R_x^2 + \dfrac{1}{C_x^2 \omega^2}}} = \frac{C_x}{\sqrt{R_x^2 C_x^2 \omega^2 + 1}} \tag{30}$$

where C_1 is the reference capacity, R_x and C_x are the ohmic and capacity components of the overall cell impedance connected in series which, in the absence of an electrochemical reaction, are equal to the resistance of the solution and to the double layer capacity, respectively.

From equation 30 it is seen that the value of C_{obs} determined by the comparison method can be equated with the double layer capacity,

---

* It should be noted that the equilibrium value of the differential capacity, related to the interfacial tension and the surface charge density by equation 2a, is a thermodynamic quantity, and that therefore the adsorption–desorption peaks on the C—E curves observed in the presence of organic substances cannot be associated with the tangential motions of mercury during adsorption–desorption processes, as was suggested[77,78].

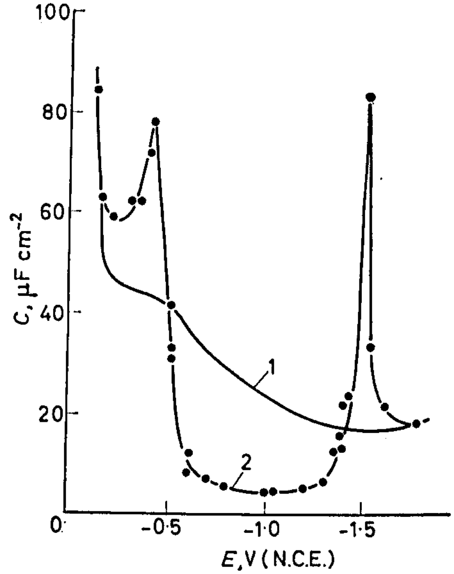

Figure 7. Differential capacity curves measured by the comparison method in solutions (**Proskurnin** *and* **Frumkin**[69])

1 1N Na_2SO_4; 2 1N Na_2SO_4 *saturated with* n-$C_8H_{11}OH$; 50 c

C_x, only at a low circular a.c. frequency ω and small solution resistance R_x when the following inequality is fulfilled

$$R_x^2C_x^2\omega^2 \ll 1 \tag{31}$$

This is an essential limitation of the comparison method. Another method for the study of adsorption of surface-active organic substances, advanced by **Breyer** and **Hacobian**[81a] and called by them 'tensammetry', suffers from the same limitation. It consists in measuring the dependence on the potential of the a.c. current flowing through the cell, $\tilde{\Delta i}$, which for an ideally polarized electrode is

$$\tilde{\Delta i} = \frac{\Delta E}{\sqrt{R_x^2 + \dfrac{1}{C_x^2\omega^2}}} = \Delta E\omega\frac{C_x}{\sqrt{R_x^2C_x^2\omega^2+1}} \tag{32}$$

As seen from comparison of equation 30 with 32, the 'tensammetric' method gives, in principle, the same results as the comparison method[82] and, consequently, is limited by condition 31.

The 'tensammetric' method was widely used to study adsorption on a mercury electrode of a great variety of organic compounds[77,78,81,83-86,174-178], but the results are only of a qualitative character. More accurate data can be obtained by means of a bridge arrangement providing separate compensation for the ohmic and the capacity components[87] or by some other arrangement permitting determination of the phase angle[88].

2. *Facts concerning Adsorption obtained from Capacitance*

The bridge arrangement[87] was first used for measuring the capacity of the double electric layer in the presence of an organic substance, n-octyl alcohol, by GRAHAME[89]. MELIK-GAIKAZJAN[90] studied the adsorption of normal fatty alcohols on a mercury electrode. He found that in the presence of n-octyl and n-hexyl alcohols, polymolecular layers are formed on the mercury surface, which results in a capacity decrease down to 0·9 μf cm^{-2}, no formation of polylayers being observed in n-C_4H_9OH and n-$C_5H_{11}OH$ solutions (cf. *Figure 29b*, curve 6, p. 213).

Measurements of differential capacity were used to investigate the adsorption on the mercury electrode of valeric acid and other derivatives containing five carbon atoms[91, 92a], of gelatin and camphor[92b], of thiourea[93] and of polyelectrolytes (polymethacrylic acid, polylysine, polyvinylpyridine)[94–96]. The method was also employed in studying[97, 98] the adsorption on mercury of surface-active tetra-alkylammonium cations $[(C_nH_{2n+1})_4N]^+$ with $n=1$–6. The behaviour of large organic cations ($n \geqslant 3$) on the mercury electrode surface is similar to that of neutral surface-active molecules (cf. [99]). Thus, at sufficiently negative potentials, these cations are desorbed from the mercury surface despite electrostatic attraction, and this effect results in a characteristic peak on the differential capacity curve.

The simultaneous adsorption of n-butyl alcohol and of tetra-alkylammonium cations with $n=1$, 2 and 4 was investigated by KIRKOV[100, 179] who showed that the desorption of butyl alcohol from the mercury at negative surface potentials is the less pronounced the larger the cation, with the height of the peak on the C—E curve decreasing in the sequence

$$K^+ > [(CH_3)_4N]^+ > [(C_2H_5)_4N]^+ > [(C_4H_9)_4N]^+$$

In a number of cases, the shape of the differential capacity curves in the presence of surface-active organic substances is more complex. In saturated solutions of n-heptyl and n-octyl alcohols, instead of two adsorption–desorption peaks, LOVELAND and ELVING[101b] observed four capacity peaks on the differential capacity curves obtained by the oscillographic method*. The two outer peaks were considered to be due to the complete desorption of alcohol molecules from the electrode surface, while the two inner ones were explained in terms of the removal of a second layer of adsorbed molecules which, at small electrode charges, form a micellar film. On blowing through the solution, even for a short time, an inert gas, which slightly reduces the alcohol concentration in the solution, the differential capacity curves assume the usual form with two desorption peaks.

The conclusion regarding formation of polymolecular adsorbed layers in the saturated solutions of aliphatic compounds containing, apparently, no micelles in the bulk of the solution, is thus arrived at by a number of independent methods, viz. determination of γ, measurement of C by the a.c. method and oscillographic determination of the capacity current.

Gupta[83a] arrived at the conclusion about the formation of condensed micellar films when studying the adsorption of methyl orange on mercury by the 'tensammetric' method. Capacity peaks associated with the formation and destruction of micellar films are observed in the C—E curves of alkyl sulphate anions with a carbon chain of sufficient length (12 or more carbon atoms)[103, 104] as well as those of sodium laurate and caprylate[105].

A typical C—E curve with the A and B peaks corresponding to the processes of formation and destruction of the micellar film and the C peak, to the total desorption of the alkyl sulphate from the electrode surface, is shown in *Figure 8*.

C—E curves of an unusual shape were observed by OSTROVSKY and FISCHER[106] in weak bases which are at the same time effective corrosion inhibitors. Thus, ethyldodecylsulphoxide in 6N HCl gives a C—E curve with two deep minima, where the capacity falls to $3\,\mu f\,\text{cm}^{-2}$ and even somewhat lower. The authors attribute the left-hand minimum to adsorption of the free base, the secondary adsorption of the sulphoxonium cation and the right-hand one to the primary adsorption of the cation.

The shape of the C—E curves measured by the a.c. method and, in particular, the height of the peaks depend on the frequency, since at

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* The oscillographic method was first used by BARCLAY and BUTLER[102] who studied the adsorption of t-amyl alcohol by measuring the charging current. In the method of Loveland and Elving[151], triangular voltage pulses are imposed on the polarographic cell and the capacity current is registered on the oscillograph screen. With a small solution resistance, this current is proportional to the double layer capacity, and two symmetrical differential capacity curves, corresponding to the rising and falling branches of the triangular pulse, are obtained on the oscillograph screen. Also a differential galvanostatic method has been developed by Kozlowska and Conway (see Chapter 5).

sufficiently high frequencies the establishment of the adsorption equilibrium lags behind the change in the potential. This question will be considered in Section VI.

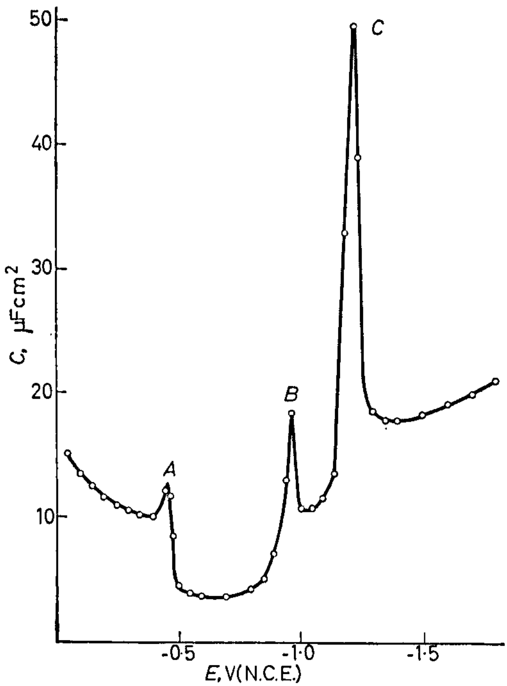

Figure 8. Differential capacity curve of 1N $Na_2SO_4 + 10^{-3}$M $C_{12}H_{25}OSO_3Na$; 400 c 25° C (Damaskin, Nikolaeva-Fedorovich *and* Ivanova[104])

IV. THE QUANTITATIVE THEORY OF THE EQUILIBRIUM C—E CURVES IN THE PRESENCE OF ALIPHATIC COMPOUNDS

1. *Connection between Adsorption Capacitance and Adsorption Isotherm*

The quantitative theory of the *C—E* curves, assuming the adsorption equilibrium to be established for every value of *E*, will now be considered.

If the adsorption of organic compounds on the electrode surface does not result in the formation of multilayers or micellar films, the surface charge is a function of only the potential and the coverage: $q=f(E, \theta)$; hence

$$\mathrm{d}q = \left(\frac{\partial q}{\partial E}\right)_\theta \mathrm{d}E + \left(\frac{\partial q}{\partial \theta}\right)_E \mathrm{d}\theta \tag{33}$$

whence

$$C = \frac{\mathrm{d}q}{\mathrm{d}E} = \left(\frac{\partial q}{\partial E}\right)_\theta + \left(\frac{\partial q}{\partial \theta}\right)_E \frac{\mathrm{d}\theta}{\mathrm{d}E} \tag{34}$$

In other words, the differential capacity measured under these conditions consists of two terms[107] one of which, the quantity,

$$C_{\mathrm{tr}} = \left(\frac{\partial E}{\partial q}\right)_\theta \tag{35}$$

can be called the true capacity, and the other,

$$C_{\mathrm{ad}} = \left(\frac{\partial q}{\partial \theta}\right)_E \frac{\mathrm{d}\theta}{\mathrm{d}E} \tag{36}$$

the added capacity or the adsorption pseudocapacity*.

To interpret quantitatively the differential capacity curves in the presence of an organic substance, it is necessary to know the relations $q=f(E, \theta)$ and $\theta=\theta(E)$, connected by equation 8 with the adsorption isotherm of organic molecules on the electrode surface.

Freundlich's isotherm resulting from Butler's theory[19], taking into account equations 23, 25 and 26, can be written in the form

$$\theta = B_0 c^n \exp\left[-\alpha(E-E_m)^2\right] \tag{37}$$

This leads to the following expressions for the electrode charge and for the true and the added capacities:

$$q = q_0 - \frac{2\alpha A}{n}(E-E_m)\theta \tag{38}$$

$$C_{\mathrm{tr}} = C_0 - \frac{2\alpha A}{n}\theta \tag{39}$$

$$C_{\mathrm{ad}} = \frac{4\alpha^2 A B_0}{n} c^n (E-E_m)^2 \exp\left[-\alpha(E-E_m)^2\right] \tag{40}$$

Analysis of equations 38–40 shows that the potentials of the maxima on the differential capacity curve are equal to†

$$E^{\max} = E_m \pm \frac{\sqrt{3}}{2\alpha} \tag{41}$$

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* The term is used here in a somewhat different sense from that in Chapter 5.

† Our acknowledgement is due to Dr. Parsons, who pointed out an inaccuracy in the original calculation.

and, hence, do not depend on the concentration of the organic substance, while the value of $(C\text{–}C_0)_{E^{\max}}/(C_0\text{–}C)_{E_m}$ is equal to $2e^{-3/2}$ i.e. the excess of the total capacity at $E_{\max}$ over C_0 amounts to ~ 44·5 per cent of its decrease at E_m(cf.[108]).

As seen from *Figure 9*, the experimental differential capacity curves do not generally correspond to the inferences from Butler's theory.

