

This kind of increase in proton-donor power probably explains the increased yield of methane obtained by electrochemical reduction of menthol in the presence of zinc salts as supporting electrolyte [14].

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ASSOCIATION OF IONS DURING THEIR SPECIFIC ADSORPTION AT A METAL/SOLUTION INTERFACE

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In studying electrochemical processes involving charge transfer in the presence of electrochemically inert specifically adsorbed species, one often observes that the processes are accelerated in comparison with analogous systems in which specific adsorption of inert components does not occur. The hypothesis that so-called bridges may be formed from reactants and adsorbed inert species within the Helmholtz layer has been postulated and given a theoretical grounding in a number of works [1-3]. The role of these bridges consists either in reducing the effective electric charge of the reactants or in providing the means for the energetically more favorable two-stage transfer of charge between the metal and reactant. In connection with the interpretation of experimental data on the effect of adsorbed counterions on electrochemical reactions involving ionic reactants, it would be of particular interest to analyze the effect of the formation of ion pairs in the Helmholtz layer during the simultaneous specific adsorption of oppositely charged ions.

Fawcett and Levine [4] have developed a two-dimensional modification of the known bulk ionic association theory [5, 6]. On the assumption that the centers of the reacting ions and adsorbed counterions lie in the same plane, they calculated the contribution made to the electrochemical potential of the reactants by the reorganization of the distribution of the counterions due to their electrostatic interaction with the reactants, and explained the accelerating effect of ionic association on electrochemical charge-transfer reactions.

It should be noted, however, that the situation in which the centers of the associating ions are located at different distances from the metal surface is much more probable (and, presumably, more common). In this case, even when neutral ion pairs are formed, the dipole moment arising during association may make a considerable contribution to the chemical potential of the associates. The object of the present work is to analyze the internal structure of the Helmholtz layer in the presence of specifically adsorbed and associatable ions of different size and different charge sign.

Let us consider the case of the joint specific adsorption of cations K and anions A from a dilute solution of a binary z-z electrolyte on the surface of a planar metal electrode ($x=0$). Suppose that the centers of the adsorbed anions are located within the Helmholtz layer at a distance $x=x_2$ from the metal, and that the centers

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of the adsorbed cations are localized in the $x=x_1$ plane ($x_2 > x_1$). We will denote the thickness of the Helmholtz layer by δ and its effective dielectric constant by ϵ . In addition, we will assume that the plane $x=(x_1+x_2)/2$ is at a distance β from the metal surface and at a distance γ from the outer Helmholtz plane ($x=\delta$). If the $\mu_C^{(ad)}$ and $\mu_A^{(ad)}$ denote the electrochemical potentials of the cations and anions in the adsorbed state, the conditions for adsorptive equilibrium for each of the ions in dilute solution will be of the form

$$\mu_C^{(ad)} = \mu_C^{(st)} + kT \ln c/c_0, \quad (1)$$

$$\mu_A^{(ad)} = \mu_A^{(st)} + kT \ln c/c_0. \quad (2)$$

where $\mu_C^{(st)}$ and $\mu_A^{(st)}$ are the standard chemical potentials of the ions in the bulk phase; c is the bulk concentration of electrolyte; and c_0 is the total concentration of the solution, including the electrolyte ions and the solvent molecules. From now on, we will assume that a thermodynamic equilibrium exists between the adsorbed ions and the neutral CA ions pairs within the Helmholtz layer. Hence, the following relation will hold:

$$\mu_{CA} = \mu_C^{(st)} + \mu_A^{(st)} + 2kT \ln c/c_0, \quad (3)$$

where μ_{CA} is the chemical potential of an ion pair in the adsorbed state.

If we disregard the short-range forces between the ion pairs and assume that each adsorbed ion occupies only one active adsorption center, the following expression can be written for the chemical potential μ_{CA} :

$$\mu_{CA} = \mu_{CA}^{(st)} + kT \ln \frac{\Gamma}{\Gamma_\infty - \Gamma} + \mu_{CA}^{(e)} \quad (4)$$

where $\mu_{CA}^{(st)}$ is the standard part of the chemical potential; Γ is the surface density of ion pairs; Γ_∞ is the maximum possible value of Γ ; and $\mu_{CA}^{(e)}$ is the electrostatic part of the chemical potential. A statistical thermodynamic method for calculating $\mu_{CA}^{(e)}$ has been developed in [7]. Using this method, we find*

