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ISOTHERMS AND COMPETITIVE ADSORPTION

By

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Treating adsorption from solution on electrodes, BOCKRIS *et al.*[1] have recently taken into account dipole-dipole interactions between solvent molecules within an adsorbed layer (consisting of solvent and adsorbate molecules) but assumed,

(i) that such interactions (strictly speaking the total energy of interaction per solvent molecule) do not depend on the coverage of the electrode by these or other molecules (but such interactions were taken as a function of orientation which, in turn, depends on the electric variable, see below),

(ii) that contributions from interactions other than dipole-dipole to the energy of adsorption are constant throughout, regardless of coverage and electric state.

BOCKRIS *et al.*'s calculations for various systems reproduced satisfactorily the *variation* of adsorption of neutral molecules *with the electric variable*, which thus turned out to be determined chiefly by the solvent's dipole-dipole interactions, in addition to its dipole-field interactions.

Assumption (i) might be questioned after comparing BOCKRIS *et al.* 's equations[1] with FRUMKIN's isotherm[2]. However, the situation at the electrode-solution interface differs qualitatively from other cases of adsorption with interaction[3] because there is, at this interface, a degree of freedom in the *orientation* of the dipoles.

Consider the following equations, which are BOCKRIS *et al.* 's expressions in their simplest form[4,5]:

$$\theta_A/(1-\theta_A) = b \exp\{B(rq^M - sB)\} \tag{1.a}$$

with

$$B = \tanh(rq^M - sB) \tag{1.b}$$

where θ_A is the coverage of the electrode by a neutral adsorbate, A, competing with the solvent molecules, S, at the interface, B is a variable expressing the excess number of solvent dipoles in one orientation over that in the other (with respect to the field), q^M is the charge density on the metal, and b, r, and s are

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constants. The constant r is a function of the dipole moment and the dielectric constant of the double layer material. The constant s is proportional to the interaction energy for a pair of nearest-neighbour solvent dipoles times an effective coordination number. This coordination number was also taken[1] as constant with coverage, whence B was calculated, at given values of r and s, as a function of q^M, and then θ_A as a function of b (which is proportional to the concentration of A); B, *i.e.* the orientation of adsorbed solvent molecules, was thus only a function of q^M but was independent of θ_A.

If the restriction on s is lifted by setting $s=s_0(1-\theta_A)$, and B is calculated as a function of both θ_A and q^M, the result is somewhat surprising, *viz.*, B varies now appreciably with θ_A, at a given value of q^M (*i.e.* the field), but the variation of θ_A with b is not affected appreciably, *cf.* Fig. 1.

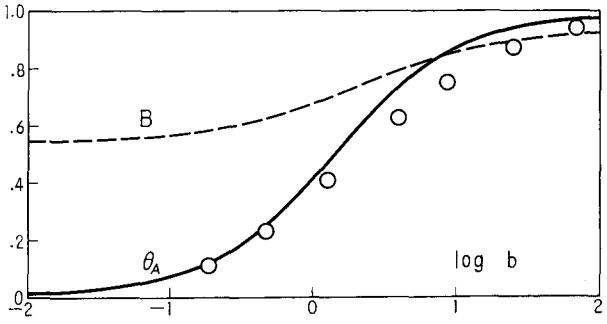

Fig. 1. Variation of B (net orientation of adsorbed solvent dipoles) and θ_A (the coverage of the electrode by a neutral adsorbate) with log b, by Eq. (1), with $r=1.70$ (corresponding to $q^M=6\,\mu C\ cm^{-2}$) and $s=2(1-\theta_A)$ (circles). The solid line gives θ_A by Eq. (1) with the constant values $B=0.55$ and $s=2.0$. The deviations between circles and the solid line are strongly reduced with decreasing q^M.

Thus, allowing s to be a simple function of coverage θ_A, as it could reasonably be, brings about a relative variation of B such that the solvent dipoles, at constant q^M, are *increasingly oriented* in parallel when the coverage θ_A, *i.e.* the fraction of neutral molecules diluting them in the adsorbed layer, increases. But the sum of dipole-dipole interactions of the solvent molecules remains approximately constant, at constant field, because the diluting effect of the adsorbate is compensated, to a considerable extent, by the increasing orientation of the solvent molecules.

This variation of orientation of the solvent dipoles is an interesting result in itself. However, to maintain approximation (i) in calculations of the effect of dipole-dipole interactions on adsorption appears to be justified as a first approximation.