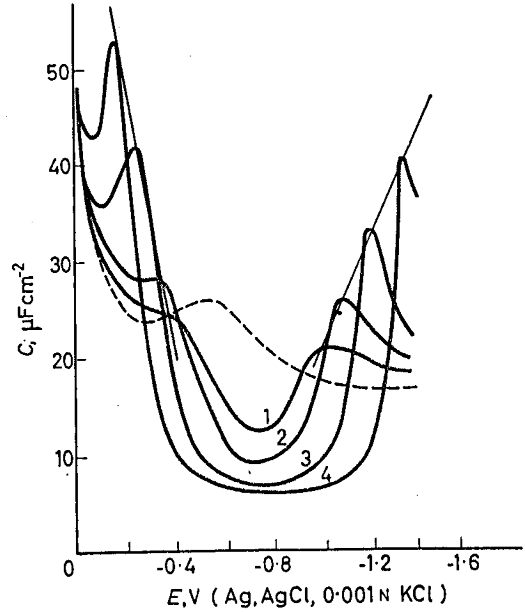

Figure 9. Differential capacity curves of 0·1N $HClO_4$ (dashed) *and of* 0·1N $HClO_4$ *with additions of valeric acid* ($x = c_{sat}$) (HANSEN, MINTURN *and* HICKSON[91])

1 x = 0·042; 2 x = 0·08; 3 x = 0·162; 4 x = 0·32; 1000 c

Only in the case of small concentrations of organic compounds of low molecular weight does an approximate agreement with this theory exist (*Figure 9*, curve 1), as noted by PARSONS[108].

According to Frumkin[12b], if there occurs no reorientation of adsorbed organic molecules due, for instance, to the π-electronic interaction, the expression for the surface charge in the presence of adsorbed organic substances is, to a first approximation, of the form

$$q = q_0(1-\theta)+q'\theta \tag{9}$$

whence

$$C = C_0(1-\theta)+C'\theta+(q'-q_0)\,\frac{d\theta}{dE} \tag{42}$$

where the first two terms on the right-hand side represent the true capacity

$$C_{tr} = C_0(1-\theta)+C'\theta \tag{42a}$$

whereas

$$C_{ad} = (q'-q_0)\,\frac{d\theta}{dE} \tag{42b}$$

If the value of C_{ad} can be neglected compared with the true capacity, which is the case at the minimum of the differential capacity curve, where $(d\theta/dE)\approx 0$, or when the experimental capacity values measured at different a.c. frequencies are extrapolated to $\omega \to \infty$ (cf. [107, 108, 110]), equation 42a can be used for the determination of the coverage θ.

The use of equation 42a, which is not purely thermodynamic, for the investigation of the adsorption isotherms was criticized by PARSONS[111]. However, as shown by BREITER and DELAHAY[112] for adsorption of n-amyl alcohol, the values of θ calculated by a thermodynamic method from the electrocapillary measurements and those determined by means of equations 9 and 42a are in fair agreement. This shows that equation 42a can be used for the study of the adsorption of organic compounds on the electrode surface. LAITINEN and MOSIER[113] applied it to the adsorption isotherms of thirty organic substances on mercury, their shape being found to correspond approximately to Langmuir's isotherm. It should be noted, however, that in a number of cases where the concentration of strongly adsorbed organic substances was small, the adsorption equilibrium probably could not be actually established when a dropping electrode with a relatively short drop time, 8–10 sec, was used[114, 115]. This limits the certainty of the conclusions regarding the shape of the adsorption isotherms.

Frumkin and Damaskin[97] found from differential capacity measurements in 1N KI solutions with varying additions of $[(C_4H_9)_4N]I$ that the adsorption isotherm of tetrabutylammonium cations on mercury has an *S*-shape, corresponding to equation 16 and indicating a strong attractive interaction between the adsorbed particles. At the same time, when the dropping electrode was used at small concentrations of $[(C_4H_9)_4N]I$, in accordance with the results of DELAHAY *et al.*[114, 115] the total quantity of adsorbed particles was found to be determined by the diffusion rate and to a first approximation could be calculated by means of Ilkovic's equation.

LORENZ *et al.*[116, 117] determined the adsorption isotherms of various amines, alcohols and organic cations from the differential capacity data by means of equation 42a. It was shown that, when the attraction forces between the adsorbed particles predominate (higher alcohols and amines), the adsorption isotherm has an *S*-shape, but when repulsion predominates—$[(CH_3)_4N]^+$, $[(C_2H_5)_3NH]^+$—it lies below that of Langmuir.

The shape of the adsorption isotherms of organic substances on mercury can be interpreted by means of equation 16. In fact, as follows from the analysis of this equation, at $a > 0$ (=attractive forces), the dependence of θ on the concentration assumes an *S*-shape*, while at $a < 0$ (=repulsive forces), equation 16 expresses approximately a logarithmic dependence of θ on c (see *Figure 10*).

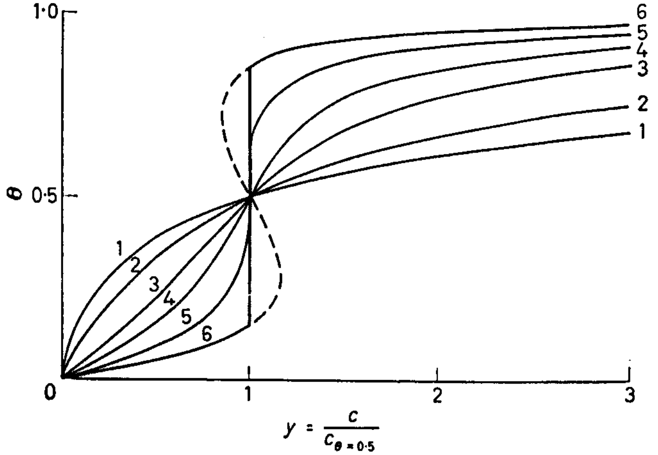

Figure 10. Adsorption isotherm calculated from equation 43 at different values of a

In order to determine the value of *a* from the experimental data, it is very convenient to express the coverage as a function of the relative concentration, $y = c/c_{\theta=0.5}$. Here, we obtain instead of equation 16

$$y = \frac{\theta}{1-\theta} \exp\left[a(1-2\theta)\right] \tag{43}$$

The dependence of θ on y for various values of *a*, calculated from equation 43, is shown in *Figure 10*. The experimental data of Lorenz *et*

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* See also Chapter 5.

al.[116, 117] on adsorption of t-amyl alcohol and of $[(C_2H_5)_3NH]^+$ are given in *Figure 11* which shows that the data for these two compounds are in good agreement with the theoretical curves calculated for $a=1{\cdot}6$ and $a=-1{\cdot}0$, respectively. Some discrepancies are probably due to the fact that no allowance was made for the change in the activity coefficient with increasing concentration of the organic substance; this results in a certain distortion of the adsorption isotherm.

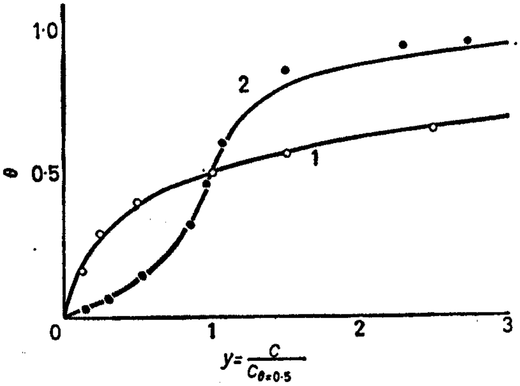

Figure 11. Adsorption isotherm calculated from equation 43 at $a=-1{\cdot}0$ *(curve 1); at* $a=1{\cdot}6$ *(curve 2)*

experimental data for ○ $[(C_2H_5)_3HN]^+$ (LORENZ, MÖCKEL *and* MÜLLER[116])
● $t\text{-}C_5H_{11}OH$ (LORENZ *and* MÜLLER[117])

It follows from equation 43 that

$$\frac{dy}{d\theta}=\exp\,[a(1-2\theta)]\,\frac{1-2a\theta+2a\theta^2}{(1-\theta)^2} \tag{44}$$

At $\theta=0$

$$\left(\frac{dy}{d\theta}\right)_{\theta=0}=\exp\,(a) \tag{44a}$$

at $\theta=0{\cdot}5$

$$\left(\frac{dy}{d\theta}\right)_{\theta=0\cdot5}=4-2a \tag{44b}$$

Equations 44a and 44b give two graphic methods for the determination of the constant a from experimental data, as illustrated by *Figure 12*. In addition, from equation 43 it follows that

$$a=\frac{2{\cdot}3}{1-2\theta}\log\left[\frac{y(1-\theta)}{\theta}\right] \tag{43a}$$

Equation 43a can be also used for the determination of a from experimental adsorption isotherms.

It follows from equation 44b that at $a=2(\mathrm{d}y)/(\mathrm{d}\theta)_{\theta=0\cdot5}=0$, i.e. there appears a vertical section on the adsorption isotherm. When $a>2$, a part of the theoretical isotherm corresponds to unstable states of the adsorption layer (the dashed section of curve 6 in *Figure 10*). The unstable states for which $\mathrm{d}\theta/\mathrm{d}c>0$ can be realized experimentally but not those for which $\mathrm{d}\theta/\mathrm{d}c<0$ (in particular, at $\theta=0\cdot5$). Under equilibrium conditions at $a>2$, a discontinuous transition is observed from a 'gaseous' layer with a small coverage to a condensed film, for which θ is close to unity. It should be noted, however, that equation 43, deduced on the basis of highly simplified assumptions, gives only semiquantitative evaluations of the phenomena occurring in the region of two-dimensional condensation which are undoubtedly of a more complicated character.

Equation 16 can be used to determine the values of $\mathrm{d}\theta/\mathrm{d}E$, necessary for a quantitative interpretation of the differential capacity

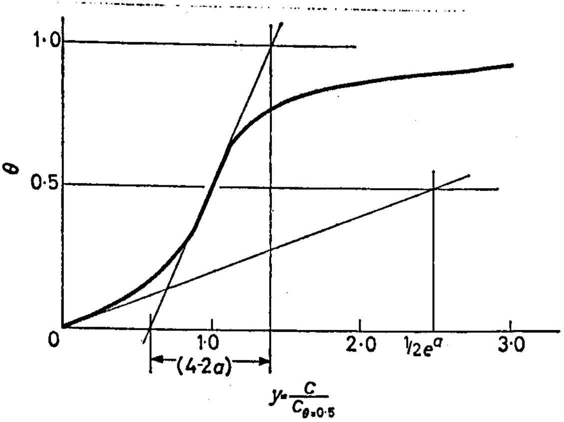

Figure 12. Determination of a from experimental adsorption isotherm (schematic)

curves (see equations 36 and 42). From equation 16, the following relation can be readily obtained

$$\frac{\mathrm{d}\theta}{\mathrm{d}E}=\frac{\mathrm{d}\ln B}{\mathrm{d}E}\,\frac{\theta(1-\theta)}{1-2\alpha\theta(1-\theta)} \tag{45}$$

It follows from equation 17 that

$$\frac{\mathrm{d}\ln B}{\mathrm{d}E} = -\frac{q_0 - C'(E-E_N)}{A} \tag{46}$$

By combining equations 42, 11, 45 and 46, one obtains

$$C = C_0(1-\theta) + C'\theta + \frac{[q_0 - C'(E-E_N)]^2}{A}h \tag{47}$$

where

$$h = \frac{\theta(1-\theta)}{1-2a\theta(1-\theta)} \tag{48}$$

Equation 47 was first deduced by Hansen *et al.*[91] and used by them to calculate the apparent coverage, θ_{app}

$$\theta_{\mathrm{app}} = \frac{C_0 - C}{C_0 - C'} = \theta\left\{1 - \frac{[q_0 - C'(E-E_N)]^2}{A(C_0 - C')}\,\frac{1-\theta}{1-2a\theta(1-\theta)}\right\} \tag{49}$$

The dependence of θ_{app} on the electrode potential calculated from this equation was in fair agreement with the experimental data obtained for adsorption of valeric acid on mercury and of some related compounds.

The use of equation 47 for quantitative interpretation of the adsorption peaks on the differential capacity curves in the presence of an adsorbed substance will now be considered. This problem was first treated by Lorenz *et al.*[116, 117] who, however, used an adsorption isotherm deduced on the basis of the concept of two-dimensional association of adsorbed molecules; the relation can be written

$$\theta = \frac{K_2\left(1 + \dfrac{1}{Bc}\right)^{\nu-1} + 1}{K_2\left(1 + \dfrac{1}{Bc}\right)^{\nu} + 1} \tag{50}$$

where K_2 = the constant of two-dimensional association of adsorbed particles and ν = degree of association, i.e. the number of molecules in an associate. When $K_2 \to \infty$, Langmuir's isotherm, 16a, is obtained from equation 50 whereas, at finite K_2 and ν, equation 50 can be satisfactorily used to explain the *S*-shape of the experimental adsorption isotherm[116]. From equation 50, Lorenz and Müller[117] deduced an approximate expression relating the width of the capacity peak at $\frac{1}{2}$ or $\frac{3}{4}$ of its height, $\Delta E_{1/2}$ or $\Delta E_{3/4}$, with the degree of association, ν:

$$\frac{2{\cdot}20}{\Delta E_{3/4}} = \frac{3{\cdot}52}{\Delta E_{1/2}} = \nu\left|\frac{\mathrm{d}\ln B}{\mathrm{d}E}\right| \tag{51}$$

It appears, however, that for quantitative interpretation of the adsorption peaks on the differential capacity curves it is preferable to use equation 16, since only one constant a is used there for the description of the two-dimensional interaction, instead of the two constants, K_2 and ν, in equation 50. Besides, equation 16 is applicable also when the repulsion forces are predominant; the corresponding calculations were carried out by DAMASKIN *et al.*[118, 119, 181].

