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THE CONGRUENCE OF THE ADSORPTION ISOTHERM WITH RESPECT TO THE ELECTRODE POTENTIAL OR CHARGE AND THE CHOICE OF AN INDEPENDENT ELECTRIC VARIABLE

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It is known that the adsorption isotherm of a solution component at constant electrode potential (E) can be obtained by a strictly thermodynamic method from the basic equation of electrocapillarity[1], which to the first approximation (that is with the concentration (c) substituted for the activity and at constant concentration of the other solution components) can be written as:

$$\mathrm{d}\sigma = -q\,\mathrm{d}E - RT\Gamma\,\mathrm{d}\ln c \tag{1}$$

where σ is the interfacial tension, q the electrode charge density, Γ the Gibbs adsorption, R the gas constant and T the absolute temperature.

In order to find the adsorption isotherm at q=const. by a thermodynamic method, it is necessary to introduce a new function[2]:

$$\xi = \sigma + qE \tag{2}$$

which enables the basic equation of electrocapillarity to be written in the form:

$$\mathrm{d}\xi = E\,\mathrm{d}q - RT\Gamma\,\mathrm{d}\ln c \tag{3}$$

The adsorption isotherms obtained from the experimental data by means of eqns. (1) and (3) are self-consistent in the sense that by calculating (by means of eqn. (1)) the Γ–c curve at E=const. and knowing the dependence of q on E at different concentrations of the adsorbed substance, it is possible to plot the Γ–c curve at q=const., which exactly coincides with the adsorption isotherm calculated by means of eqn. (3). Thus, with a strictly thermodynamic approach to the investigation of the adsorption isotherms, the choice of an electric variable is of no fundamental importance and is determined by considerations of expediency or convenience. For instance, in studying the adsorption of inorganic ions, it is more convenient to consider the isotherms at q=const., since according to the Gouy–Chapman theory, the diffuse layer structure is determined by the value of the charge.

This is not the case, however, when the thermodynamic approach to the investigation of adsorption on electrodes is supplemented by some model assumptions, in particular by the assumption of the congruence of the adsorption isotherm with respect to one of the electric variables. The condition of the congruence of the isotherm with respect to the potential can be written in the form of an equation:

$$Bc = f(\Gamma) \tag{4}$$

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and a similar condition of congruence with respect to the electrode charge as the equation:

$$Gc = f(\Gamma) \tag{5}$$

where $B = B(E)$ and $G = G(q)$ represent adsorption equilibrium constants, which are functions of E and q, respectively, and $f(\Gamma)$ is a function of Γ*. The discussion in connection with the choice of an electric variable[3-5] is essentially bound up with the question as to whether eqns. (4) and (5) are compatible, and if not, which of them agrees better with the experimental data. Let us consider this question in more detail.

It was shown by PARSONS[5] for the case of adsorption on mercury of n-butanol from its solutions in 0.1 N NaF used as a supporting electrolyte, that the curves of the dependence of the two-dimensional pressure at constant potential, $\Delta\sigma = \sigma_0 - \sigma$, or at constant charge, $\Delta\xi = \xi_0 - \xi$, upon log c, measured at different E or q, respectively, will coincide with the accuracy of the order of 3–4 dyn cm^{-1} if these curves are shifted along the abscissa (the values of σ_0 and ξ_0 are for a pure supporting electrolyte solution). Since the shape of the adsorption isotherm is determined by those of the $\Delta\sigma$–log c curves at E=const., or of the $\Delta\xi$–log c curves at q=const. (see eqns. (1) and (3)), it can be concluded from PARSONS' data that eqns. (4) and (5) are compatible and thus it is possible to choose the one that is more convenient for use. A similar conclusion was drawn also from PAYNE's studies[6] on the adsorption on mercury of NO_3^- and ClO_4^- anions.

The analysis of eqns. (4) and (5) shows, however, that their compatibility depends on the fulfilment of definite conditions since they correspond to different models of the adsorption layer. In fact, it follows from eqns. (1) and (4) that:

$$\frac{\partial \ln B}{\partial E} = -\left(\frac{\partial \ln c}{\partial E}\right)_\Gamma = \frac{1}{RT}\left(\frac{\partial q}{\partial \Gamma}\right)_E \tag{6}$$

which gives after integration,

$$q = RT\left(\frac{\partial \ln B}{\partial E}\right)\Gamma + q_0 = A\left(\frac{\partial \ln B}{\partial E}\right)\theta + q_0 \tag{7}$$

where $\theta = \Gamma/\Gamma_m$; Γ_m is the limiting value of Γ, q_0 the value of q at $\theta = 0$ and $A = RT\Gamma_m$. Let the charge at $\theta = 1$ and the given potential be q', then

$$q' = A\left(\frac{\partial \ln B}{\partial E}\right) + q_0 \tag{8}$$

It follows from (7) and (8) that:

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

from which the true differential capacity, C_{true}, is

$$C_{\text{true}} = \left(\frac{\partial q}{\partial E}\right)_\theta = C_0(1-\theta) + C'\theta \tag{10}$$

where $C_0 = \mathrm{d}q_0/\mathrm{d}E$ and $C' = \mathrm{d}q'/\mathrm{d}E$.