Assumption (ii) concerns interactions of the LONDON type. No justification

other than simplicity can be given here. To lift this restriction tentatively, one may note that the adsorption of one molecule, A', of the neutral adsorbate A by displacement of adsorbed molecules, S', of the solvent S according to

$$A'(sol)+nS'(ads)\rightleftharpoons A'(ads)+nS'(sol)$$

is accompanied by

1. a gain of, loosely speaking, cohesive energy between A' and other adsorbed A-molecules, proportional to θ_A: E_1;
2. a loss of cohesive energy between S' and other adsorbed S-molecules, proportional to $\theta_S=1-\theta_A$ (and to the number, n, of solvent molecules displaced by one molecule of A): E_2;
3. analogously, a variation in adhesive energy between A- and S-molecules: E_3.

In the usual case, $n>1$, but to allow for this in the present estimate is algebraically cumbersome. Assume, therefore, a hexagonal surface pattern where $n=1$, for the moment. Then, E_1 will be proportional to $3\theta_A E_A^c$, E_2 to $-3(1-\theta_A)$ E_S^c, and E_3 to $3(-\theta_A+\theta_S)E^a=3(1-2\theta_A)E^a$, where superscripts c and a refer to cohesion and adhesion (per molecule; the factor 3 constitutes half the number of pairs over which is to be summed, *i.e.* allows for the fact that one does not account twice for the same interaction). Adding up, there should appear in the adsorption equation a term

$$\exp\{(6E^a-3E_A^c-3E_S^c)\theta_A\}\exp(3E_S^c-3E^a).$$

The second exponential can be incorporated into the constant b of Eq. (1), but the first gives rise to a term, proportional to θ_A, such as first introduced by FRUMKIN[2], so that Eq. (1) may be written

$$\theta_A/(1-\theta_A)=b\exp\{B(rq^M-sB)\}\exp(a\theta) \qquad (2)$$

where

$$a=6E^a-3E_A^c-3E_S^c.$$

The model used to derive the nature of the term $\exp(a\theta)$ is too crude to admit a quantitative estimate. However, if the terms E are roughly set proportional to $\alpha_i\alpha_j r_{ij}^{-6}$, where the polarisabilities, α, of the molecules i and j under consideration are of the same magnitude, then one can predict that the term involving distance, r_{ij}^{-6}, which is governed by the size of the molecules, will be decisive for the relative magnitudes of E wherever $n>1$, and hence $|E_2|>|E_3|>|E_1|$, similarly $|E_S^c|>|E^a|>|E_A^c|$, and E_S^c determines a.

The effect upon the adsorption isotherm of displacing from the interface solvent molecules that attract each other turns out to be the same as that of placing there adsorbate (A) molecules that attract each other. The *former* effect

depends sharply on the size and probably on the shape of the molecules of A but the contribution of it to the value of a is basically a function of the molecular constants of S.

It appears difficult at present to develop a quantitative theory of a because the value of r_{SS} cannot be determined with sufficient accuracy. This development, however, might be desirable before attempting the complete analysis of systems containing more than one adsorbate (*i.e.* A_1 and A_2 besides S)[6,7]. It must be noted, in this connexion, that it is not justified to introduce empirically interaction constants a as obtained at constant potential[8] into the equations of BOCKRIS *et al.*[1] because the character of isotherms changes appreciably when going to the charge scale[9,10]; qualitatively, it appears that the values of a become smaller in this case, as shown with some isotherms in Fig. 2.

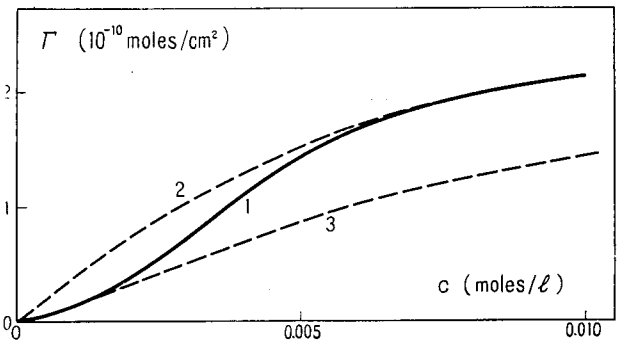

Fig. 2. Experimental results for the adsorption of phenol from 0.1 N aqueous LiCl. Curve 1: at −800 mV against a calomel electrode in the same solution. Curve 2: at $q^M = -2.4$ μC cm^{-2}. Curve 3: at $q^M = -5$ μC cm^{-2}. Here, $q^M = -2.4$ μC cm^{-2} is the charge density at −800 mV for $c = 0.01$ moles/l, $q^M = -5$ μC cm^{-2} is the charge density at −800 mV for $c \to 0$.

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