It follows from equation 47 that

$$C_{\text{ad}} = \frac{[q_0 - C'(E-E_N)]^2}{A}\,h \tag{47a}$$

As shown by calculations[180], at not too low values of a ($a \geqslant 1$) the change in the additional capacity with the potential is primarily determined by the change in the function h. Under these conditions, the position of the maxima on the C—E curves will be determined to a first approximation by the maximum of the value h. Evaluating from equation 48, $\mathrm{d}h/\mathrm{d}\theta$ and assuming $\mathrm{d}h/\mathrm{d}\theta = 0$, we obtain

$$\theta_{\max} = 0{\cdot}5 \quad h_{\max} = \frac{1}{4-2a} \tag{52}$$

Hence, the theoretical dependence of the peak potentials, $E_{\max}$, on the concentration of the adsorbed organic substance can be determined. In fact, assuming $\theta = 0{\cdot}5$, one finds from equation 16

$$\ln c = -a - \ln B = -a - \ln B_0 + \frac{\Delta\gamma_e + C'E^{\max}\left(E_N - \dfrac{E^{\max}}{2}\right)}{A} \tag{53}$$

2. *Degree of Applicability of the Theory*

In *Figure 13* the results of the calculation using equation 53 are compared with the experimental data of Lorenz and Müller[117] for t-$C_5H_{11}OH$ with 1N KF as supporting electrolyte, the constants $a = 1{\cdot}6$, $B_0 = 25{\cdot}4$, $A = 1{\cdot}045$, $C' = 4{\cdot}4$, $E_N = 0{\cdot}5$ and the experimental C_0—E curve[120] in 0·9N NaF being used in the calculation. The constants A, C' and E_N were taken from Frumkin[12b], where they had been obtained from electrocapillary measurements, and the value of a found from the shape of the adsorption isotherm of t-amyl alcohol[117]. Similar calculations were made for n-$C_5H_{11}OH$ using the data of Melik-Gaikazjan[90].

Figure 13 shows that the experimental data of the dependence of peak potentials on the concentration of the organic substance fall on the theoretically calculated curve which, to a first approximation—at

C_0=const and $\Delta\gamma_e=\frac{1}{2}C_0(E_{\max})^2$—is of a parabolic shape. A more accurate calculation by DAMASKIN and TEDORADSE[180] shows that this approximation corresponds to the condition $a \geqslant 1$ and to sufficiently

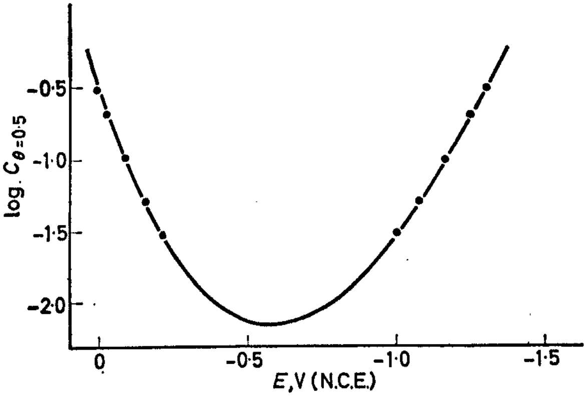

Figure 13. Dependence of potential of adsorption–desorption peaks on concentration of t-$C_5H_{11}OH$ *in presence of* 1N KF

Curve calculated from equation 53; points, experimental data (LORENZ *and* MÜLLER[117])

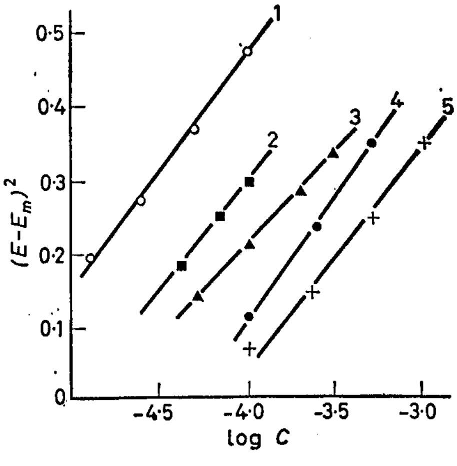

Figure 14. Dependence of potentials of adsorption–desorption peaks on concentration of organic substances (LORENZ *and* MÖCKEL[109])

1 *cyclohexanol;* 2 *isoamylalcohol;* 3 *n-butyl alcohol;* 4 *methylethylketone;* 5 *n-valeric acid*

high concentrations of the organic substance. At low concentrations, the position of the maxima on the C—E curves tends to approach the value determined from equation 41. If $a > 0{\cdot}5$, with a decreasing concentration of the organic substance, the peaks on the C—E curves at first draw together and then again move apart, approaching the value $E_m \pm \sqrt{3}/2\alpha$. At $a<1$ and in particular at $a=0$, which corresponds to Langmuir's isotherm, even at large concentrations of the organic substance an appreciable deviation of the C—E curves from the parabolic relationship, corresponding to the condition $\theta^{\max}=0{\cdot}5$, is observed. Thus the conclusion concerning the linear dependence of $(E^{\max}-E_m)^2$ on log c, drawn by Lorenz and Möckel[109], SENDA and TACHI[121] as well as by KAMBARA[122] from analysis of Langmuir's equation, cannot be considered to be correct, and the experimentally obtained linear relationship between log c and $(E^{\max}-E_m)^2$ (*Figure 14*) seems to be due to the fact that, for the organic substances investigated, $a \geqslant 1$ and, therefore, their adsorption on mercury does not obey Langmuir's equation. The inference from the theories of Doss[123] and of BREYER[81a] about a linear relationship between the peak potential and the logarithm of the concentration of the adsorbed substance in the general case is also incorrect. This relationship, as shown by numerical calculation[180], if Langmuir's isotherm ($a=0$) is applicable, is obtained over a definite although rather wide range of concentrations of the organic substance (change in c by two orders). In the general case, however, if the measurements have been made over not too great a concentration range of the organic substance, the sections of the two branches of the ln $c-E_{\max}$ parabola can, of course, be approximated by two intersecting straight lines.

3. *Height of Capacitance Peak and Concentration*

Let us consider the effect of the concentration of the organic substance on the height of the adsorption peaks. This problem can be solved analytically, provided $C_0=\text{const.}$ In this case, $q_0=C_0E$ and $\Delta\gamma_e=\frac{1}{2}C_0E^2$; since, at the maximum, $\theta=0{\cdot}5$, we obtain from equations 47 and 53

$$C_{\max} = \frac{C_0+C'}{2}+\frac{1}{4-2a}\,\frac{[(C_0-C')E+C'E_N]^2}{A} \tag{54}$$

$$(C_0-C')E^2+2EE_NC' = 2A(\ln c+a+\ln B_0) \tag{55}$$

By introducing equation 55 into 54, we find

$$C_{\max} = \frac{C_0+C'}{2}+\frac{C_0-C'}{2-a}(a+\ln B_0)+\frac{(C'E_N)^2}{2A(2-a)}+\frac{C_0-C'}{2-a}\ \ln c \tag{56}$$

or, by combining all constants

$$C_{\max} = \text{const}_1+\text{const}_2 \log c \tag{56a}$$

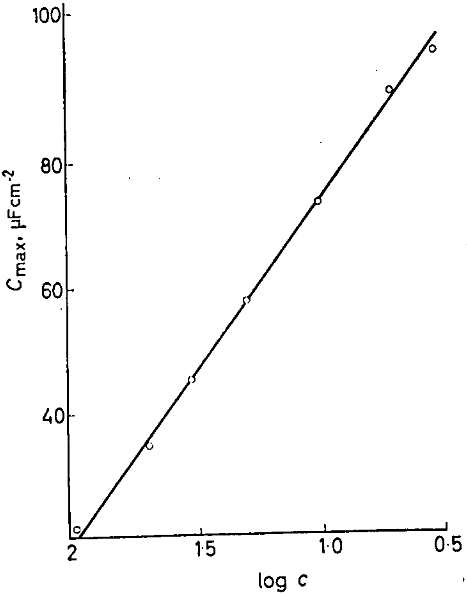

Figure 15. Dependence of height of cathodic capacity peak on concentration of t-$C_5H_{11}OH$ (DAMASKIN *and* GRIGORJEV[119])

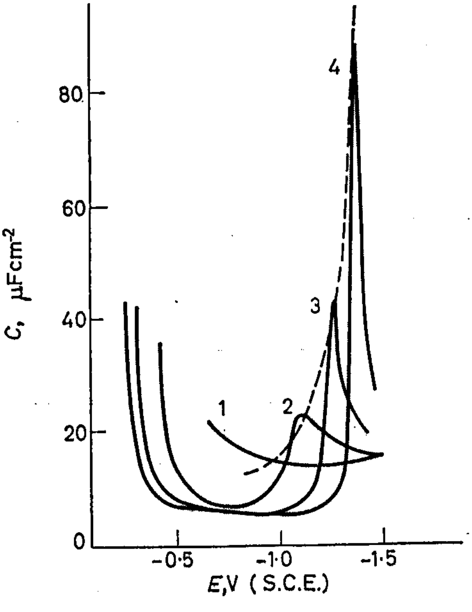

Figure 16. Differential capacity curves observed in 1N KCl *with additions of methylethylketone:* 1 0; 2 0·1M; 3 0·25M; 4 ·50M; 1,590 c (LORENZ *and* MÖCKEL[109])

Thus the height of the adsorption peak must change linearly with the logarithm of the concentration of the adsorbed substance[118, 119]. This conclusion was also drawn independently by Senda and Tachi[121] on the basis of the Langmuir adsorption isotherm. As seen from *Figure 15*, the linear dependence of C_{max} on $\log c$, predicted by equation 56a, is in good agreement with the experimental data (cf. [121]). Good agreement between calculated and experimental values of the constants, const_1 and const_2, is also observed in the case of t-$C_5H_{11}OH$, using the value $a = 1{\cdot}5$, whereas the use of the Langmuir isotherm under the same conditions ($a = 0$) results in a considerable discrepancy between theory and experiment (*Table 4*).

Since $\log c$ has been shown to depend linearly on $(E_{\mathrm{max}})^2$ and C_{max} on $\log c$, the line connecting the tops of the adsorption peaks on the differential capacity curves, measured at different concentrations of the organic substance, must be of parabolic shape. *Figure 16* confirms the correctness of this conclusion. It is valid though only for equilibrium curves of differential capacity corresponding to $\omega \rightarrow 0$, which are approximated by the C—E curves measured in solutions with a sufficiently high concentration of the organic substance at low frequencies. If the solubility of the organic substance is low, the capacity at the maximum, compared with $C_{\mathrm{max}}(\omega = 0)$, decreases owing to the slowness of diffusion, the more the lower the concentration of the organic substance. Therefore, the line connecting the tops of the maxima on the C—E curves then approaches a straight line (see *Figure 9*). In addition, the above dependence is limited by the fulfilment of condition $a \geqslant 1$.

Table 4

Comparison of Theory and Experiment for Constants in the Relation of Capacitance Maximum to Solute Concentration

	Experiment	*Calculated with* $a = 1{\cdot}5$	$a = 0$
const_1	135	132	31
const_2	54	57	14

4. *Shape of Adsorption Peaks*

The shape of the adsorption peaks[118] will now be considered. If the value of h determined by equation 48 is not equal to h_{max} (see equation 52), then by solving equation 48 relative to θ and assuming h to represent a certain fraction of $h_{\max}$, one obtains from equation 52

$$\theta_i = \tfrac{1}{2}(1 \pm r)\nu \qquad i = 1, 2 \ldots \tag{57}$$

where

$$r_{1/4} = \sqrt{\frac{6-3a}{8-3a}};\ r_{1/2} = \sqrt{\frac{2-a}{7-a}};\ r_{3/4} = \sqrt{\frac{2-a}{8-a}};\ r_{7/8} = \sqrt{\frac{2-a}{16-a}} \tag{58}$$

the subscript index of r giving the ratio $h/h_{\max}$.

It follows from equation 45 that

$$\mathrm{d}\ln B = \frac{1-2a\theta(1-\theta)}{\theta(1-\theta)}\,\mathrm{d}\theta \tag{59}$$

By integrating from θ_1 to θ_2, where the values θ_1 and θ_2 are determined by equation 57, and using the Lagrange theorem of the mean, one obtains for the width of the capacity peaks, ΔE, the expression

$$\Delta E = \frac{2}{\left|\dfrac{\mathrm{d}\ln B}{\mathrm{d}E}\right|}\left(\ln\frac{1+r}{1-r} - ar\right) \tag{60}$$

where the values of r are given by equation 58 and the value of $\left|\dfrac{\mathrm{d}\ln B}{\mathrm{d}E}\right|$ approximately corresponds to the maximum potential, $E^{\max}$, on the C—E curve.

