

U.D.C. 541.183 If $\epsilon = \epsilon(\varphi, \theta)$, then

$$C = \left(\frac{\partial \epsilon}{\partial \varphi}\right)_\theta + \left(\frac{\partial \epsilon}{\partial \theta}\right)_\varphi \frac{d\theta}{d\varphi} = \left(\frac{\partial \epsilon}{\partial \varphi}\right)_\theta + \frac{1}{A} \left(\frac{\partial \epsilon}{\partial \theta}\right)_\varphi \frac{0}{f'(\theta) - 2a\theta}. \quad (7)$$

EQUATION TO ADSORPTION ISOTHERM AND SHAPE OF PEAKS ON DIFFERENTIAL CAPACITANCE CURVES

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I have noted in several papers¹⁻³ good agreement between experimental curves for differential capacitance in the presence of aliphatic compounds and the corresponding curves calculated on the basis of the Frumkin isotherm⁴. Parsons⁵ has introduced a correction, representing the attraction interaction between adsorbed particles, into the equation of state of Helfand, Frisch, and Lebowitz (HFL)⁶, so that the resulting equation can reproduce the sigmoid shape of the experimental adsorption isotherms. It was of interest to study the influence of the shape of the adsorption isotherm on the way in which the differential capacitance C varies with the electrode potential φ in the presence of an organic substance, and to settle the question whether, by appropriate choice of the constants, similar good agreement could be obtained between experimental and calculated $C-\varphi$ curves based on the corrected HFL isotherm^{5,6}.

As has been shown previously⁷, the most general equation of state for the surface layer, embracing both the Frumkin isotherm and the corrected HFL isotherm, can be written

$$\Delta\sigma = A[f(\theta) - a\theta^2], \quad (1)$$

where $\Delta\sigma$ is the decrease in interfacial tension due to adsorption of the organic substance $A = RT\Gamma_m$ (Γ_m being the limiting value of the adsorption Γ), $\theta = \Gamma/\Gamma_m$, a is a measure of the interaction between adsorbed molecules, and $f(\theta)$ is a function determined by the choice of adsorption isotherm — for the Frumkin isotherm⁴ $f(\theta) = -\ln(1-\theta)$, and for the HFL isotherm^{5,6} $f(\theta) = \theta/(1-\theta)^2$.

Simultaneous solution of Eqn. (1) and the Gibbs equation readily gives the general equation to the adsorption isotherm

$$\ln B + \ln c = \int \frac{f'(\theta)}{\theta} d\theta - 2a\theta, \quad (2)$$

where B is a function only of φ , c is the concentration of the organic substance, and $f'(\theta) = df(\theta)/d\theta$.

Differentiating Eqn. (2) with respect to φ with c or θ constant yields, on the assumption that a can vary with potential, the equations

$$\frac{d \ln B}{d\varphi} = \left[\frac{f'(\theta)}{\theta} - 2a \right] \frac{d\theta}{d\varphi} - 2\theta \frac{da}{d\varphi}, \quad (3)$$

$$\left(\frac{\partial \ln c}{\partial \varphi} \right)_\theta = - \left(\frac{d \ln B}{d\varphi} + 2\theta \frac{da}{d\varphi} \right). \quad (4)$$

From the reciprocity relation applied to the fundamental equation of electrocapillarity, it follows that

$$\left(\frac{\partial \ln c}{\partial \varphi} \right)_\theta = - \frac{1}{A} \left(\frac{\partial \epsilon}{\partial \theta} \right)_\varphi, \quad (5)$$

where ϵ is the charge on the electrode surface. From Eqns. (3)–(5) we have

$$\frac{d\theta}{d\varphi} = \frac{1}{A} \left(\frac{\partial \epsilon}{\partial \theta} \right)_\varphi \frac{\theta}{f'(\theta) - 2a\theta}. \quad (6)$$