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* In our treatment we neglect the difference between the total potential drop and the potential drop in the adsorbed layer; this does not lead to serious errors in the concentration range considered.

Thus, the assumption that the adsorption isotherm is congruent with respect to the potential corresponds to the model of the surface layer in the form of two parallel capacitors[7]. There are water molecules between the plates of one, and particles of adsorbed substance between the plates of the other.

On the other hand, it follows from eqns. (3) and (5) that:

$$\frac{\partial \ln G}{\partial q} = -\left(\frac{\partial \ln c}{\partial q}\right)_{\Gamma} = -\frac{1}{RT}\left(\frac{\partial E}{\partial \Gamma}\right)_{q} \tag{11}$$

which gives on integration:

$$E = -RT\left(\frac{\partial \ln G}{\partial q}\right)\Gamma + E_0 = -A\left(\frac{\partial \ln G}{\partial q}\right)\theta + E_0 \tag{12}$$

where E_0 is the value of E at $\theta = 0$, corresponding to a given charge, q. If the potential at a given charge, q, and at $\theta = 1$ is E',

$$E' = -A\left(\frac{\partial \ln G}{\partial q}\right) + E_0 \tag{13}$$

From eqns. (12) and (13) we find:

$$E = E_0(1-\theta) + E'\theta \tag{14}$$

and further

$$\frac{1}{C_{\text{true}}} = \left(\frac{\partial E}{\partial q}\right)_{\theta} = \frac{1-\theta}{C_0} + \frac{\theta}{C'} \tag{15}$$

Thus, the assumption that the adsorption isotherm is congruent with respect to the charge corresponds to the model of two capacitors connected in series.

It can be readily seen that the difference between these two models disappears at $C_0 = C'$, when eqns. (10) and (15) give the same result: $C_{\text{true}} = C_0$. In other words, at $C_0 = C'$, the model of two parallel capacitors does not contradict the summation of the potential differences in the solvent layer and in the adsorbed substance layer. Thus, the compatibility of eqns. (4) and (5) is determined by the fulfilment of the condition, $C_0 = C'$. This condition is approximately fulfilled in the case of adsorption of NO_3^- and ClO_4^- anions on mercury, which accounts for PAYNE's experimental data[6].

If the condition $C_0 = C'$ is fulfilled, the choice of an independent variable is not of fundamental importance and is determined, as has been pointed out above, by considerations of expediency. Such is not the case with the adsorption on mercury of neutral molecules of aliphatic compounds. Here C_0 is much larger than C', eqns. (4) and (5) become incompatible and the choice depends on how well the models corresponding to one of them agree with experimental data.

Before the different methods of comparing eqns. (4) and (5) with experimental data are considered, it should be noted that in the case of adsorption of neutral organic molecules, it is hardly possible to explain the physical meaning of the model of two capacitors connected in series. Other conditions being equal, this fact gives preference to the isotherms that are congruent with respect to the electrode potential.

As has been pointed out above, the method of two-dimensional pressure used by PARSONS[5] for the analysis of the system, 0.1 N $NaF + n\text{-}C_4H_9OH$, where $C_0/C' \approx$

4–5, did not bring out the difference between eqns. (4) and (5), although judging by the results of the analysis of these equations, this difference must exist. Let us demonstrate this result to be due to an insufficient sensitivity of the method of two-dimensional pressure. To this end, let us assume that the adsorption of the organic substance rigorously obeys eqn. (4), the quantities C_0 and C' being independent of the potential. In this case,

$$q_0 = q_\mathrm{m} + C_0(E - E_\mathrm{m}) \quad \text{and} \quad q' = q_\mathrm{m} + C'(E - E_\mathrm{m}) \tag{16}$$

where E_m and q_m are the abscissa and the ordinate of the intersection point of the straight lines of the q_0–E and q'–E dependencies (see Fig. 1), which corresponds to the maximum adsorption of the organic substance and to the minimum on the differential capacity curves. Introducing (16) into eqn. (8), we obtain:

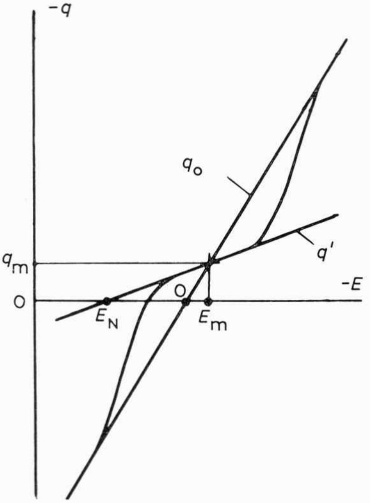


Fig. 1. Schematic representation of dependence of electrode charge on potential in the presence of aliphatic compounds at C_0 = const. and C' = const.