Equations 52 and 60 combined with 58 permit us to calculate the change in the shape of the peak on the differential capacity curves with increasing values of the attraction constant. The results of this calculation are given in *Figure 17*. As seen from this figure, the height of the peak (or, more exactly, the quantity h) increases and the width of the peak decreases with a rise in a. At $a=2$, as follows from equations 58 and 60, $\Delta E=0$ and, according to 52, $h_{\max} \to \infty$. In other words, the peak on the C—E curve degenerates into a vertical line with an indefinite value of the capacity. Data of this kind were obtained by Damaskin and Nikolaeva-Fedorovich[98] with 1N KI in 10^{-3}N $[(C_4H_9)_4N]I$ solution (*Figure 18*).

At smaller concentrations, 0·01N of KI, no degeneration of the adsorption–desorption peak into a vertical line occurs. Apparently, by neutralizing the positive charges of the tetrabutylammonium cations, the presence of the I^- ions in the adsorbed layer increases their mutual attraction, which results in a rise in a.

As already pointed out, at $a > 2$ the coverage changes discontinuously from small θ to θ approaching unity with a rise in the concentration and with a lowering of $|E|$. The intermediate, unstable, values of the coverage result in unstable capacity values. Since some of the unstable θ values can be realized, a hysteresis loop during the determination of the differential capacity curve can be observed by quickly changing the electrode polarization in different directions. On the other hand, if $a > 2$, some of the values of θ, including $\theta = 0{\cdot}5$, and the corresponding capacity peaks cannot be realized ($d\theta/dc < 0$). One

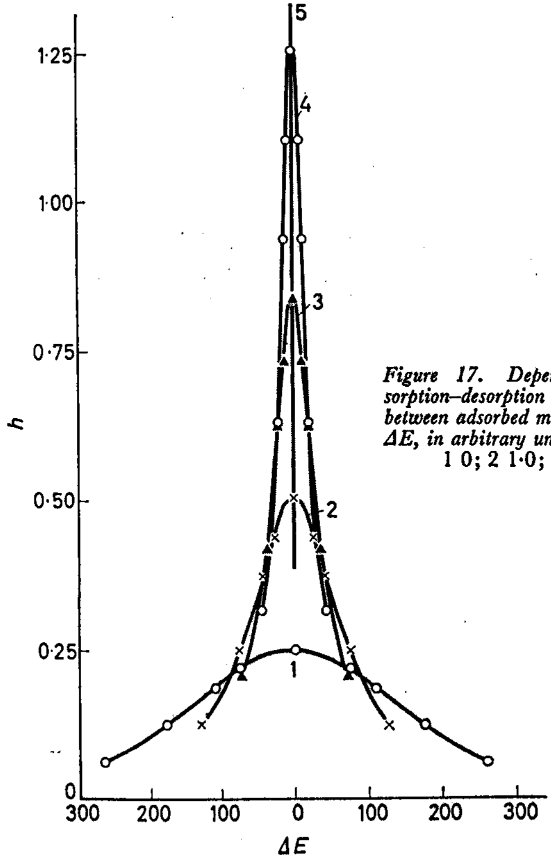

Figure 17. Dependence of shape of adsorption–desorption peak on interaction between adsorbed molecules.
ΔE, in arbitrary units (Damaskin[118]) *: a=* 1 0; 2 1·0; 3 1·4; 4 1·6; 5 2

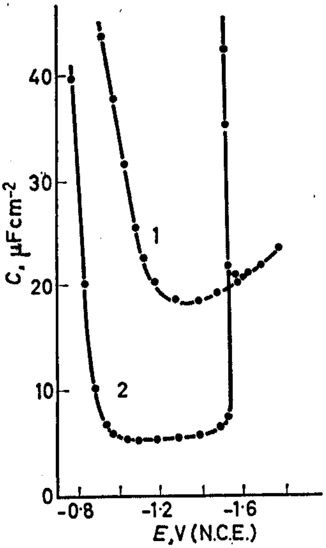

Figure 18. Differential capacity curves of solutions (DAMASKIN *and* NIKOLAEVA-FEDOROVICH[98])

1 1N KI; 2 1N KI + 10^{-3}N $[(C_4H_9)_4N]I$; 400 c, 25° C

should expect to observe the phenomena described in the case of organic compounds with sufficiently long carbon chain, where the value of *a* can readily exceed 2. In fact, all the phenomena, i.e. unstable capacity values, the hysteresis loop and absence of the desorp-

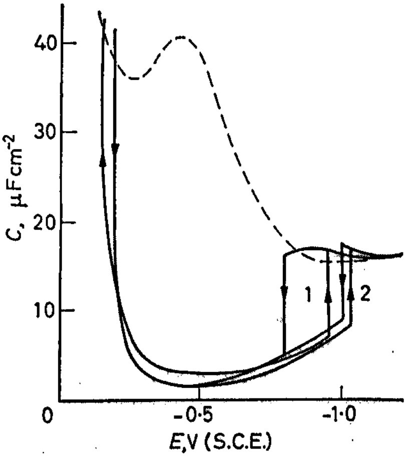

Figure 19. Differential capacity curves of 1N KCl *(dashed) and of* 1N KCl *with additions of nonylic acid* (LORENZ[110])

1 *c* = 2 c_{sat}; 2 *c* = c_{sat}; 1,590 c

tion peak were observed by Lorenz[110] when determining the C—E curves in nonylic acid solutions (*Figure 19*).

From equations 60 and 58, at $a=0$, we obtain

$$\frac{3{\cdot}52}{\Delta E_{1/2}} = \frac{2{\cdot}20}{\Delta E_{3/4}} = \left|\frac{\mathrm{d}\ln B}{dE}\right| \tag{51a}$$

which is in agreement with Lorenz's[117] conclusion for the case of the Langmuir isotherm when, by definition, $\nu=1$ (see equation 51). If $a\neq 0$, we obtain for ν from equations 51 and 60

$$\nu_{1/2} = \frac{3{\cdot}52}{2\left(\ln\dfrac{1+r_{1/2}}{1-r_{1/2}} - ar_{1/2}\right)} \qquad \nu_{3/4} = \frac{2{\cdot}20}{2\left(\ln\dfrac{1+r_{3/4}}{1-r_{3/4}} - ar_{3/4}\right)} \tag{61}$$

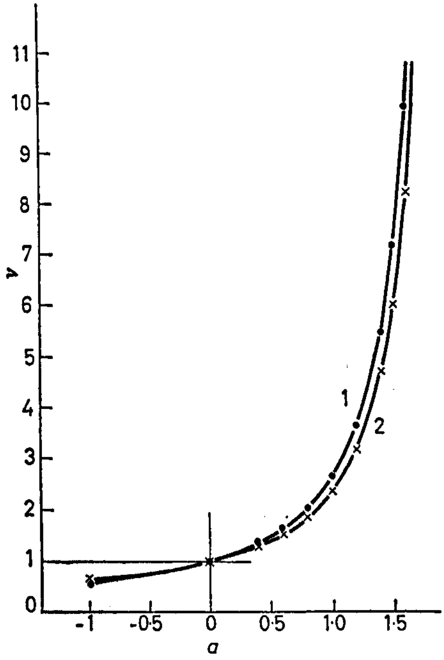

Figure 20. Dependence of 'degree of association', ν, on the attraction constant, a, calculated from equations 61 and 58: 1 $\nu_{3/4}$; 2 $\nu_{1/2}$

The calculation of the values of $\nu_{1/2}$ and $\nu_{3/4}$ from equation 61 (*Figure 20*) shows that $\nu_{1/2}=\nu_{3/4}$ only at $a=0$ whereas, at $a>0$, $\nu_{3/4}>\nu_{1/2}$ and, at $a<0$, $\nu_{3/4}<\nu_{1/2}$. This conclusion is in good agreement with the experimental data of Lorenz and Müller[117], as shown by Damaskin[119].

By differentiating equation 53 with respect to the potential which, at $\theta = 0{\cdot}5$ is equal to $E_{\max}$, we obtain

$$\frac{\mathrm{d}\ln c}{\mathrm{d}E_{\max}} = -\frac{\mathrm{d}\ln B}{\mathrm{d}E} - \frac{\mathrm{d}a}{\mathrm{d}E} \tag{62}$$

If the attraction constant, a, is assumed to be independent of the potential

$$\frac{\mathrm{d}\ln c}{\mathrm{d}E_{\max}} = -\frac{\mathrm{d}\ln B}{dE} \tag{62a}$$

From equations 60 and 62a, it follows that

$$f\,(a) = \log\frac{1+r}{1-r} - \frac{a}{2{\cdot}3}r = \frac{1}{2}\frac{\mathrm{d}\log c}{\mathrm{d}E_{\max}}\varDelta E \tag{63}$$

where the dependence of r on a is given by the relations 58. Thus, knowing the slope of the $\log c$—$E_{\max}$ curves and the width of the capacity peaks, $\varDelta E$, the attraction constant, a, at the peak potentials can be found by means of the $f\,(a)$–a graph. The values of a for t-$C_5H_{11}OH$ with 1N KF as supporting electrolyte, determined by this method from the values of $\varDelta E$ and $(\mathrm{d}\ln c)/(\mathrm{d}E_{\max})$ of Lorenz and Müller[117], are presented in *Figure 21.* As is seen, a changes nearly linearly with the electrode potential and, hence, the hypothesis that $a = \text{const}$ (or, correspondingly, $\nu = \text{const}$)[117, 124], represents only a first approximation, as already stated by Frumkin[12b]. The dependence of the value of a on the electrode potential necessitates a reconsideration of the applicability of equations 63, 58 and 47, as they were deduced under the condition $a = \text{const}$. Such analysis was made by DAMASKIN[181] who showed that, with a varying value of a, equations 63 and 58 are valid with sufficient accuracy, if $a \geqslant 1$. At the same time, for the differential capacity in the presence of an organic substance, instead of equation 47 we obtain

$$C = C_0(1-\theta) + C'\theta + \left[q_0 + C'(E_N^0 - E) - 2A\theta\frac{\mathrm{d}a}{\mathrm{d}E}\right]^2 \frac{h}{A} \tag{47a}$$

where h is expressed by equation 48 as before. Unlike equations 63 and 58, equation 47a is valid at any value of a.

It follows from equation 52 that a small change in a may greatly affect the height of the capacity adsorption–desorption peak, if a is close to 2. Thus, a change in a from 1·6 to 1·8 doubles the value of $h_{\max}$ which is proportional to the height of the peak. *Figure 22a* and *b* compares the differential capacity curves experimentally measured in 0·9N NaF with different additions of t-amyl alcohol, and those calculated[119] from equation 47 with $\alpha = \text{const} = 1{\cdot}6$. Shape and disposition of the theoretical and experimental curves are seen to be in good agreement. The experimental anodic capacity peaks, however, are appreciably higher than those calculated, while the cathodic are somewhat lower. As in *Figure 21*, this indicates an increase in a with the rise in the positive value of the electrode potential.

In fact, when the linear change in the value of a with the potential is taken into consideration, the discrepancy between the calculated and the experimental curves is practically eliminated, as shown in *Figure 23*. Good agreement between the experimental and calculated differential capacity curves, taking into account the dependence of a on E, was also observed by DAMASKIN and LERKH[182] for adsorption on mercury of normal and iso-amyl alcohols from 1N Na_2SO_4 solutions, as well as by Damaskin and Venkatesan for adsorption of n-valeric acid from 0·1N Na_2SO_4 solutions.

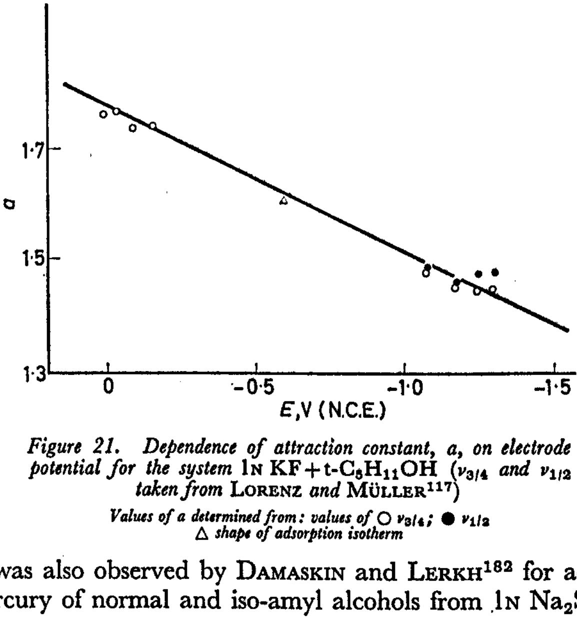

Figure 21. Dependence of attraction constant, a, on electrode potential for the system 1N KF + t-$C_5H_{11}OH$ *($\nu_{3/4}$ and $\nu_{1/2}$ taken from* LORENZ *and* MÜLLER[117])

Values of a determined from: values of ○ $\nu_{3/4}$; ● $\nu_{1/2}$
△ *shape of adsorption isotherm*

The linear dependence of a on E for these compounds does not correspond to equation 20 (according to which a linear relation should exist between a and the square of the potential); it can be expressed as

$$a = a_0 + k_0 E \qquad (64)$$

where k_0 is a certain constant, with the value 0·25 for t-$C_5H_{11}OH$ with 1N KF as supporting electrolyte. By using equations 16 and 8, one obtains for the value of the surface charge

$$q = q_0(1-\theta) + C'(E - E_N^0)\theta + k_0 A \theta^2 \qquad (65)$$

By comparing equation 65 with equations 9 and 11 and introducing the supplementary term from equation 65 into the quantity E_N one obtains

$$E_N = E_N^0 - \frac{k_0 A}{C'}\theta \tag{66}$$

where $E_N^0 = E_N$ at $\theta = 0$.

