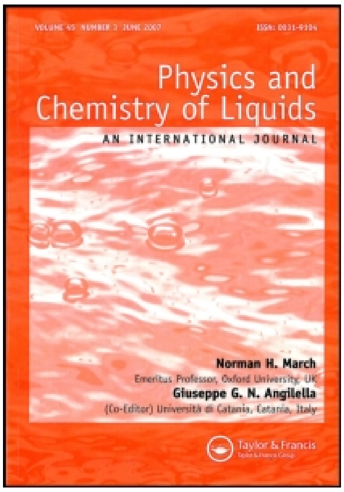

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E. Gileadi[a]
[a] Institute of Chemistry, Tel Aviv University, Romat, Aviv, Israel

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Tafel Slopes in Relation to the Replacement of Adsorbed Water by Organic Molecules

E. GILEADI

Institute of Chemistry, Tel Aviv University, Romat Aviv, Israel

INTRODUCTION

In the lecture presented by Prof. Reddy the role of water in determining the potential dependence of electrosorption of neutral organic molecules has been discussed. The process one considers is that of the replacement of a number of water molecules n by each organic molecule adsorbed. The dipole moments of the adsorbed water molecules interact with the electrical field in the double layer and hence cause a potential (or charge) dependent adsorption of the neutral organic molecule, even if the latter possesses no permanent dipole moment. The theory of this phenomenon has been worked out by Bockris, Devanathan and Muller. Corrections for lateral interactions between the adsorbed water molecules and for the permanent dipole moment of the electrosorbed neutral organic molecule have been made.[1,2]

A different approach has been taken much earlier by Frumkin,[3] who considered that the potential dependence of electrosorption of neutral species was caused by the change of energy of the double layer capacitor when water molecules were replaced by organic molecules having a lower dielectric constant.

In the present note, the influence of this competition between organic and water molecules for sites on the surface on electrode kinetics will be considered.

THE COMBINED ADSORPTION ISOTHERM

Let the adsorption isotherm be written in the form

$$f(\theta) = K(E)c \qquad (1)$$

In the discussion to follow, we shall not concern ourself with the form of the function $f(\theta)$. For the potential dependence of the adsorption equilibrium constant $K(E)$, two distinct cases have traditionally been considered. If adsorption involved charge transfer (e.g. when the adsorbed species is an intermediate in a sequence of steps occuring during an electrochemical reaction) the function $K(E)$ can be written in simple form as

$$K(E) = K^0 \exp\left[\frac{EF}{RT}\right] \tag{2}$$

If adsorption does not involve charge transfer the situation is much more complex. The form of the function $K(E)$ for this case was given by Bockris *et al.* as

$$K(E) = K^0 \exp - \left[\frac{nz(\mu X - z\varepsilon m)}{kT}\right] \tag{3}$$

where μ is the dipole moment of water, X is the electrical field in the double layer, ε is the interaction energy between neighbouring water molecules, m is a two dimensional coordination number representing the number of nearest neighbours and z is given by

$$z = \frac{N\uparrow - N\downarrow}{N\uparrow + N\downarrow} \tag{4}$$

where $N\uparrow$ and $N\downarrow$ are numbers of water molecules in the two possible orientations per unit area of the interphase.

Consider now the adsorption of an organic molecule

$$RH_{sln} \rightleftarrows RH_{ads}. \tag{5}$$

Equation (3) is clearly applicable to describe the potential dependence of the adsorption equilibrium constant $K(E)$.

Suppose now that the same species is adsorbed but in a different way, so that charge-transfer occurs.

$$RH_{sln} \rightleftarrows R_{ads} + H^+ + e_M \tag{6}$$

Here Eq. (2) would seem at first applicable. This, however, cannot be expected to give a complete description of the equilibrium in Eq. (6) since the adsorbed species R may take up nearly as much place on the electrode surface as the molecule RH, and the effect of competition with water should be taken into account. Thus the adsorption equilibrium in Eq. (6) can be best represented by a *combined isotherm* which takes into account the potential dependence $K(E)$ represented by both Eqs. (2) and (3). It was shown by Gileadi and co-workers[4,6] that the expression for the combined isotherm can be greatly simplified if one considers only the high-field approximation. Under these conditions one obtains