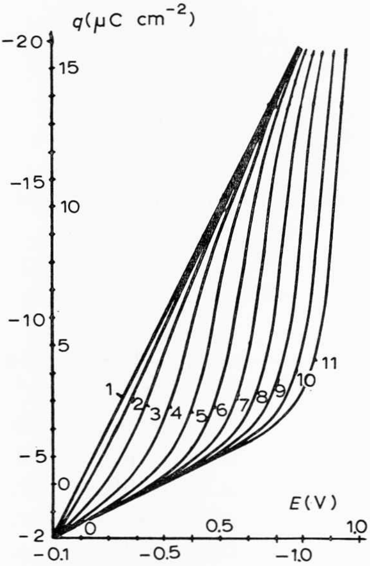


Fig. 2. Dependence of electrode charge on potential at different concns. of organic substance theoretically calcd. using the model of two parallel capacitors. Organic substance concn.: (1), 0; (2), 2.51 × 10^{-2}; (3), 6.3 × 10^{-2}; (4), 0.159; (5), 0.398; (6), 1.0; (7), 2.51; (8), 6.3; (9), 15.9; (10), 39.8; (11), 100 *M*.

$$\frac{\partial \ln B}{\partial E} = -\frac{C_0 - C'}{A}(E - E_\mathrm{m}) \tag{17}$$

which on integration gives:

$$B = B_\mathrm{m} \exp[-\alpha(E - E_\mathrm{m})^2] \tag{18}$$

where $\alpha = (C_0 - C')/2A$ and B_m is the value of B at $E = E_\mathrm{m}$.

Equation (18) in combination with the equation of Frumkin's isotherm[8] leads to:

$$Bc = \{\theta/(1-\theta)\} \exp(-2a\theta) \tag{19}$$

where a—the parameter of intermolecular interaction—enables the θ–E dependence to be calculated for different concentrations of the organic substance, provided all the parameters contained in these equations are given. Then, by means of the equation

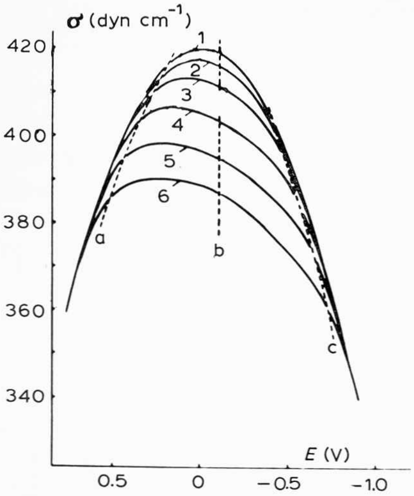
$$q = q_{\mathrm{m}} + [C_0(1-\theta) + C'\theta](E - E_{\mathrm{m}}) \tag{20}$$

which is obtained by substituting (16) into (9), it is possible to calculate a set of q–E curves, and by means of the equation[8]:

$$\sigma = \tfrac{1}{2}C_0E^2 + A\,[\ln(1-\theta) + a\theta^2] \tag{21}$$

—a set of electrocapillary curves in the presence of different concentrations of organic substance. These data are sufficient for plotting the $\Delta\sigma$–log c curves at different E, which, as specified by the conditions of the calculations, should coincide when shifted along the abscissa, and the $\Delta\xi$–log c curves at different q, which should not coincide when shifted in a similar manner.

We have performed this calculation choosing parameters similar to those corresponding to the 0.1 N NaF + n-C_4H_9OH system[9]: $C_0 = 20\ \mu\mathrm{F\ cm^{-2}}$, $C' = 5\ \mu\mathrm{F\ cm^{-2}}$, $A = 1\ \mu\mathrm{J\ cm^{-2}}$, $a = 1$, $B_{\mathrm{m}} = 10\ \mathrm{l\ mol^{-1}}$, $\alpha = (C_0 - C')/2A = 7.5\ \mathrm{V^{-2}}$, $E_{\mathrm{m}} = -0.1$ V