The terms on the right-hand side of Eqn. (7) represent respectively the true and the additional capacitance of the double layer⁸. Since $(\partial \epsilon / \partial \theta)_\varphi$ varies monotonically with potential⁹, the position and form of the adsorption peak on the $C-\varphi$ curve are determined, at not too small values of a ,¹⁰ by the parameter

$$h = \frac{\theta}{f'(\theta) - 2a\theta}. \quad (8)$$

The function h passed through a maximum

$$h^{\max} = \frac{\theta^{\max}}{f'(\theta^{\max}) - 2a\theta^{\max}},$$

where $\theta^{\max}$ is found from the condition $dh/d\theta = 0$, which is equivalent to

$$\theta f''(\theta) = f'(\theta). \quad (9)$$

Expressing a in terms of $h^{\max}$, we obtain for h

$$h = 1 / \left[\frac{f'(\theta)}{\theta} - \frac{f'(\theta^{\max})}{\theta^{\max}} + \frac{1}{h^{\max}} \right]. \quad (10)$$

Putting $m = h/h^{\max}$, we obtain the equation

$$\frac{f'(\theta)}{\theta} = \frac{f'(\theta^{\max})}{\theta^{\max}} + \frac{1-m}{mh^{\max}}, \quad (11)$$

solution of which gives two values θ_i : $\theta_1 < \theta^{\max}$ and $\theta_2 > \theta^{\max}$.

We must now pass from θ_i values to the corresponding potentials φ_i on the $C-\varphi$ curve. We use for this purpose Eqn. (6), from which it follows that

$$\frac{1}{A} \left(\frac{\partial \epsilon}{\partial \theta} \right)_\varphi d\theta = \frac{d\theta}{h} = \left[\frac{f'(\theta)}{\theta} - \frac{f'(\theta^{\max})}{\theta^{\max}} + \frac{1}{h^{\max}} \right] d\theta. \quad (12)$$

Integrating this equation from $\theta^{\max}$ to θ_i and neglecting the variation of $(\partial \epsilon / \partial \theta)_\varphi$ with φ in the region of the peak (a sufficiently narrow peak), we obtain the corresponding deviations in the potential from $\varphi^{\max}$

$$\frac{1}{A} \left(\frac{\partial \epsilon}{\partial \theta} \right)_\varphi \max (\varphi_i - \varphi^{\max}) \simeq \int_{\theta^{\max}}^{\theta_i} \left[\frac{f'(\theta)}{\theta} - \frac{f'(\theta^{\max})}{\theta^{\max}} + \frac{1}{h^{\max}} \right] d\theta. \quad (13)$$

Having specified $h^{\max}$ from Eqns. (10), (11), and (13), we can calculate the dependence of h on the potential, and ascertain the effect of the equation to the isotherm on the shape of the peak on the $C-\varphi$ curve. For the Frumkin isotherm we find, solving Eqns. (11) and (13), that

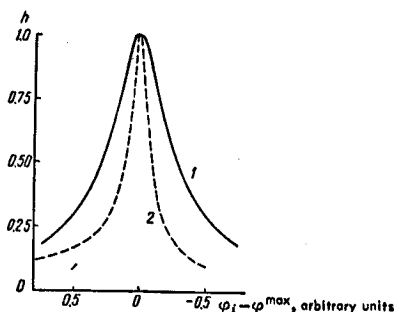
$$\frac{1}{A} \left(\frac{\partial \epsilon}{\partial \theta} \right)_\varphi \max (\varphi_i - \varphi^{\max}) = \pm \left[\ln \frac{1+r}{1-r} - \frac{r}{2} \left(4 - \frac{1}{h^{\max}} \right) \right], \quad (14)$$

where

$$r = \sqrt{\frac{1-m}{4mh^{\max} + 1 - m}}.$$

For the HFL isotherm, it follows from Eqn. (13) that, since $\theta^{\max} = 0.215$,^{5,7}

$$\begin{aligned} \frac{1}{A} \left(\frac{\partial \epsilon}{\partial \theta} \right)_\varphi \max (\varphi_i - \varphi^{\max}) \simeq & \ln \frac{\theta_i}{1-\theta_i} + \frac{2-\theta_i}{(1-\theta_i)^2} - \\ & - \left(11.68 - \frac{1}{h^{\max}} \right) \theta_i - \frac{0.215}{h^{\max}} + 0.907. \end{aligned} \quad (15)$$



Potential dependence of function h , defining shape of peak on $C-\phi$ curves, calculated on the basis of:

1) Frumkin isotherm; 2) corrected HFL isotherm, $h^{\max} = 1$.

