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POTENTIAL DISTRIBUTION ACROSS THE ELECTROACTIVE-POLYMER FILM BETWEEN THE METAL AND SOLUTION AS A FUNCTION OF THE FILM CHARGING LEVEL

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Abstract—The distribution of the electrostatic potential across the electroactive-polymer film between the metal electrode and the solution has been analysed theoretically at various charging levels. The content of the film is determined by the electronic equilibrium with the metal and the exchange by co- and counterions with the solution. The electronic and ionic concentrations inside the film are assumed to be well below their saturation values. Two limiting shapes of the potential profile have been found, with a plateau region inside the film separating two space-charge layers near the interfaces, and with the potential drop distributed within the whole film, like that in an insulating film. In its turn, profiles with the bulk-film region have been separated into three different types, referred to as the "membrane", "electron-counterion" and "semiconductor" forms. Depending on the electronic and ionic parameters of the system, the profile may show various scenarios of evolution among these states upon sweeping the electrode polarization. Available ways to distinguish between these variants are discussed. Copyright © 1996 Elsevier Science Ltd

Key words: electroactive-polymer film, electron conducting polymers, potential profile, interfacial potential drops, ion exchange with the solution.

INTRODUCTION

Electroactive-polymer coated electrodes (including electron conducting and redox polymers as well as related systems) are considered as prospective materials for numerous applications based on their ability to be charged and discharged repeatedly in a quasi-reversible manner as well as on modification of electrochemical reactions of species from the solution. However, those prospectives are hindered due to the high complexity of processes in such films[1, 2].

During the initial period of these studies the attention was mostly paid to the electronic exchange between the film and the electrode changing the charging level of the film which was characterized in a close analogy to redox reactions of solute species at the bare metal surface. In particular, it was assumed implicitly that the variation of the electrode potential resulted mostly in the polarization of only one interface, between the metal and the film, while the potential drop at the polymer/solution boundary was considered to be constant[3]. Potential applications based on the exchange with the solution by ions and neutral species initiated later a more thorough investigation of this process which has revealed

* Author to whom correspondence should be addressed. † Present address: Dept Applied Physics, Fukui University, 9-1, Bunkyo 3-chome, Fukui-shi, 910 Japan. a complex picture of participation of both counterand co-ions as well as solvent molecules. See[2, 4, 5] for a review.

A theoretical analysis of the both interfacial potential drops varying as functions of the overall polarization has been carried out in Ref.[6]. It demonstrated that a traditional hypothesis on the dominant compensation of the varying electronic charge in the film by counter-ions (i.e. with no co-ion contribution) must be accompanied by a strong change of the film/solution potential drop modifying considerably the quasi-equilibrium film properties, such as charging curves, kinetics of redox reactions of solute species at the film surface, etc.

That approach[6] treated the film-coated electrode as a three-phase system, with the electronic equilibrium between the film and the metal as well as with the ion exchange between the film and the solution. One can expect it is justified for sufficiently thick films where the electric double layers at both interfaces of the film are much thinner than its thickness. This approximation can be violated for thin films, especially at low charging levels.

In this case the electrostatic-potential profile must be found for the whole system, metal/film/solution, without splitting it into separate bulk and interfacial regions. Such an analysis based on numerical calculations is carried out in this paper. It has enabled us to make conclusions on the qualitative features of the profile, at various charging levels of the film, depending on the electronic and ionic parameters of the film. We find the shape of the potential profile inside the film, the conditions of applicability of the previous three-phase model, the relation between the two interfacial potential drops and the overall polarization, and the relation between the potential drop inside the solution and the overall film/solution interfacial potential (an important quantity in redox kinetics at such boundaries).

It has been demonstrated below that one can expect at least three different types of the profile evolution with variation of the charging level in (quasi)-equilibrium conditions. Then, some ways of distinguishing between them are discussed, based on available, or possible experimental techniques.

MODEL

It is assumed that the film is in the equilibrium with respect to electronic exchange with the metal electrode, and to exchange of single-charged cations and anions with the solution. The transfer of an electron from the metal into the film (or an ion from the solution into the film) is accompanied by the change of its standard chemical potential from $\mu_e^{0(m)}$ to $\mu_e^{0(f)}$ (from $\mu_{k,a}^{0(s)}$ to $\mu_{k,a}^{0(f)}$ for cations or anions, correspondingly).

The shape of the potential distribution depends on these electronic and ionic parameters of the film as well as of its dielectric properties (characterized below by the film dielectric constant, ε^{f}) which are considered as identical for each point inside this medium. To minimize the number of parameters, the simplest model is considered below corresponding to sufficiently low levels of film charging. Then, one may disregard effects of the electronic-energy dispersion[7, 8], short-range interactions between the charged species inside the film[9], or between a species and the interfacial boundary (image forces), as well as the electron or ion concentration saturation[6, 9].