$$K(E) = K^0 \exp\left[\frac{EF}{RT}\cdot\left(1 - \frac{\mu_m}{e_0\delta}\right)\right] \qquad (7)$$

where e_0 is the charge of the electron and δ is the diameter of a water molecule.[4] Introducing the proper numerical values into Eq. (7) one has

$$K(E) = K^0 \exp\left[\frac{EF}{RT}\cdot(1 - 0.14n)\right] \qquad (8)$$

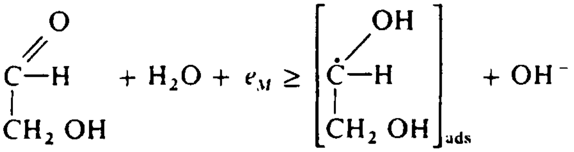
INFLUENCE OF MOLECULAR SIZE ON THE TAFEL SLOPE

The Tafel slopes derived using the combined isotherm and their dependence on molecular size (i.e. on the parameter n), for different mechanism have been discussed by Gileadi and Stoner recently.[7] Since the standard free energy is influenced by the size of the molecule adsorbed (cf. Eq. (8)) the standard free energy of activation in a step in which an adsorbed intermediate is formed on the surface or desorbed from it will also be affected by the size parameter n. This may be expressed as an additional potential dependence of the specific rate constant

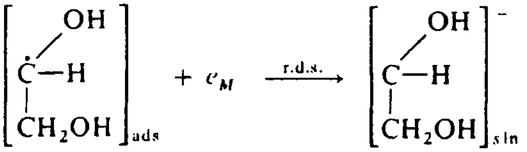
$$k(E) = k^0 \exp \pm \left[0.14\beta n\left(\frac{EF}{RT}\right)\right] \qquad (9)$$

The positive and negative signs refer to desorption and adsorption steps, respectively.

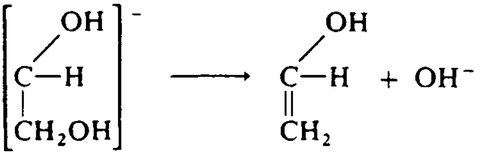
This theory[7] has been applied recently by Kirowa-Eisner and Gileadi[8] to evaluate the mechanism of reduction of glycol aldehyde at the dropping mercury electrode in alkaline solutions. The mechanism was found to be as follows:



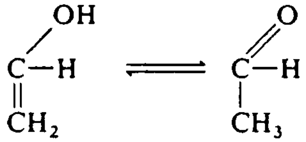
$$\mathrm{O{=}CH{-}CH_2OH} + H_2O + e_M \geq \left[\mathrm{\dot{C}H(OH){-}CH_2OH}\right]_{ads} + OH^- \qquad (10)$$



$$\left[\mathrm{\dot{C}H(OH){-}CH_2OH}\right]_{ads} + e_M \xrightarrow{\text{r.d.s.}} \left[\mathrm{CH(OH){-}CH_2OH}\right]^-_{sln} \qquad (11)$$



(12)



(13)

The corresponding rate equation, using the combined isotherm, turns out to be

$$i = K\, C_{GA} C_{OH^-}^{-1} \exp\left[\left(\frac{EF}{RT}\right)(1.5 - 0.07n)\right] \tag{14}$$

where the symmetry factor β has been taken to be equal to one half. The reaction-order parameters found experimentally were equal to those predicted from equation (14) and the Tafel slope ($b = -49 \pm 2$ mV at 3.4°C) is in agreement with the same equation for $n = 5 - 6$. ($2.3RT/F = 54$ mV at this temperature).

In a further study[9] the reduction of acetaldehyde and formaldehyde was compared to that of glycolaldehyde. The same kinetic behaviour was observed for all three aldehydes, but the Tafel slope decreased with molecular size to $b = -40 \pm 2$ for aceltaldehyde and $b = -36 \pm 2$ for formaldehyde, corresponding to $n = 1$-3 and $n = 0$-1, respectively. Thus a definite dependence of the Tafel slope on the size of the molecule was observed in this series of aldehydes. Many more experiments will have to be done, preferably in homologous series of compounds, to verify the generality of the observation that the Tafel slope depends on the size of one of the adsorbed intermediates in the reaction sequence.

Added in Proof: In a recent study of the reduction of nitroalkenes, a similar effect of the size of the adsorbed intermediate on the Tafel slope was observed.[10]

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