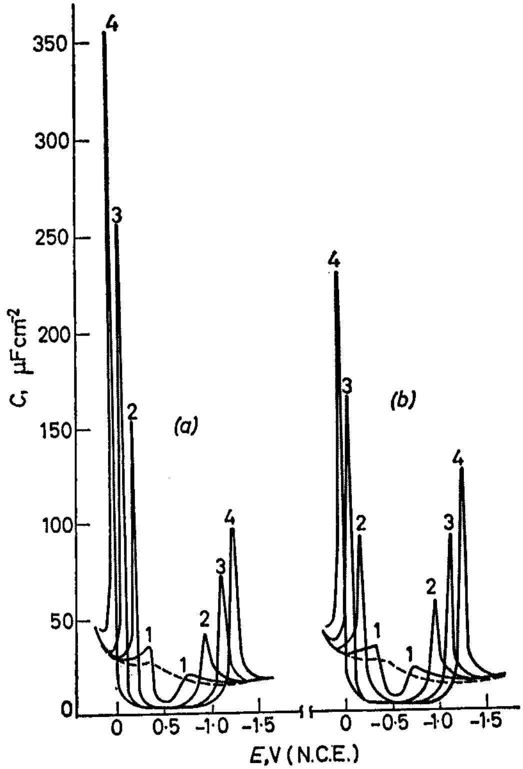

Figure 22. Differential capacity curves of 0·9N NaF (*dashed*) *and of* 0·9N NaF *with additions of* t-$C_5H_{11}OH$ (DAMASKIN *and* GRIGORJEV[119])

1 0·3M; 2 0·1M; 3 0·03M; 4 0·01M

(*a*) *experimental data*, 400 c; (*b*) *calculated from equation 47 at* a = const

Thus, a formally linear change with the potential in the value of a found experimentally may result from a change with the coverage in the effective value of E_N. However, since the value of E_N is associated with the adsorbed molecules having a dipole moment, the result obtained can be interpreted as caused by a change in the orientation of the adsorbed molecules with an increase in the coverage. At $k_0=0{\cdot}25$, $A=1{\cdot}045$, $C'=4{\cdot}4$ and $E_N^0=0{\cdot}5$ according to equation 66, $E_N=0{\cdot}5-0{\cdot}059\theta$, i.e. the maximum change in E_N for t-$C_5H_{11}OH$ with 1N KF as supporting electrolyte amounts to ~12 per cent.

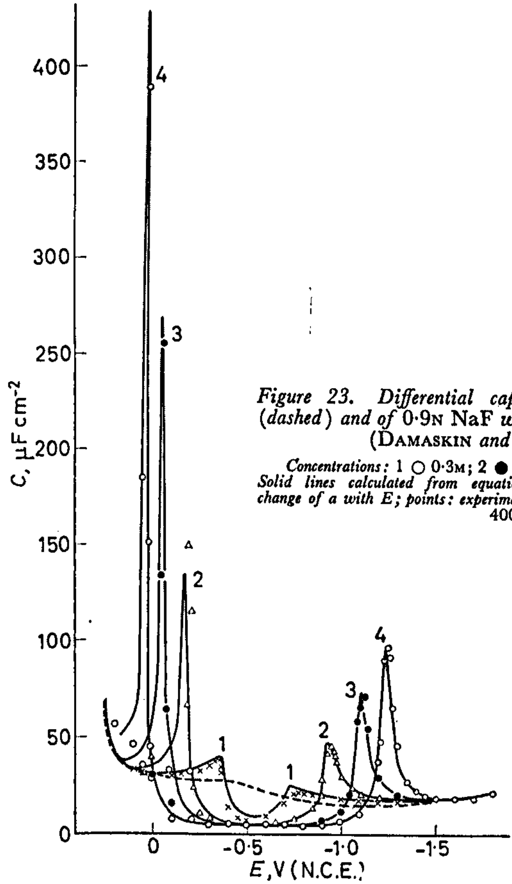

Figure 23. Differential capacity curve of 0·9N NaF *(dashed) and of* 0·9N NaF *with additions of* t-$C_5H_{11}OH$ (DAMASKIN *and* GRIGORJEV[119])

Concentrations: 1 ○ 0·3M; 2 ● 0·1M; 3 △ 0·03M; 4 × 0·01M
Solid lines calculated from equation 47 with allowance for linear change of a with E; points: experimental data in corresponding solutions; 400 c

As stated in discussing equation 20, the assumption about the constancy of the quantities A, a_0 and B_0 when there exists a dependence of E_N on θ, can be regarded only as a first approximation.

For pyridine adsorption, a much greater value of $k_0=-2{\cdot}8$ is obtained experimentally. This can be interpreted as a result of a strong dependence of the effective dipole moment of pyridine molecules on the coverage, the opposite sign of the k_0 value indicating that the quantity E_N becomes more positive with increasing coverage.

The repulsive interaction between pyridine molecules observed by Conway and Barradas[21] at positive surface charges, changes into an attractive one at $q_0 < 0$. The existence of the latter is evidenced both by the shape of strongly pronounced cathodic peaks on the C—E curves (*Figure 24*) and by the S-shape of adsorption isotherms at negative surface charges (*Figure 4*). As shown by DAMASKIN and KLJUKINA[125], at $q_0 < 0$, the pyridine molecules are oriented vertically to the mercury surface, which is in agreement with the conclusion of Conway and Barradas[21]. Under these conditions, the experimental data—adsorption isotherms, dependence of $E_{\max}$ on log c and of θ, C and γ on E—can be quantitatively described on the basis of the above theory, taking into consideration the linear dependence of a on E. Upon a transition to $q_0 < 0$, there is a decrease in the maximum possible coverage, which provides the conditions for reorientation of adsorbed pyridine molecules and for π-electron interaction between these and the positively charged mercury surface.

This accounts for the fact that under the above conditions there is already no agreement between the experimental and the calculated data[125]. Similar results were obtained by DAMASKIN, MISHUTUSHKINA, GEROVICH and KAGANOVICH[183] for adsorption on mercury of aniline from 1N KCl and KI solutions. The differential capacity curves determined in these solutions greatly resemble the C—E curves obtained in the presence of aliphatic compounds. The resemblance, however, is only superficial. While in the presence of aliphatic compounds, both maxima on the C—E curves are associated with the adsorption–desorption processes, in the case of aniline only the cathodic maxima, which are well expressed by the theoretically calculated differential capacity curves, correspond to these processes. The anodic maxima, which in the case of aniline in 1N KCl are very pronounced, correspond to the process of reorientation of adsorbed organic molecules on the mercury surface: the vertical orientation of molecules, which is characteristic of a negatively charged surface, is substituted by a horizontal one, in which case the π-electrons of the benzene ring interact with the positive charges on the mercury surface. The approximate coincidence between the double-layer capacity in 1N KCl and that in the presence of aniline in the region of large positive surface charges can be accounted for by the fact that the π-electrons of the benzene ring penetrate into the metal and neutralize the positive charges of the mercury surface. This results in the monolayer of the horizontally oriented molecules, characterized by the presence of electronic 'holes', beginning to play the role of the positively charged metal surface and attracting chlorine anions[184].

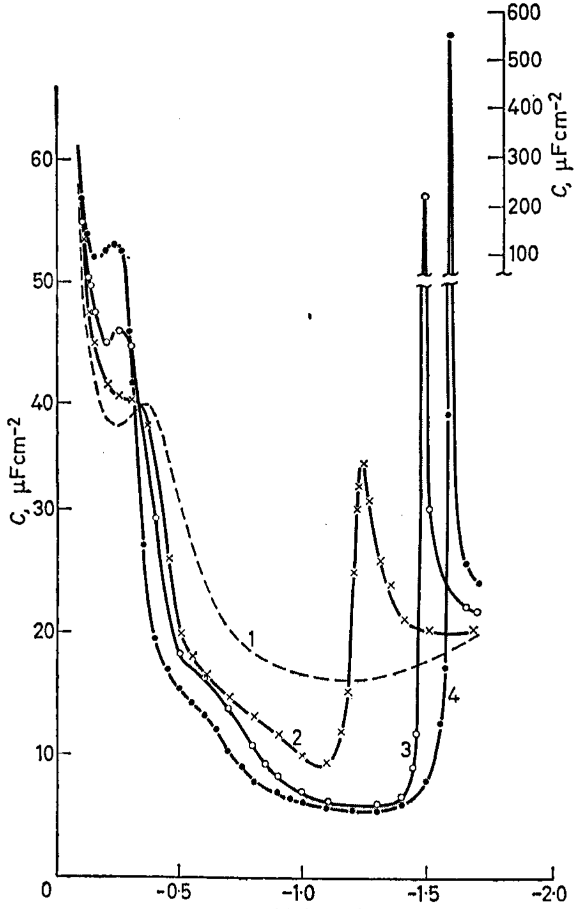

Figure 24. Differential capacity curves of 0·1N KCl *with additions of pyridine:* 1 0; 2 0·06M; 3 0·1M; 4 0·3M; 400 c (DAMASKIN *and* KLJUKINA[125])

These examples show that great care must be exercised in extending the quantitative interpretation of the adsorption phenomena presented here, in which no allowance was made for π-electron interaction, to aromatic and heterocyclic compounds. The inapplicability of equations 15 and 16 in the case of adsorption of aromatic compounds at some intermediate potentials at which a transition occurs with an increase in θ from the repulsive to the attractive interaction, as found by Blomgren, Bockris and Jesch[36], should be particularly emphasized.

As follows from equations 16 and 17, under the assumption that C_0 = const and condition 64 is observed, the potential of maximum adsorption, E_m, is expressed by the condition

$$E_m = -\frac{C'}{C_0 - C'} E_N^0 + \frac{2k_0 A}{C_0 - C'} \theta_m \tag{67}$$

where θ_m = maximum coverage at a given concentration of the organic substance. It follows from this equation that, at large k_0, the potential of maximum adsorption, corresponding to the minimum on the differential capacity curves, should be greatly dependent on θ_m and, consequently, on the concentration of the organic substance. This conclusion is in fair agreement with the experimental data for pyridine (*Figure 24*), as well as for phenol where a large negative value of k_0 ($k_0 = -2{\cdot}05$) is observed.

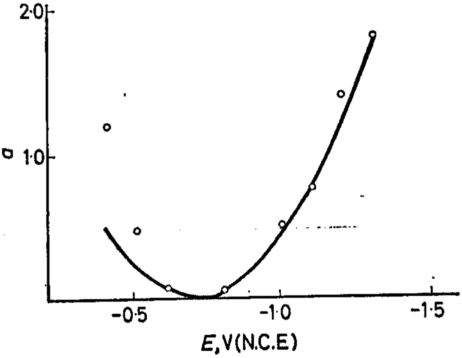

Figure 25. Dependence of attraction constant, a, on electrode potential (DAMASKIN, VAVŘIČKA *and* GRIGORJEV[126])

Curve calculated from equation 68; points: experimental data for 1N Na_2SO_4 + $[(C_4H_9)_4N]_2SO_4$

5. *Tetrabutylammonium Cation*

The linear change in *a* with the electrode potential observed in the case of a number of organic compounds cannot be regarded as a general rule. In fact, as shown by DAMASKIN *et al.*[126], the value of the attraction constant, determined from the shape of the adsorption isotherm for $[(C_4H_9)_4N]^+$ cations from 1N Na_2SO_4 solutions, to a first approximation changes with the potential according to the equation

$$a = a_0+(k-1)\,\frac{(C_0-C')E^2+2C'E_NE}{2A} \tag{68}$$

resulting from equations 20 and 17 (*Figure 25*). Thus, in this case, one should expect a change in the electrode charge with θ_s in agreement with equation 19, and a corresponding change in the true capacity of the electrode, according to the equation

$$C_{\mathrm{tr}} = C_0(1-k\theta_s)+C'k\theta_s+(k-1)(C_0-C')\theta_s^2 \tag{69}$$

A direct verification of equation 69 was carried out[126] by measuring the dependence of the capacity of a growing mercury drop on time in $1\,\mathrm{N}\ Na_2SO_4$ solutions containing small additions of $[(C_4H_9)_4N]^+$.