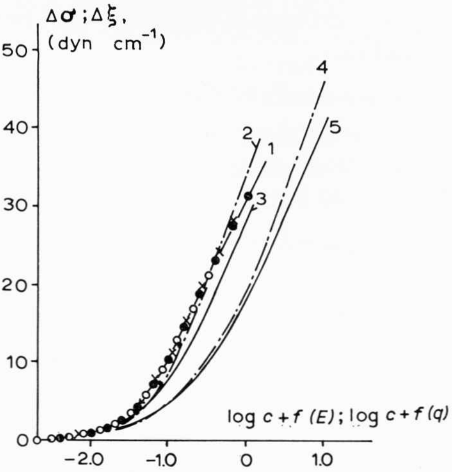


Fig. 3. Electrocapillary curves at different organic substance concns. theoretically calcd. using the model of two parallel capacitors. Organic substance concn.: (1), 0; (2), 2.5×10^{-2}; (3), 6.3×10^{-2}; (4), 0.159; (5), 0.398; (6), 1.0 M. Dashed lines connect the points with a constant surface charge: (a), $q = +4$; (b), $q = -2$; (c), $q = -8\ \mu\mathrm{C\ cm^{-2}}$.

Fig. 4. Dependence of two-dimensional pressure at E = const. ($\Delta\sigma$) and at q = const. ($\Delta\xi$) on the log of organic substance concn. calcd. using the model of two parallel capacitors: (1), $q = -2\ \mu\mathrm{C\ cm^{-2}}$; (○ ○), $E = +0.3$ V; (● ●), $E = 0$; (× ×), $E = -0.3$ V; (2), $q = -8$; (3), $q = +4$; (4), $q = -16$; (5), $q = +12\ \mu\mathrm{C\ cm^{-2}}$. The functions $f(E)$ and $f(q)$ are chosen so that all curves should coincide in the range of $\Delta\sigma$ and $\Delta\xi$ values of the order of 0.3–0.5 dyn cm⁻¹.

and $q_{\mathrm{m}} = C_0E_{\mathrm{m}} = -2\ \mu\mathrm{C\ cm^{-2}}$. The calculated $\Delta\sigma$–log c and $\Delta\xi$–log c curves were shifted along the abscissa until they coincided at the smallest values of $\Delta\sigma$ or $\Delta\xi$ (of the order of 0.3–0.5 dyn cm⁻¹).

Some of the results obtained are presented in Figs. 2–4. As expected, the $\Delta\sigma$–log c curves measured at different E coincide completely (Fig. 4). As to the $\Delta\xi$–log c curves, in the range of charges where the adsorption of ordinary organic compounds leads to an appreciable decrease in interfacial tension, the discrepancy in the calculated values of $\Delta\xi$ does not exceed 3–4 dyn cm^{-1}, *i.e.*, lies approximately within the scatter of the experimental data (see ref. 5). In order to find the discrepancy in the $\Delta\xi$–log c curves, which lies definitely outside the experimental error limits, it would be necessary to investigate the dependence of $\Delta\xi$ on log c at charges that are much more removed from q_m, *e.g.*, at $q=12$ and $q=-16$ μC cm^{-2} (see curves 4 and 5 in Fig. 4). Under such conditions, however, the product $B_m \cdot c$ should reach 50 to 1000, which cannot be realized in practice owing to the limited solubility of organic substances with high surface activity. The two-dimensional pressure method cannot be used, therefore, as a criterion in choosing one of the two equations, (4) and (5). It is of interest to seek for other more sensitive methods.

One such method suggested[10] consists in the analysis of the experimental dependence of the shift of the point of zero charge, $E_{q=0}$, on the adsorption value of the organic substance, Γ. Provided that $C_0=$const. and $C'=$const., it follows from Fig. 1 that the equations of the straight lines, q_0, E, and q', E can be written as:

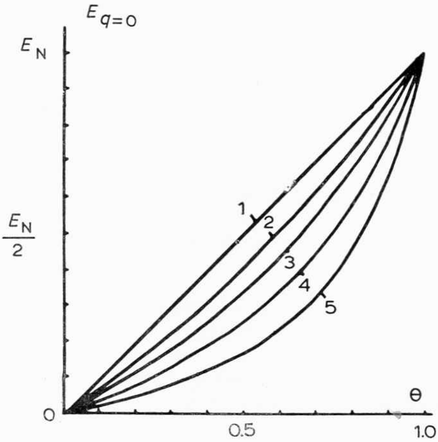
$$q_0 = C_0 E \quad \text{and} \quad q' = C'(E - E_N) \tag{22}$$

where E_N is the limiting value of E, corresponding to $\theta=1$. Thus, when the adsorption isotherm is congruent with respect to the potential, we obtain from eqns. (9) and (22):

$$E_{q=0} = E_N\theta/[(C_0/C')(1-\theta)+\theta] \tag{23}$$

On the other hand, when the adsorption isotherm is congruent with respect to the charge, we obtain from eqn. (14), taking into consideration that at $q=0$, $E_0=0$ and $E'=E_N$ (see Fig. 1):