$$\begin{aligned} \mu_{CA}^{(e)} = & -\frac{4\pi\chi}{\epsilon} \left(q - \frac{\chi\Gamma}{\delta} \right) - \frac{\chi^2}{\epsilon} \int_0^\infty \left(\frac{\text{ch } \lambda\beta \text{ ch } \lambda\gamma}{\text{sh } \lambda\delta} - \frac{1}{2} \right) \lambda^2 d\lambda + \\ & + \frac{\pi^{1/2}\chi^2\Gamma}{\epsilon\delta^2} \sum_{k=1}^\infty (-1)^k k \cos\left(\frac{k\pi\beta}{\delta}\right) \cos\left(\frac{k\pi\gamma}{\delta}\right) \left\{ 2K_1\left(\frac{k}{\delta}\sqrt{\frac{\pi}{\Gamma}}\right) - \frac{k}{\delta}\sqrt{\frac{\pi}{\Gamma}} K_2\left(\frac{k}{\delta}\sqrt{\frac{\pi}{\Gamma}}\right) \right\}. \end{aligned} \quad (5)$$

Here, χ denotes the projection of the dipole moment of the ion pairs on the x axis, averaged over all ion pairs, q represents the average electronic charge density on the metal surface, and K_2 is a Bessel function of the second kind (McDonald function). On the basis of the assumptions made above, χ is negative and equal to

$$\chi = -ez(x_2 - x_1). \quad (6)$$

By combining expressions (3) and (4), we obtain the following transcendental equation for the ion-pair density Γ :

$$B \left(\frac{c}{c_0} \right)^2 = \frac{\Gamma}{\Gamma_\infty - \Gamma} \exp \left(\frac{\mu_{CA}^{(e)}}{kT} \right), \quad (7)$$

where

$$B = \exp \left\{ - \left(\frac{\mu_{CA}^{(st)} - \mu_C^{(st)} - \mu_A^{(st)}}{kT} \right) \right\}. \quad (8)$$

* In deriving formula (5) it was assumed, and will be assumed in all that follows, that the potential drop in the diffuse layer is negligible owing to the great difference in the dielectric constants of the bulk phase and the Helmholtz layer.

Let us assume now that the ion pair CA takes part in an irreversible electrode reaction with slow charge transfer. The following expression can be written for the rate of such a reaction:

$$v = A\Gamma \exp \left\{ -\frac{\beta \Delta \mu_{CA}^{(e)}}{kT} \right\}, \quad (9)$$

where A is a coefficient independent of the electrode potential φ_0 and the electric parameters of the Helmholtz layer; $\Delta \mu_{CA}^{(e)}$ is the change in the electrostatic part of the chemical potential of the ion pair as a result of the reaction and β is a numerical coefficient ($0 \leq \beta \leq 1$):

If only one of the ions making up the ion pair, for example the anion A, were to take part in the electrode reaction, the expression for the reaction rate would be of the form

$$v = A\Gamma_A \exp \left(-\frac{\beta \Delta \mu_A^{(e)}}{kT} \right). \quad (10)$$

Here, $\Delta \mu_A^{(e)}$ is the change in the electrochemical potential of the adsorbed anion as a result of the reaction. For the case where two parallel layers of specifically adsorbed oppositely charged ions are present in the Helmholtz layer, $\mu_A^{(e)}$ can be calculated if the distribution of local electrostatic potential in the Helmholtz layer is known. This distribution has been found in [8]. On the basis of the results obtained in this work, we can write an expression for $\mu_A^{(e)}$ in explicit form:

$$\begin{aligned} \mu_A^{(e)} = & -ez\varphi_0 \left(1 - \frac{x_2}{\delta} \right) + \frac{e^2 z^2}{4\epsilon\delta} \int_0^1 \frac{dt}{1-t} \{ 2 - t - x_2/\delta - t^{x_2/\delta-1} \} + \\ & + \frac{16e^2 z^2 \Gamma_A^2 \delta^3}{\pi^2 \epsilon} \sum_{k=1}^{\infty} \frac{1}{k^4} \sin^2 \left(\frac{k\pi x_2}{\delta} \right) \left\{ 2 - \frac{k^2 \pi}{\delta^2 \Gamma_C} K_2 \left(\frac{k}{\delta} \sqrt{\frac{\pi}{\Gamma_C}} \right) \right\} - \\ & - \frac{8e^2 z^2 \Gamma_A^2}{\pi^2 \epsilon} \sum_{k=1}^{\infty} \frac{1}{k} \sin \frac{k\pi x_1}{\delta} \sin \frac{k\pi x_2}{\delta} K_1 \left(\frac{k}{\delta} \sqrt{\frac{\pi}{\Gamma_A}} \right), \end{aligned} \quad (11)$$

where K_1 is a McDonald function of the first order.