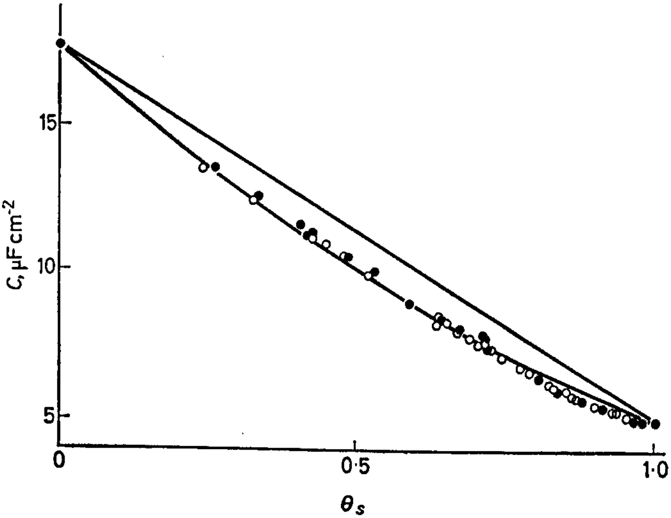

Figure 26. *Dependence of* C_{tr} *on* $\theta_s=\Gamma/\Gamma_m$ (DAMASKIN, VAVŘIČKA *and* GRIGORJEV[126])

Curve calculated from equation 69; straight line calculated from equation 42a; points: experimental data for $1\,\mathrm{N}\ Na_2SO_4+x.10^{-5}\,\mathrm{N}\ [(C_4H_9)_4N]^+$ *at* $E=0{\cdot}8$ (N.C.E.): ○ $x=3{\cdot}5$; ● $x=4{\cdot}0$

Under the conditions of the experiment, the adsorption of organic cations was practically irreversible and determined by their diffusion rate to the surface of the dropping electrode[114, 97]. The equation used to calculate the dependence of $\theta_s=\Gamma/\Gamma_m$ on time was

$$\theta_s = 0{\cdot}74\,\frac{D^{1/2}t^{1/2}c}{\Gamma_m}\left(1+3{\cdot}4\,\frac{D^{1/2}t^{1/6}}{m^{1/3}}\right) \tag{70}$$

which is similar to the well known diffusion equation* of KOUTECKY[128], taking $D=5{\cdot}1\,.\,10^{-6}$ cm^2 sec^{-1} and $\Gamma_m=2{\cdot}07\,.\,10^{-10}$ mole cm^{-2}. As seen from *Figure 26*, the experimental points thus obtained fall on the theoretical C—θ_s curve calculated from equation 69.

The result obtained shows that equation 42a, which indeed was considered[111, 129] to be in need of verification, is not quite exact in the general case. As seen from equations 19 and 65, the change in the interaction between the adsorbed particles with the electrode potential observed in the experiment is an indication of the presence of the terms containing θ_s^2 in the expressions for the surface charge and, consequently, for the true capacity as well. Therefore, the data obtained from the differential capacity measurements by means of equation 42a, even with $C_{ad}=0$, can only serve as a first approximation. Equation 68 can be used as the next approximation for determining adsorption isotherms from differential capacity measurements. However, the shape of the isotherm and, consequently, the value of the attraction constant a calculated from it do not change essentially[126].

6. *Thiourea*

The thermodynamic approach to the investigation of the adsorption of organic compounds, based on Gibbs's equation, 1, and on experimental capacity data or on the interfacial tension, requires a graphical differentiation which greatly lowers the accuracy of calculations. PARSONS[130a] used the method of calculation based on comparison of the experimental values of surface pressure with the data obtained by integrating Gibbs's equation, into which that of the corresponding adsorption isotherm had been substituted. He applied this method[130b] to the data of Schapink *et al.*[93] who measured the differential capacity in 0·1N solution of NaF with varying additions of thiourea. The experimental data on the adsorption of thiourea on mercury proved to agree best not with the Langmuir isotherm, as was supposed by the authors, but with an isotherm expressed by the equation with virial coefficients

$$\ln c - \frac{\Delta \bar{G}_A^0}{RT} = \ln \Gamma + 2\beta\Gamma \tag{71}$$

where $\Delta \bar{G}_A^0/RT$ is the first virial coefficient giving the value of the free energy of adsorption at $\theta=0(\Delta \bar{G}_A^0)$, and β the second virial coefficient, representing a measure of the repulsive interaction between the

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* KORYTA[127] was the first to calculate the surface coverage of a growing mercury drop by means of the diffusion equation.

adsorbed particles. If the repulsive force is accounted for by the rigidity of a circular molecule, the virial coefficient is twice the molecular area. Since the experimental value of the second virial coefficient obtained by Parsons is much greater than that calculated according to this relationship, the existence of an appreciable electrostatic repulsion should be assumed. He showed that a considerable part of the free energy of adsorption of thiourea is due to covalent bonding of the adsorbed molecules with the mercury surface. This accounts for the difference in the behaviour of thiourea at the mercury–solution and at the air–solution interface at which the substance is negatively adsorbed[17]. The electrostatic component, $\Delta \bar{G}_A^0$, which to a first approximation linearly depends on E, is interpreted by Parsons by assuming that all dipoles of thiourea are perpendicular to the surface and directed towards it with their negative ends. This assumption also provides an explanation of the fairly large repulsive interaction between the adsorbed molecules of thiourea, cf.[21].

A similar method was used by PARRY and PARSONS[185] to study the adsorption on mercury of benzenedisulfonate ions; as they showed, this can be described with sufficient accuracy by TEMKIN's isotherm[186]. But the method of comparison of calculated and experimental curves for the surface pressure–electrode charge dependence, as was later noted by Parsons[163], is not very sensitive to the form of the adsorption isotherm. A much more sensitive function is the differential capacity of the electrode. For this reason, PARSONS[187] theoretically calculated the C—E curves for the linear and square $\Delta \bar{G}_A^0$ dependences on E with the help of adsorption isotherms of Henry, Freundlich, Langmuir, Temkin and the isotherm with virial coefficients. The comparison of the equations obtained with the experimental adsorption data on mercury of molecules of thiourea[93] and of n-$C_5H_{11}OH$[112] showed, however, that the adsorption isotherms considered can be used to describe the experimental C—E curves only to a first approximation. The adsorption isotherm obtained by Parsons[163] from the equation of state of Helfand, Frisch and Lebowitz[164] by adding to it a term for the interaction between the adsorbed particles is in better agreement with the experimental data on the dependence, at $q = \text{const}$, of the differential capacity upon the concentration of thiourea[93] and of benzene disulfonate[185] and I^- ions. In Parsons' opinion, this equation is preferable to equation 16, since it has been deduced under the assumption of non-localized adsorption. This argument cannot be agreed with, however[165]. Moreover, Parsons' isotherm seems to be inapplicable in the case of adsorption on mercury of aliphatic compounds[188].

7. *Devanathan's Method of Evaluating Adsorption: Discussion*

A different interpretation of the experimental data on the adsorption of thiourea[93] was given by DEVANATHAN[131a]. According to him

$$\frac{\mathrm{d}\Gamma}{\mathrm{d}q} = \left(\frac{1}{C}-\frac{1}{C_0}\right)\frac{e_0}{K_{\mathrm{org}}} \tag{72}$$

where e_0 is the elementary charge, K_{org} a quantity with the dimensions of capacity and equal to $\epsilon/2\pi l$, ϵ being the dielectric constant in the layer between the metal surface and the Gouy plane and l the effective length of organic dipoles of moment μ, equal to μ/e_0.

In the deduction of equation 72, a relation is used according to which the potential difference, $\Delta\phi_{\mathrm{org}}$ in Devanathan's notation, between metal and dielectric in the presence of a layer of adsorbed dipoles, is equal to

$$\Delta\phi_{\mathrm{org}} = 2\pi\Gamma\mu/\epsilon \tag{73}$$

Instead of the generally accepted coefficient 4, a value of 2 is used in the right-hand side of equation 73. The reason for this substitution is given as follows: the potential of a dipole layer of limited dimensions in the dielectric, which diminishes with distance as the solid angle subtended by the layer at a given point decreases, vanishes at infinite distance from the layer, while the potential in the metal remains constant. As a result, the potential difference between two points situated at large distances from the interface in the metal and in the dielectric, respectively, proves to be equal to half the potential drop within the dipole layer $4\pi\Gamma\mu/\epsilon$. The application of this argument to a dipole layer on both sides adjoining a dielectric leads to the conclusion that, at a sufficient distance from the interface, the oriented dipole layer does not give rise to any net potential difference at all. This concept, however, cannot be accepted. Indeed, imagine a dipole layer covering a disc having a radius R. The change in the potential in the dielectric outside the layer occurs only at distances x comparable to R whereas, if the condition $x \ll R$ is fulfilled, the coefficient 4 enters into the expression for the potential difference between two points on both sides of the dipole layer. As the plane boundary between two phases can be regarded as infinitely extended, the coefficient in the right-hand side of equation 73 must be 4 at any distances from the dipole layer of the points between which the potential difference is being determined. The same value 4 is obtained also for a closed interface[132] (e.g. a mercury drop in an electrolyte solution)*.

In deducing equation 72, Devanathan assumed further[131a] that the introduction of an organic substance into the surface layer had no effect on the dielectric constant and that the potential differences depending on the charge of the metal surface, on the presence of specifically adsorbed ions and on that of organic molecules, respectively, were additive (equation 8). The physical meaning of this further assumption seems obscure.

Equation 72 can be deduced from equation 12, assuming C_0, the capacity of the double layer at $\Gamma=0$, to be a constant and $C'=C_0$. In this case, it follows from equation 12 that

$$q = C_0\left(E - E_N\frac{\Gamma}{\Gamma_m}\right) \tag{74}$$

$$C = \frac{\partial q}{\partial E} = C_0\left(1 - \frac{E_N}{\Gamma_m}\frac{\partial \Gamma}{\partial E}\right) = C_0\left(1 - \frac{E_N}{\Gamma_m}\frac{\partial \Gamma}{\partial q}C\right) \tag{75}$$

whence

$$\frac{\partial \Gamma}{\partial q} = \left(\frac{1}{C} - \frac{1}{C_0}\right)\frac{\Gamma_m}{E_N} \tag{76}$$

The quantity E_N in Frumkin's theory has the same significance as Devanathan's $\Delta\phi_{\text{org}}$ at $\Gamma=\Gamma_m$. By expressing it in terms of μ and ϵ, according to equation 73, we obtain an equation identical with 72. However, judging by the capacity values at different magnitudes of q given by Parsons[130b], the assumption that $C_0=C'$ in the case of thiourea is only a very rough approximation.

Knowing the value of K_{org} from equation 72, the dependence of Γ on q can be found and, consequently, Γ itself since at sufficiently negative q its value approaches zero. In order to calculate K_{org}, Devanathan used the experimental value of $\mu=4{\cdot}89$ D for thiourea and that of $\epsilon=7{\cdot}2$, which he considers to be the most probable on the basis of the capacity measurements in solutions of potassium halides. The values of Γ thus calculated are in approximate agreement with the

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* Devanathan[131] quotes some papers in which the coefficient 2 was used in the expression for the potential difference. However, these papers referred not to an adsorbed dipole located outside the metal but to that formed by an adsorbed ion and the image induced in the metal, or by a chemisorbed atom and the lattice atom in the case of an ionic type of bond[133]. The controversial question[134,189] about the value of the coefficient in this case will not be further discussed. It should be mentioned, however, that LANGMUIR, who was actually the first to propose the value 2 for the coefficient under discussion in layers formed by adions[135a], used the value 4 for layers or oriented polar molecules[135b].

thermodynamic data, but this disappears if the coefficient 4 is substituted for the coefficient 2 in equation 73.

The method for the evaluation of adsorption advanced by Devanathan is of great simplicity, but the arbitrariness of a number of assumptions concerning the deduction of equation 72, the choice of the value of ϵ within the double layer, the normal to the surface orientation of all adsorbed dipoles and the maintenance of the values of μ in the field of the double layer render the reliability of the results so obtained doubtful.

In a later paper, DEVANATHAN[131b] applied his theory to the adsorption of aliphatic compounds with a polar group and a hydrocarbon chain. Pointing out that the assumption about the constancy of ϵ during adsorption cannot be valid in this case, he introduces into the quantity $1/C$, determined from equation 72, a correction to allow for this change. He proceeds from a relation somewhat similar to our equation 9, viz.

$$\epsilon = \epsilon_s(1-\theta)+\epsilon_0\theta = \epsilon_s(1-\alpha\theta) \qquad (77)$$

where ϵ_s is the dielectric constant in the absence of organic molecules, ϵ_0 that of the hydrocarbon chain and $\alpha=(\epsilon_s-\epsilon_0)/\epsilon_s$ (Devanathan's notations).