$$E_{q=0} = E_N\theta \tag{24}$$



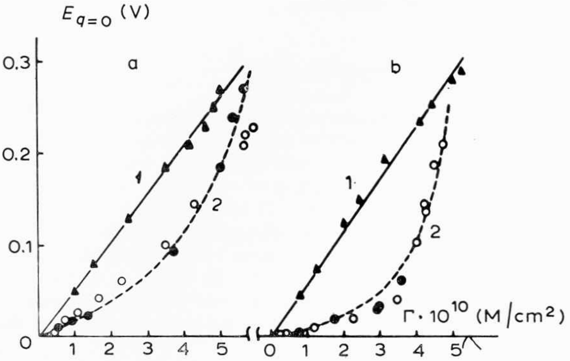


Fig. 5. Dependence of adsorption potential on surface coverage calcd. by means of eqn. (23) for the following values of the ratio C_0/C': (1), 1; (2), 1.5; (3), 2; (4), 3; (5), 5.

Fig. 6. Dependence of adsorption potential on adsorption of *n*-propanol (a) and caproic acid (b) at the soln./air (1) and soln./mercury (2) interfaces. The data have been obtained: (○ ○), from the maximum on the electrocapillary curves; (● ●), from the minimum on the differential capacity curves in dilute solns.; (---), calcd. by means of eqn. (23) at: (a), E_N = 0.31 V, C_0/C' = 3.5; Γ_m = $6 \cdot 10^{-10}$ mole cm^{-2}; (b), E_N = 0.29 V, C_0/C' = 7, Γ_m = $5 \cdot 10^{-10}$ mole cm^{-2}.

It follows from a comparison of eqns. (23) and (24), that a characteristic feature of the systems obeying eqn. (4) is the non-linearity of the dependence of $E_{q=0}$ on θ (or on Γ), which increases with increasing C_0/C' (see Fig. 5). As expected, at $C_0=C'$ both models give the same result.

Figure 6 shows the experimental dependencies of $E_{q=0}$ on Γ for the case of adsorption on mercury of *n*-propanol (a) and *n*-caproic acid (b) obtained by two methods. It is clear from the figure that these dependencies deviate appreciably from the straight line and agree well with eqn. (23). The same result was obtained for the case of adsorption on mercury of *n*-valeric acid and *n*-amylamine[10]. It should be noted that curves of the dependence of $E_{q=0}$ on Γ of a similar shape were obtained for camphor[11], *n*-butylamine[12] and some other aliphatic compounds[13], although they were explained differently, *viz.*, by the change in the orientation of adsorbed dipoles. Since in the same systems at the solution/air interface an approximately linear dependence of the adsorption potential drop on Γ is observed (see Fig. 6), this explanation cannot be considered as correct. Recently, a non-linear dependence of $E_{q=0}$ on Γ at the solution/mercury interface has been obtained also in the presence of tetrapropyl- and tetrabutyl-ammonium cations[14]. The results obtained show that in all the systems investigated, the assumption of the adsorption isotherm being congruent with respect to the electrode potential is in better agreement with experiment than the same assumption with respect to the electrode charge. It should be emphasized, however, that at $C_0/C' \leqslant 2$ (*e.g.*, in the case of adsorption on mercury of acetanilide molecules[15]) the curvature of the dependence of $E_{q=0}$ on θ (or on Γ) becomes insignificant, as is evident from Fig. 5, and owing to the scatter of the experimental points, this method cannot be used for the choice between eqns. (4) and (5).

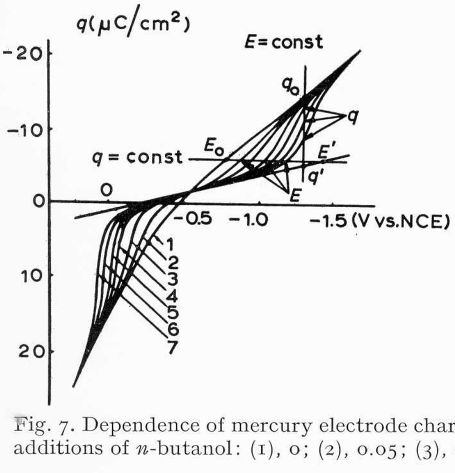


Fig. 7. Dependence of mercury electrode charge on potential in 0.1 *N* Na_2SO_4 solns. with different additions of *n*-butanol: (1), 0; (2), 0.05; (3), 0.1; (4), 0.2; (5), 0.4; (6), 0.6; (7), 0.8 *M*.