The quantities Γ_A and Γ_C entering into expression (11) can be calculated from joint adsorption isotherms, which are described by the following system of equations [9]:

$$B_{Ac} = \frac{\Gamma_A}{\Gamma_{A\infty} - \Gamma_A} \exp \left(\frac{\mu_A^{(e)}}{kT} \right), \quad (12)$$

$$B_{Cc} = \frac{\Gamma_C}{\Gamma_{C\infty} - \Gamma_C} \exp \left(\frac{\mu_C^{(e)}}{kT} \right), \quad (13)$$

$$B_A = \frac{1}{c_0} \exp \left\{ -\frac{(\mu_A^{(ad)})_{st} - \mu_A^{(st)}}{kT} \right\}, \quad (14)$$

$$B_C = \frac{1}{c_0} \exp \left\{ -\frac{(\mu_C^{(ad)})_{st} - \mu_C^{(st)}}{kT} \right\}, \quad (15)$$

where $(\mu_A^{(ad)})_{st}$ and $(\mu_C^{(ad)})_{st}$ are the standard chemical potentials of the ions in the adsorbed state. An expression for the electric component of the electrochemical potential $\mu_C^{(e)}$ can be obtained from Eq. (11) by replacing x_2 by x_1 and Γ_A by Γ_C .

It would be of interest to compare the values of $\Delta \mu_{CA}^{(e)}$ and $\Delta \mu_A^{(e)}$ for the case of some simple reaction in order to estimate the effect of ionic association on the rate of electrochemical processes taking place in the adsorbed state. We have examined the one-electron irreversible electrochemical reduction of doubly charged anions, which proceeds according to the scheme

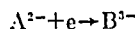


TABLE 1. Changes in the Electrostatic Part of the Chemical Potential of Doubly Charged Anions $\Delta\mu_A^{(e)}$ and Neutral Ion Pairs $\Delta\mu_{CA}^{(e)}$ in an Elementary Act of One-Electron Transfer

Parameters	e, V				
	0.0	0.4	0.6	0.8	1.0
$\Delta\mu_A^{(e)} \cdot 10^{12}$ erg	-0.22	-0.01	0.08	0.19	0.28
$\Delta\mu_{CA}^{(e)} \cdot 10^{12}$ erg	-0.53	-0.32	-0.19	-0.11	0.01

on the assumption that specifically adsorbed K^{2+} cations are present in the Helmholtz layer as well as the adsorbed A^{2-} anions. We used the following values for the parameters of the Helmholtz layer in the calculations: $\delta = 6 \text{ \AA}$, $x_2 = 2x_1 = 4 \text{ \AA}$, $\epsilon = 8$. Since the ion pair acquires a negative charge of $-e$ at the end of the electrochemical reaction, it can be shown that $\Delta\mu_{CA}^{(e)}$ and $\Delta\mu_A^{(e)}$ are interconnected by the relation

$$\Delta\mu_{CA}^{(e)} = \Delta\mu_A^{(e)} - \mu_{CA}^{(e)} \quad (16)$$

In calculating the adsorption isotherm on the basis of Eq. (7), we assumed that $B = 3.2 \cdot 10^7$, $c_0 = 56$ mole/liter, $c = 10^{-2}$ mole/liter, and $\Gamma_\infty = 10^{14}$ particles/cm². The results of the calculations are given in Table 1 for several values of the potential of the cathodically polarized electrode (the potential is reckoned from the electrocapillary maximum in a solution of unadsorbed electrolyte).

As can be seen from Table 1, the association of specifically adsorbed ions may substantially accelerate electron transfer at a metal solution interface. This conclusion is in qualitative agreement with the results of an analysis performed in [4]. However, in the presence of significant potential jumps generated by ion pairs (these jumps were not taken into account in [4]), the degree to which electron transfer is accelerated may be considerably higher than in cases where the dipole moments of the ion pairs are parallel to the electrode surface.

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