It is inferred from equation 77 that the effect of the transition from ϵ_s to ϵ on the capacity can be allowed for by the relation

$$C = \frac{\epsilon}{4\pi l} = C_0(1-\alpha\theta) \qquad (78)$$

$$\frac{1-\alpha\theta}{C} = \frac{1}{C_0} \qquad (78a)$$

By introducing a correction into the expression for C from equation 72 with the help of equation 78a, Devanathan finds

$$\frac{1-\alpha\theta}{C} = \frac{1}{C_0}+\frac{e_0}{K_{\text{org}}}\frac{\partial\Gamma}{\partial q} \qquad (79)$$

or

$$\frac{1-\alpha\theta}{C} = \frac{1}{C_0}+\beta\frac{\partial\theta}{\partial q} \qquad (79a)$$

The deduction of equations 78 and 79 cannot be agreed with, since C denotes the differential capacity, whereas equation 78 is evidently concerned with the integral capacity. Moreover, equation 72 itself cannot be valid, as has been shown above, in the case when $C_0 \neq C'$. The correct expression for $(1-\alpha\theta)/C$ which would be in accordance with the assumption involved in equation 77 can be readily obtained for the case when the dipole effect is absent: in this case

$$q = \frac{4\pi\epsilon}{l}E = \frac{4\pi\epsilon_s(1-\alpha\theta)}{l}E = C_0(1-\alpha\theta)E \tag{80}$$

By differentiating equation 80 with respect to q, after some elementary transformations, we find

$$\frac{1-\alpha\theta}{C} = \frac{1}{C_0}+\frac{\alpha}{\Gamma_m}\frac{\partial\Gamma}{\partial q}E \tag{81}$$

The second term on the right-hand side of equation 81 is absent in equation 78a, but in its order of magnitude it is comparable with the second term on the right-hand side of equation 79, and at $|\alpha E| > |E_N|$ exceeds the latter in its absolute value. An expression for $(1-\alpha\theta)/C$, in which both the dipole effect and the change in capacity for adsorption of an organic substance are allowed for, can be obtained from equation 42 on assuming that

$$q_0 \approx C_0 E \tag{82}$$

and

$$q' = C'(E-E_N) \tag{83}$$

and, following Devanathan, on supposing that the capacities for $\theta=1$ and $\theta=0$ (in our notation, C' and C_0) are proportional to the dielectric constants, i.e.

$$\frac{C'}{C_0} = \frac{\epsilon_0}{\epsilon_s} = 1-\alpha \tag{84}$$

(the subscript 0 in our notation pertains to the unoccupied part of the surface, in Devanathan's to the covered one). From equations 42, 83 and 84, by substituting $e_0\Gamma_m K_{\text{org}}^{-1}$ for E_N, we readily obtain

$$\frac{1-\alpha\theta}{C} = \frac{1}{C_0}+\frac{\partial\Gamma}{\partial q}\left(\frac{e_0}{K_{\text{org}}}\frac{C'}{C_0}+\frac{\alpha E}{\Gamma_m}\right) \tag{85}$$

Equation 85 differs from 79 both in the coefficient before the first term in the brackets, which is considerably less than unity, and, what is of special importance, in that there is a second term present; it agrees with equation 79 only at $C'=C_0$, i.e. $\alpha=0$.

The use of the dielectric constant determined by equation 77 in the capacity calculation is based on the assumption that the adsorption of an organic substance has no effect on the thickness of the electric double layer. According to Devanathan, this assumption is confirmed by the fact that the minimum capacity value in aqueous solutions of aliphatic compounds with a hydrocarbon chain and a polar group amounts to 5–6 μF cm^{-2}, independently of the chain length. However, the minimum capacity in solutions of octyl alcohol[69] is 4·5 μF cm^{-2}, in those of nonylic acid[110], ~2 μF cm^{-2}, in the presence of a monolayer of cetyl alcohol, 1·03 μF cm^{-2} and of a monolayer of oleic acid[79], 1·15 μF cm^{-2}. In cetyl alcohol, the thickness of the monolayer, calculated from the capacity, is close to the chain length. In these cases there are no indications of the formation of polymolecular layers. Thus, there is no doubt that an increase in chain length results in an increase in the thickness of the electric double layer. Besides, the low capacity values observed when polylayers are formed also show that the adsorbed hydrocarbon chains hinder the hydrated ions in approaching the Hg surface.

According to Devanathan, the polar group of an organic compound has no effect on the quantities contained in equation 79. As supposed in earlier work (e.g.[17]), Devanathan assumes the adsorbed molecules to be oriented with the hydrocarbon chain towards the interface. Under these conditions, the polar group must be located far from the interface and since, according to Devanathan's views, the electric field of the dipole layer in the dielectric decreases with the distance from it, the polar group should have no effect on the values measured, e.g. E_N; the effect observed is completely determined by the fact that $n = 1{\cdot}806$ molecules of water are displaced during the adsorption of one hydrocarbon chain. The dipole moment, μ, used in calculating K_{org} from equation 73 should therefore be equated with $-n\mu_w$, where μ_w is the dipole moment of water. A similar concept was advanced by KAMIENSKY[136] to explain the shifts in the potential in the case of the adsorption of organic compounds at the water–air interface; it leads, however, to impossible values of chemical hydration energies of cations and anions[39].

A final choice between the assumptions which underlie equation 9 and 77 can be made only on the basis of experimental data. Probably, at relatively high electrolyte concentrations, when the planes located in the solution at molecular distance from the metal surface can be regarded as equipotential to a first approximation, equation 9 represents a better approximation. It is possible, however, that in solutions with very low concentration of the electrolyte and at small values of $|E|$, i.e. under the conditions when the potential drop occurs mainly in the diffuse double layer, equation 77 may be of use.

On the basis of the above considerations, Devanathan finds the values of α and β in equation 79a. The expression obtained was used to calculate θ from the capacity values of n-amyl alcohol solutions measured by Breiter and Delahay[112]. The values of θ in the case of maximum adsorption are in fair agreement with those calculated[112] from equation 9; this is to be expected since, at $(\partial \Gamma)/(\partial q) = 0$, equations 79 and 85 become identical.

8. *Adsorption from Non-aqueous Solutions*

The adsorption of organic substances on the electrode surface also affects the shape of the differential capacity curves measured in non-aqueous organic solvents. However, the data available are rather scarce[137-144, 190-192]. The decrease in the double layer capacity observed on all *C—E* curves obtained in organic solvents, compared to that in aqueous solutions, appears to result both from the lowering of the dielectric constant in the double layer and from an increase in the thickness of the latter. The fact that a decrease in the capacity is also observed with solutions in *N*-methylformamide[143], for which the macroscopic dielectric constant is much higher than that of water[145], is at variance with the assumption of a proportionality between the macroscopic dielectric constant of the solvent and the effective dielectric constant in the double layer[144]. The incorrectness of this assumption was noted early[41].

If the effective dielectric constant of an organic solvent within the double layer is much smaller than that of water, a desorption of this solvent by small additions of water is observed at sufficiently negative electrode charges; this results in the appearance of characteristic peaks on the differential capacity curve[142, 193], in agreement with the results of electrocapillary measurements[37, 41].

Finally, it is of interest to note that the characteristic hump observed in aqueous solutions on the differential capacity curves in the vicinity of the p.z.c. is absent in the case of most of organic solvents. Solutions in *N*-methylformamide[143] and formamide[144, 191] are an exception but, in contrast to water, the hump observed on the *C—E* curves is greatly shifted in the direction of negative surface charges. The problem of the nature of this hump has not yet been sufficiently clarified[146-148, 168, 194].

V. DEPENDENCE OF THE *C—E* CURVES ON THE NATURE OF THE METAL

In contrast to the electrocapillary method, differential capacity measurement can be used to study the adsorption of organic compounds on solid electrodes as well. Here the consideration will be confined to the cases for which a pronounced dependence of adsorption on potential is observed and there is no reason to expect far-reaching chemical changes to occur in the process of adsorption, e.g. of the kind that can take place during the adsorption on platinum. Adsorption–desorption peaks were observed in the presence of amyl alcohol on the *C—E* curves obtained with lead[149] and thallium[150] electrodes; in the presence of a mixture of thymol, β-naphthol and diphenylamine with copper, silver, tin, lead, bismuth and Tl-amalgam electrodes[151] as well as with solid mercury[152]. A differential capacity curve for a silver electrode in 1N Na_2SO_4 solution saturated with n-hexyl alcohol[153] is given in *Figure 27.*

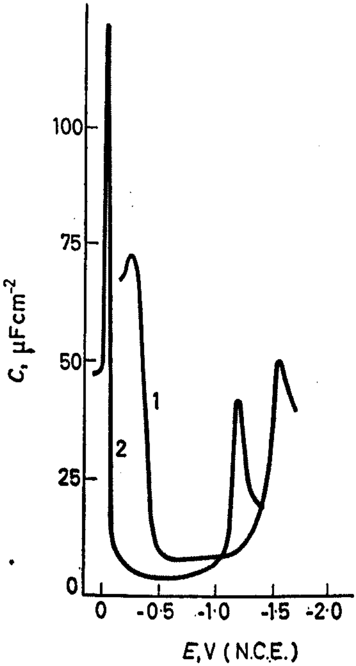

Figure 27. Differential capacity curves of 1N Na_2SO_4 *saturated with* n-$C_6H_{13}OH$ (Leikis[153])

1 silver electrode, 2 mercury electrode

To a first approximation, the differential capacity curves obtained with solid electrodes in the presence of organic substances are similar to the corresponding ones obtained with liquid mercury. Upon adsorption of organic molecules, a decrease in the capacity, as against that in the pure supporting solution, is observed. With an increase in the electrode charge, the organic substance is desorbed, which results in the appearance of a characteristic peak on the differential capacity curves. With electrodes of Pb, Ag, Ga, Sb in N Na_2SO_4 saturated with $C_6H_{13}OH$, the cathodic adsorption–desorption peaks are located at about the same distance from the p.z.c. of these metals, as shown by LEIKIS and SEVASTYANOV[154]. With solid electrodes, the peaks on the *C—E* curves are less pronounced than with liquid mercury (cf. *Figure 27*), owing perhaps to the inhomogeneity of the surface. In the case of gallium, however, the transition from the liquid to the solid state has practically no effect[154] upon the *C—E* curve (*Figure 28*).

In *Figure 29* are presented the data obtained by PETRY *et al.*[155] for the adsorption of n-$C_6H_{13}OH$ on mercury (*b*) and on a 40 per cent thallium amalgam (*a*). Identical additions of hexyl alcohol to 0·1N KCl are seen to result in a much greater decrease in the capacity at the p.z.c. in the case of mercury ($E_{p.z.c.} \cong -0{\cdot}50$ V N.C.E.), than of a 40 per cent thallium amalgam ($E_{p.z.c.} \approx -0{\cdot}93$ V N.C.E.), this effect being especially pronounced at small concentrations of $C_6H_{13}OH$. This result is an indication of a larger adsorption energy of hexyl alcohol at the mercury–solution than at the amalgam–solution interface. As a consequence, the peak on the *C—E* curves is observed at higher negative charges with mercury than with the thallium amalgam for the same concentrations of hexyl alcohol (*Table 5*).