Another method for choosing between eqns. (4) and (5) is based on the analysis of the experimental *E*–*q* curves, measured at different concentrations of organic substance, by means of eqns. (9) and (14). This method can be explained by taking as an example the case of the system, 0.1 *N* $Na_2SO_4+n\text{-}C_4H_9OH$, for which we have measured the differential capacity curves and obtained the *q*–*E* curves by a numerical "backward" integration of the former*. The data obtained are given in Fig. 7, where an explanation of the graphical determination of the values of q_0, q and q' at a given E and of the values of E_0, E and E' at a given q is also presented. As the quantity C' is usually assumed constant in this method, the dependence of q' on E (or E' on q, which is the same thing) is a straight line with slope C', passing through a common intersection point of all q–E curves.

Thus, eqns. (9) and (14) can be used for calculating the adsorption isotherm in the θ–c coordinates both at E=const. and at q=const. When these isotherms are calculated at the point with coordinates (E_m, q_m), eqns. (10) and (15) are used, respectively, since at the minimum on the C–E curves at $E = E_m$, $C = C_{\text{true}}$. Then, the isotherms obtained can be given in relative coordinates, *e.g.*, θ *vs.* $y = c/c_{\theta=0.3}$. This enables the shape of the isotherms obtained at different E or q to be compared. The results of such a comparison for the system, 0.1 N $Na_2SO_4 + n\text{-}C_4H_9OH$, is shown in Fig. 8. It is clear from the figure that the isotherms obtained are congruent with respect to the potential and incongruent with respect to the charge.

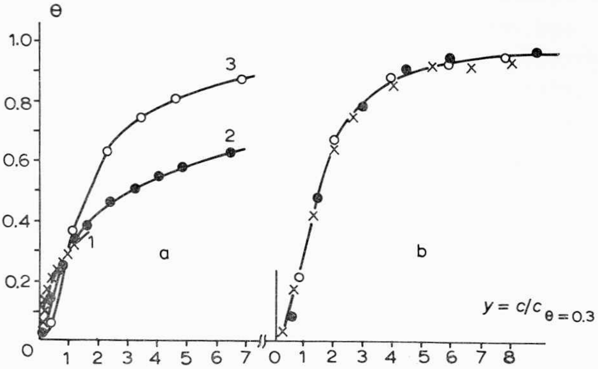


Fig. 8. Adsorption isotherms of n-butanol in the coordinates θ *vs.* $y = c/c_{\theta=0.3}$. (a), at q = const.: (1), $q = -9$; (2), $q = -6$; (3), $q = -1.55$ μC cm^{-2}. (b), at E = const.: (○ ○), $E = -0.55$; (● ●), $E = -0.8$; (× ×), $E = -1.0$ V (NCE).

In order to compare the sensitivity of this method with that of the two-dimensional pressure, we obtained by means of the "backward" integration of the q–E curves shown in Fig. 7, the corresponding electrocapillary curves and plotted the $\Delta\sigma$–log c curves for the potentials: −0.2, −0.55, −1.0 V (NCE) and $\Delta\xi$–log c curves for the charges +7.0, −1.55, −9.0 μC cm^{-2}. The data obtained are shown in Fig. 9. Owing to the low sensitivity of the two-dimensional pressure method, it is impossible to choose between eqns. (4) and (5) which is in agreement with PARSONS' results[5] and the model calculation given above.

Let us consider one more method, which enables a choice to be made between the models of two parallel- and two series-connected capacitors. This method consists in a theoretical calculation of the q–E curve and a comparison of its shape with that of the experimental charge–potential curve. Such a calculation for the model of

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* The "backward" integration method proposed by GRAHAME *et al.*[16] consists in carrying out the integration from a sufficiently negative potential, E, at which the substance being investigated has been completely desorbed from the surface, so that a corresponding quantity (q or σ) in a pure supporting electrolyte solution can be used as a constant of integration.

two parallel capacitors has already been considered by us above, a comparison of Figs. (2) and (7) shows the shapes of the theoretically-calculated and experimental q–E curves to be in good agreement.

It follows from Fig. 1 that in the case of the model of two series-connected capacitors at $C_0 = \text{const.}$ and $C' = \text{const.}$ we have

$$E_0 = E_\mathrm{m} + (q - q_\mathrm{m})/C_0 \quad \text{and} \quad E' = E_\mathrm{m} + (q - q_\mathrm{m})/C' \tag{25}$$

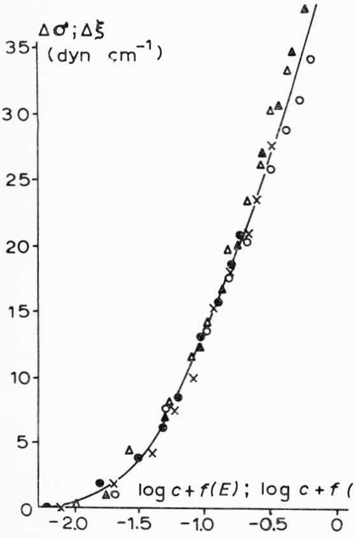
Substituting (25) into (13), we obtain:

$$\frac{\partial \ln G}{\partial q} = -\frac{C_0 - C'}{AC_0C'}(q - q_\mathrm{m}) \tag{26}$$

which on integration gives:

$$G = G_\mathrm{m} \exp[-\beta(q - q_\mathrm{m})^2] \tag{27}$$

where G_m is the value of G at $q = q_\mathrm{m}$ and $\beta = (C_0 - C')/2AC_0C' = \alpha/C_0C'$.