In order to determine θ_i in this expression, it is necessary to solve Eqn. (11), which is most simply accomplished graphically, by determining the abscissae of the points of intersection of the function $h(\theta)$ with the horizontal straight lines $h = mh^{\max}$.

The results of such a calculation for $h^{\max} = 1$ are illustrated in the diagram. It is seen that, for the same height of capacitance peak, its width according to the corrected HFL isotherm must be less, by a factor of ~ 2.7 , than if adsorption of the organic substance had obeyed the Frumkin isotherm. On the other hand, if the adsorption had obeyed the corrected HFL isotherm, and we had determined the value of $h^{\max}$ (which is analogous to a) from the experimental peak width, by the method described previously⁹ on the assumption that the Frumkin isotherm is valid, the capacitance peak calculated in this way would have been about double the height of the experimental peak. This marked difference in peak width for the same value of $h^{\max}$, or in $h^{\max}$ at the same peak width, obtained for the Frumkin and HFL isotherms, cannot be eliminated by varying the value of A occurring in Eqns. (7) and (13). In fact, from the equation

$$\frac{1}{A} \left(\frac{\partial \epsilon}{\partial \theta} \right)_{\varphi^{\max}} = - \left(\frac{\partial \ln c}{\partial \varphi} \right)_{\theta^{\max}} = - \frac{\partial \ln c}{\partial \varphi^{\max}}, \quad (5a)$$

A is unambiguously defined by the slope of the experimental curve of $\log c$ plotted against $\varphi^{\max}$ and by the choice of equation for the variation of the charge on the electrode with θ at constant φ . The relationship proposed by Frumkin⁴

$$\epsilon = \epsilon_0(1 - \theta) + \epsilon'\theta, \quad (16)$$

(where ϵ_0 and ϵ' are the values of ϵ at $\theta = 0$ and 1 respectively), which agrees well with experiment in the case of the adsorption of aliphatic compounds, is usually chosen for this purpose.

Thus from the good agreement between calculated and experimental $C-\phi$ curves¹⁻³ it must be concluded, not only that the adsorption of the compounds can be described by the Frumkin isotherm, but also that it is impossible to represent the adsorption of these compounds by the corrected HFL isotherm.

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SUMMARY

1. A generalised formula (7) is obtained, unconnected with an actual equation of state, for differential capacitance in the presence of an organic substance.
2. It is shown that the adsorption of the organic compounds investigated previously¹⁻³ cannot be described by the corrected isotherm of Helfand et al.

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DISSOCIATION OF IONS DERIVED FROM PROPANE IN A DOUBLE MASS-SPECTROMETER

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Study of the dissociation of various fission and molecular ions in a double mass-spectrometer permits the observation of many rules governing their breakdown, which cannot be established from the molecules mass spectra obtained by means of a mass-spectrometer with a single magnetic analyser. This is because, according to the existing concepts^{1,2}, the mass spectrum of a polyatomic molecule forms as a result of consecutive and competing breakdown reactions involving the initial and fission ions during their residence in the ion source. As a result various processes leading to the formation of a given type of ion become superimposed which, in the presence in the mass spectrum of many types of ion, greatly complicates the analysis of the mass spectrum by means of the usual type of mass-spectrometer. The double mass-spectrometer permits the separate investigation of the dissociation of initial and fission ions. Having measured in this way the cross-sections for the formation of various ions from the original molecular ions and from fission ions, it is possible to obtain some information concerning the structure of the initial ions, their energy state, and the modes of their breakdown. With this aim in view we investigated the dissociation of various ions derived from propane, occurring as a result of collisions with neon atoms.