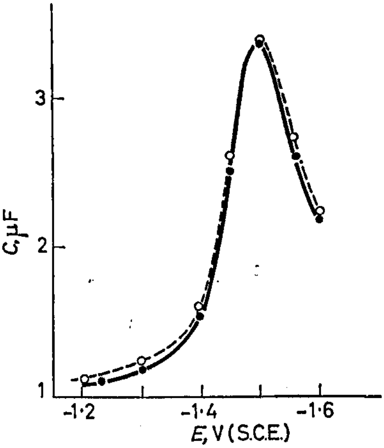

Figure 28. Cathodic branches of C—E *curves of gallium electrode in* 1N Na_2SO_4, *saturated with* n-$C_6H_{13}OH$; 2,000 c (LEIKIS *and* SEVASTYANOV[154])

Solid line, liquid gallium, dashed, solid gallium

On the other hand, the surface charges on mercury and on the 40 per cent thallium amalgam corresponding to the desorption peaks of large organic cations are seen to be approximately identical, although

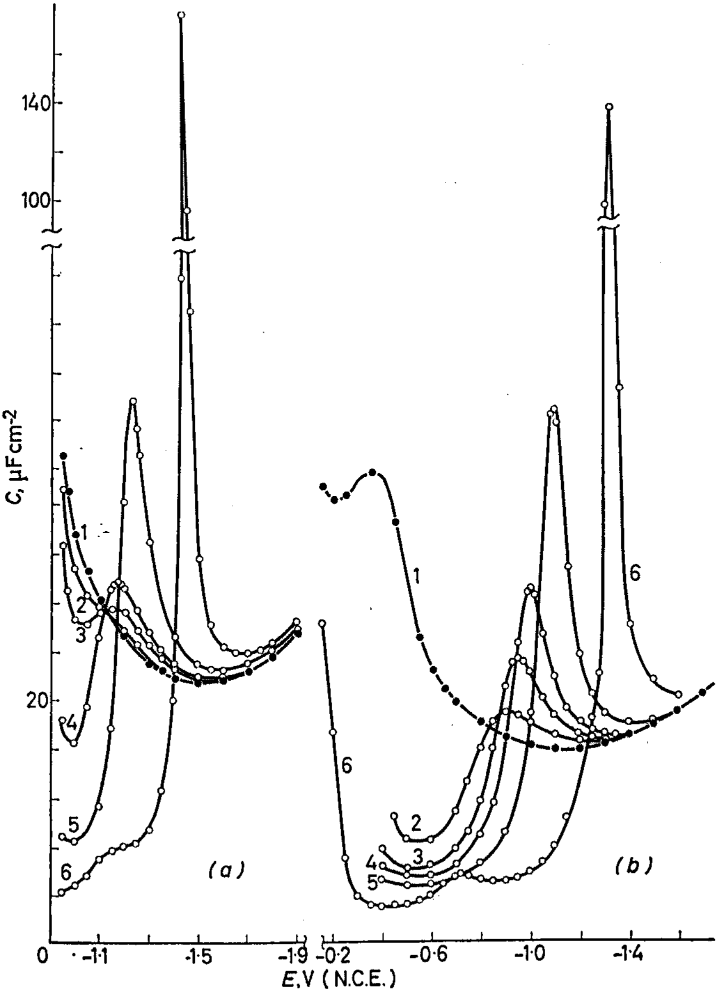

Figure 29. Differential capacity curves of 0·1N KCl *with additions o* n-$C_6H_{13}OH$ (PETRY *et al.*[155])

1 0; 2 10^{-3}M; 3 $3{\cdot}10^{-3}$M; 4 $5{\cdot}10^{-3}$M; 5 10^{-2}M; 6 *sat. with* n-$C_6H_{13}OH$
(*a*) 40 *per cent thallium amalgam;* (*b*) *mercury;* 400 c

still somewhat smaller in the case of the amalgam. This can be explained by the negative adsorption of Tl atoms at the amalgam–solution interface[50] which decreases the surface concentration of the amalgam at large cathodic polarizations.

Table 5

Charge at which Peak is observed as a Function of Metal

Supporting electrolyte	*Adsorbed substance*		Hg		40 per cent Tl (Hg)	
			$-E_{\max}$	$-q_{\theta=0\cdot5}$	$-E_{\max}$	$-q_{\theta=0\cdot5}$
0·1N KCl	$n-C_6H_{13}OH$	$5\cdot10^{-3}$M	1·0	9·75	1·18	6·9
		10^{-2}M	1·09	11·20	1·24	8·4
		sat.	1·32	14·90	1·45	13·2
10^{-2}N Na_2SO_4	$[(C_4H_9)_4N]^+$	10^{-4}N	1·75	21·0	1·80	20·55
		10^{-3}N	1·80	21·95	1·85	21·45
	$[(C_5H_{11})_4N]^+$	10^{-4}N	1·75	21·0	1·81	20·6
		10^{-3}N	1·82	22·35	1·87	21·85
	$[(C_6H_{13})_4N]^+$	10^{-4}N	1·79	21·7	1·84	21·25

VI. ADSORPTION KINETICS OF ORGANIC COMPOUNDS

By means of the a.c. method, it is possible to study the kinetics of adsorption of organic substances on the electrode surface. This problem was first considered by Frumkin and Melik-Gaikazyan[107, 90]. They showed that, at small deviations from equilibrium, the value of the adsorption pseudocapacity, C_{ad} (see equation 36), when measured by the a.c. method is the function of the frequency, ω, decreasing from the equilibrium value corresponding to $\omega=0$ (C_{ad}, $\omega=0$) to zero at $\omega \to \infty$, the character of the dependence of C_{ad} on ω being determined by the nature of the rate-determining step in the process of adsorption of the organic compound. Thus, if diffusion is rate-determining, the dependence of C_{ad} on ω is given by the equation

$$C_{ad}(\omega) = C_{ad(\omega=0)} \frac{2\left(\dfrac{\sqrt{\omega}}{M}+1\right)}{\left(\dfrac{2\sqrt{\omega}}{M}+1\right)^2+1} \qquad (85)$$

where

$$M = \frac{\sqrt{2D}}{\left(\frac{\partial \Gamma}{\partial c}\right)_E} \tag{87}$$

D is the diffusion coefficient of the organic substance and c its concentration in the bulk of the solution.

By studying the frequency dependence of the differential capacity values in the region of adsorption–desorption peaks in solutions containing normal aliphatic alcohols, Melik-Gaikazyan[90] showed that this dependence is fairly well represented by equation 86, and consequently the diffusion of alcohol molecules to the electrode surface is the rate-determining step in the process of adsorption of these alcohols. This result is in agreement with the conclusions drawn from the study of the influence of butyl alcohol on polarographic maxima of the second kind[1-3].

The decrease in C_{ad} with frequency results in the disappearance of the adsorption–desorption peaks on the C—E curves determined at high frequencies. With a rise in the frequency the curve asymptotically approaches the C_{tr}—E curve (*Figure 30*). At a given frequency, the lowering of the peaks is the more pronounced the smaller the concentration of the adsorbed substance*.

Two limiting cases were considered in the above theory: that when the rate of the process is determined by the diffusion and that when it depends on the rate of the adsorption itself.

Berzins and Delahay[156] gave a more general solution of the problem by taking into consideration the rates of both the diffusion process and of adsorption. In deducing the basic equation, they assumed that the adsorption of organic compounds proceeds in accordance with Langmuir's isotherm and that the constants of the rate of the adsorption and desorption processes are exponential functions of the electrode potential. A deduction free from these limitations was given later by Lorenz[110]. If the adsorption process is characterized at a given frequency by the capacity $C(\omega)_{ad}$ and the resistance by $R(\omega)_p$, connected in parallel in the equivalent electric circuit, and if

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* When the experimental data on the adsorption–desorption peaks are compared with the predictions of relations calculated theoretically on the basis of the assumption that the adsorption equilibrium is established, it is necessary to make certain that the above condition is observed. A convenient criterion[117, 118] of the establishment of equilibrium is the coincidence between the values of the charge q, determined by integrating over the C—E curves for the solution of the organic compound between the potentials corresponding to the complete desorption of the organic substance on the anodic and cathodic branches, and the value of q found by the same method in the absence of the substance adsorbed.

there are two rate determining steps, diffusion and adsorption, then, according to Lorenz

$$C_{\mathrm{ad}(\omega)} = C_{\mathrm{ad}(\omega=0)} \frac{\dfrac{\sqrt{\omega}}{M}+1}{\left(\dfrac{\sqrt{\omega}}{M}+N\omega\right)^2+\left(\dfrac{\sqrt{\omega}}{M}+1\right)^2} \tag{88}$$

$$R_{p(\omega)} = \frac{\left(\dfrac{\sqrt{\omega}}{M}+N\omega\right)^2+\left(\dfrac{\sqrt{\omega}}{M}+1\right)^2}{C_{\mathrm{ad}(\omega=0,}\,\omega\left(\dfrac{\sqrt{\omega}}{M}+N\omega\right)} \tag{89}$$

where

$$N = -\frac{1}{\left(\dfrac{\partial v}{\partial \Gamma}\right)_{E,c_0}} \tag{90}$$

v = rate of the adsorption step and c_0 = concentration of the organic substance at the electrode surface.

In limiting cases, when $N \rightarrow 0$ (slow diffusion) or $D \rightarrow \infty$ (slow adsorption), equations 88 and 89 are transformed into the corresponding equations of Frumkin and Melik-Gaikazyan[107]. Equations 88 and 89 can be used to determine the rate of the adsorption step of the overall process. A series of investigations of this problem were carried out by LORENZ *et al.*[109, 110, 157–159].

As shown by Lorenz and Möckel[109], for comparison of theory with experiment it is more convenient to make use of the frequency dependence of the phase angle, δ, rather than that of C_{ad}. From equations 88 and 89 it follows that

$$\cot\delta = \frac{1+\dfrac{M}{\sqrt{\omega}}}{1+MN\sqrt{\omega}} \tag{91}$$

whence, knowing the value of the diffusion coefficient, the limiting adsorption and the equation of the adsorption isotherm, the exchange rate of the adsorption–desorption process can be determined. This method was used by Lorenz *et al.* in a study of the kinetics of adsorption on mercury of a number of organic compounds. It was shown that the time constant of the adsorption step, although small, has a finite measurable value of the order of 10^{-5} sec.

According to Lorenz[110], in the case of organic compounds with a carbon chain of sufficient length, a process of two-dimensional association is taking place in the surface layer, which to a considerable extent complicates the frequency dependence of cot δ. In this case this dependence can be fairly well represented by the equation

$$\cot\delta = \frac{k_1\left(k_2+k_1\dfrac{\sqrt{\omega}}{M}\right)+\left(\dfrac{\omega}{w_0}\right)^2\left(k_3+\dfrac{\sqrt{\omega}}{M}\right)}{\left[k_1^2+\left(\dfrac{\omega}{w_0}\right)^2\right]\left(\dfrac{\omega}{v_0}+\dfrac{\sqrt{\omega}}{M}\right)+\dfrac{\omega}{w_0}(k_1k_3-k_2)} \tag{92}$$

if it is assumed that the exchange rate of two-dimensional association, w_0, is within 10–1,000 sec^{-1}; k_1, k_2 and k_3 are constants characterizing the process of the two-dimensional association.

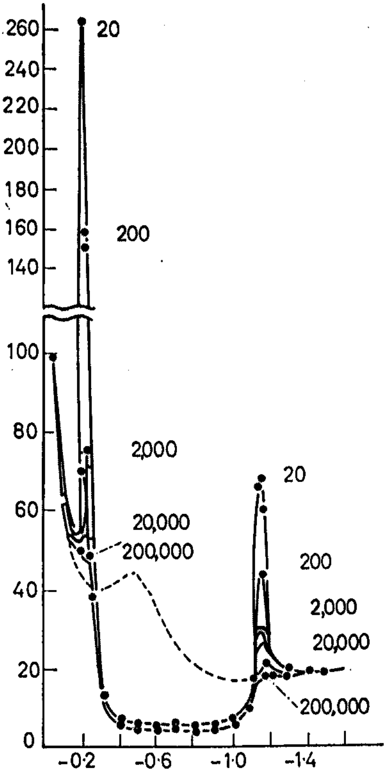

Figure 30. Differential capacity of 1N KCl+5·10^{-3}M n-$C_6H_{13}OH$ *at different frequencies;* 25° C; *dashed line,* 1N KCl (Melik-Gaikasyan[90])

According to Lorenz[195], the frequency dependence of the differential capacity in concentrated solutions of an indifferent electrolyte with small additions of a specifically adsorbed substance can be used for the determination of the partial charge transfer, if a covalent bond between the adsorbed particles and mercury is formed. According to LORENZ and KRÜGER[196] a partial charge transfer and, consequently, the formation of a covalent bond are observed in the case of adsorption on mercury of thiourea and of I^- ions, whereas in the case of adsorption of molecules of various aliphatic compounds as well as of tetraalkylammonium cations no partial charge transfer occurs.

A new coulostatic method to study the adsorption kinetics of organic substances was proposed by DELAHAY and MOHILNER[197]. It consists in a small charge, δq, being imparted to the electrode within a very short time τ, e.g. 1 μsec, whereupon at open circuit, a change in the potential occurs due to the quantity Γ approaching a new equilibrium value; the charging is assumed to proceed so fast that the change in Γ within the time τ may be neglected. Evidently, the changes in the potential δE are expressed by the equation

$$\delta E = \left(\frac{\partial E}{\partial q}\right)_\Gamma \delta q + \left(\frac{\partial E}{\partial \Gamma}\right)_q \delta \Gamma$$

A quantitative expression is given for the value of $\delta\Gamma$, assuming the equilibrium adsorption to follow Temkin's logarithmic isotherm[186] and the desorption rate to be proportional to the activity of the adsorbed substance being exponentially dependent on the coverage. The role played by diffusion is also taken into account[198]. From the time dependence of δE the rate of exchange between the adsorbed layer and the bulk of the solution can be found, if it is not too large, i.e. if the kinetics of the adsorption process proper is not disguised by the diffusion rate.

Delahay and Mohilner also discuss the connection between the applicability of Temkin's logarithmic isotherm and the fulfilment of the condition that the Esin and Markov coefficient (a term proposed by GRAHAME[199]), $(\partial E/\partial \ln c)_q$, is constant with varying c.

It is of interest to extend the coulostatic method upon other adsorption isotherms as well, since Temkin's logarithmic isotherm, based on the assumption of the existence of a strong repulsive interaction between adsorbed molecules which corresponds to negative values of a in equation 16, is but of limited applicability to adsorption of neutral molecules.

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