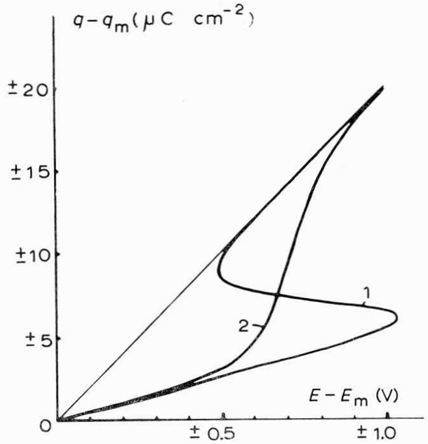


Fig. 9. Dependence of two-dimensional pressure on the log of concn. of *n*-butanol: (○), $E = -0.55$ V, $q = -1.55$ μC cm^{-2}; (●), $E = -1.0$ V; (×), $E = -0.2$ V (NCE); (△), $q = +7$ μC cm^{-2}; (▲), $q = -9$ μC cm^{-2}.

Fig. 10. Dependence of charge on potential theoretically calcd. using the model of (1), two series-connected capacitors; (2), two parallel capacitors.

The condition $q = \text{const.}$ becomes identical with the condition $E = \text{const.}$ in the point q_m, E_m, as all q–E curves cross in this point. The value of G_m should, therefore, be numerically equal to that of B_m in eqn. (18) and the parameter of intermolecular interaction, *a*, contained in the isotherm

$$G_\mathrm{m} c \exp[-\beta(q - q_\mathrm{m})^2] = \{\theta/(1 - \theta)\} \exp(-2a\theta) \tag{28}$$

should not differ from the value of *a* in eqn. (19). Thus, in eqn. (28) it was assumed that $G_\mathrm{m} = 10$ l mole^{-1}, $\beta = 0.075$ (cm^2/μC)^2 and $a = 1$. When the dependence of θ on

$(q-q_m)$ had been calculated by means of this equation, it was possible using the equation

$$E-E_m=\{(1-\theta)/C_0+\theta/C'\}(q-q_m) \tag{29}$$

(which is obtained by substituting (25) into (14)) to calculate the q–E curve in the coordinates $(q-q_m)$ *vs.* $(E-E_m)$. The q–E curve thus calculated for the concentration, $c=1.32$ *M*, is shown in Fig. 10, where it is compared with the charge–potential curve calculated under the same conditions, but using the model of two parallel capacitors.

It is evident from the figure that the q–E curve calculated using the model of two series-connected capacitors has an anomalous form and in a certain charge range corresponds to negative differential capacity values. For the shape of the above curve to be in agreement with that of the experimental q–E curves, it is necessary to assume that the parameter of intermolecular interaction, a, contained in Frumkin's isotherm (28) decreases sharply and even becomes negative with the charge moving away from q_m. This fact testifies that the experimental isotherms are incongruent with respect to the electrode charge, and has already been noted[4], although proved incorrectly as pointed out by PARSONS[5].

Thus, in the case of adsorption on mercury of aliphatic compounds, when the capacity in the supporting electrolyte solution, C_0, is much larger than the capacity in the presence of the adsorbed substance, C', and hence eqns. (4) and (5) are incompatible, the experimental data are better described by the isotherms that are congruent with respect to the potential than by those that are congruent with respect to the charge. This result is to be expected, since the surface layer model corresponding to the isotherm that is congruent with respect to the electrode potential has a more real physical significance.

The congruence of the adsorption isotherm with respect to the potential is an approximation that corresponds to the exact realization of the model of two parallel capacitors, *i.e.*, to the strict equipotentiality of both sides of the electric double layer[17]. This approximation is best realized in the case of adsorption on mercury of aliphatic compounds, although even in this case, owing to the discrete nature of the adsorbed dipoles of organic substance, the condition of equipotentiality of the ionic side of the double layer is somewhat impaired. For this reason, in describing C–E curves in the presence of aliphatic compounds quantitatively, it is necessary to introduce an additional correction for some small changes in α with the potential[18], *i.e.*, for the deviations of the real system from an ideal one described by an isotherm that is strictly congruent with respect to the electrode potential.

SUMMARY

In a strictly thermodynamic approach to the investigation of the adsorption isotherm, the choice of an electric variable is of no fundamental importance and is determined by considerations of expediency or convenience. This is not the case, however, when the thermodynamic approach to the investigation of adsorption is supplemented by the assumption of the congruence of the adsorption isotherm with respect to the electrode potential or charge. These assumptions are only compatible provided the double-layer capacity in the supporting electrolyte solution, C_0, does

not differ from the capacity, C', at complete surface coverage with adsorbed substance. If C_0 markedly exceeds C' as, for example, in the case of adsorption of aliphatic compounds on mercury, the assumption of the congruence of the adsorption isotherm with respect to the electrode potential is in better agreement with the experimental data. Moreover, this assumption corresponds to a clear and consistent physical picture of the surface layer in the presence of adsorbed molecules of organic substance (the model of two parallel capacitors).

ADDENDUM

The conclusions of this paper are not inconsistent with the latest experimental results of DUTKIEWICZ, GARNISH AND PARSONS[19], which were kindly communicated to us by Dr. PARSONS before publication. In fact, adsorption of glycols reduces only slightly the capacity of a mercury electrode. Therefore, the adsorption behaviour of butane-1,4-diol and 2-butyne-1,4-diol can be described within experimental error by means of eqn. (4) as well as eqn. (5). In the case of adsorption of *n*-butanol and ether however, it follows from Figs. 6–9 in ref. 19 that the experimental data deviate from both the models investigated, these deviations being rather less significant for the model of two parallel capacitors. Thus, the deviation of the experimental points on the q–Γ curves (see Figs. 6 and 8 in ref. 19) from a mean linear dependence amounts to no more than 0.5 μC cm^{-2}, which only slightly exceeds the accuracy in the charge determination. On the other hand, the deviation of the experimental points in Figs. 7 and 9 from the mean linear dependence, in some cases is as large as 0.10–0.15 V. Finally, in connection with the paper under discussion, it should be stressed once more that the choice of the independent electrical variable based on considerations of convenience (*e.g.*, the possibility of obtaining symmetrical curves for cathodic and anodic adsorption regions of an organic substance) cannot serve as a criterion for the choice of the independent variable. This can be decided only on the basis of an analysis of the physical significance of the underlying model.

REFERENCES

1 A. N. FRUMKIN, *Z. Physik. Chem.*, 103 (1923) 55.
2 R. PARSONS, *Trans. Faraday Soc.*, 51 (1955) 1518; 55 (1959) 999.
3 R. PARSONS, *J. Electroanal. Chem.*, 7 (1964) 136.
4 B. B. DAMASKIN, *J. Electroanal. Chem.*, 7 (1964) 155.
5 R. PARSONS, *J. Electroanal. Chem.*, 8 (1964) 93.
6 R. PAYNE, *J. Phys. Chem.*, 69 (1965) 4113; 70 (1966) 204.
7 A. N. FRUMKIN, *Z. Physik*, 35 (1926) 792.
8 A. N. FRUMKIN, *Z. Physik. Chem.*, 116 (1925) 466.
9 B. B. DAMASKIN, A. A. SURVILA AND L. E. RYBALKA, *Elektrokhimiya*, 3 (1967) 146.
10 A. N. FRUMKIN, B. B. DAMASKIN, V. M. GEROVICH AND R. I. KAGANOVICH, *Dokl. Akad. Nauk SSSR*, 158 (1964) 706.
11 A. G. STROMBERG AND L. S. ZAGAINOVA, *Zh. Fiz. Khim.*, 31 (1957) 1042.
12 I. ZWIERZYKOWSKA, *Roczniki Chem.*, 39 (1965) 101.
13 R. G. BARRADAS, P. G. HAMILTON AND B. E. CONWAY, *J. Phys. Chem.*, 69 (1965) 3411.
14 B. B. DAMASKIN, R. I. KAGANOVICH, V. M. GEROVICH AND S. L. DIATKINA, *Elektrokhimiya*, in press.
15 R. PARSONS AND F. G. R. ZOBEL, *Trans. Faraday Soc.*, 62 (1966) 3511.
16 D. C. GRAHAME, E. M. COFFIN, J. I. CUMMINGS AND M. A. POTH, *J. Am. Chem. Soc.*, 74 (1952) 1207.
17 A. N. FRUMKIN, B. B. DAMASKIN AND A. A. SURVILA, *Elektrokhimiya*, 1 (1965) 738.
18 B. B. DAMASKIN, *Usp. Khim.*, 34 (1965) 1764.
19 E. DUTKIEWICZ, J. D. GARNISH AND R. PARSONS, *J. Electroanal. Chem.*, 16 (1968) 505.