The film is treated as a thin plane uniform layer of thickness L, so that all characteristics (electrostatic potential, ϕ , and concentrations, $c_{e,k,a}$) depend on only one spatial coordinate, x, normal to the both interfacial boundaries.

We make approximations for the film region in analogy with the Gouy-Chapman theory for an electrolyte solution, taking into account all three forms of mobile species, e, k and a:

$$\frac{\varepsilon^{f} d^{2} \phi(x)}{dx^{2}} = -4\pi\rho(x),$$

$$\rho(x) = F[c_{e}(x) + c_{k}(x) - c_{a}(x)]$$
for 0 < x < L,
(1)
$$(x) = c^{0} \exp\left(\left(\frac{F}{c_{e}}\right)[\phi^{m} - \phi(x)] + \frac{\Delta\mu_{e}^{0(mf)}}{c_{e}}\right)$$

$$c_{e}(x) = c_{e}^{0} \exp\left(\left(\frac{T}{RT}\right) \left[\phi^{m} - \phi(x)\right] + \frac{\Delta\mu_{e}}{RT}\right)$$
$$\Delta\mu_{e}^{0(mf)} = \mu_{e}^{0(m)} - \mu_{e}^{0(f)}, \qquad (2)$$

$$c_{s,k}(x) = c^{s} \exp\left(\pm \frac{F}{RT} \phi(x) - \frac{\Delta \mu_{a,k}^{O(fs)}}{RT}\right)$$
$$\Delta \mu_{a,k}^{O(fs)} = \mu_{a,k}^{O(f)} - \mu_{a,k}^{O(s)}, \tag{3}$$

To simplify the formulae, all varying characteristics inside the film are denoted here without an upper index, f. The electronic species are positively single charged, as usual for most electron-conducting polymers[1, 2]. The Boltzmann formulae for ions, equation (3), contains the bulk-electrolyte ionic concentration, c^s , and the bulk-solution potential value is taken as the reference point. Its analogue for the electronic species, equation (2), refers the potential inside the film, ϕ , to that of the metal, ϕ^m , while c^0_{e} , is taken as standard for the electronic concentration in this medium.

Equation (1) represents the electrostatic Poisson equation and includes all contributions to the local charge density, $\rho(x)$. It replaces the local electroneutrality condition which is only applicable in the bulk film, beyond the double-layer regions at the interfaces. The treatment of this paper enables one to consider in a unified manner both sufficiently thick films where the usual three-phase approach does hold, and a more complicated case of overlapping space-charge regions.

Equations (2) and (3) can be derived from the equilibrium conditions for the interfacial exchange of the corresponding species, e, k, or a, for the low-concentration case[9].

Differential equations (1)-(3) are supplemented by the continuity condition for the potential at both interfaces,

$$\phi(\mathbf{x}) = \phi^{s}$$
 at the film/solution boundary, $\mathbf{x} = 0$ (4)

 $\phi(\mathbf{x}) = \phi^{\mathsf{m}}$ at the film/metal boundary, $\mathbf{x} = L$ (5)

 ϕ^{s} being the potential drop inside the solution, ϕ^{m} , potential of the metal with respect to the bulk solution.

An additional boundary condition at the film/ solution interface follows from the continuity of the electric displacement combined with the Gouy-Chapman relation for the electric-field strength at any point inside the solution:

$$\frac{d\phi(x)}{dx} = (\varepsilon/\varepsilon^{f}) (32\pi RT c^{s}/\varepsilon)^{1/2} \sinh F \phi^{s}/2RT$$

at the film/solution boundary, $x = 0$ (6)

Equations (1)-(6) contain numerous parameters of the system. However, the potential profile depends in reality only on a few of their combinations. To show it one can use dimensionless variables:

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$$\psi(s) = \frac{F\phi(x)}{RT}, \quad \psi^{s} = \frac{F\phi^{s}}{RT}, \quad \psi^{m} = \frac{F\phi^{m}}{RT}$$
(7)
$$s = \left(\frac{x}{L_{D}^{s}}\right) \left(\frac{\varepsilon}{\varepsilon^{t}}\right),$$

$$s^{max} = \left(\frac{L}{L_{D}^{s}}\right) \left(\frac{\varepsilon}{\varepsilon^{t}}\right),$$

$$L_{D}^{s} = \left(\frac{\varepsilon RT}{8\pi F^{2}c^{p}}\right)^{1/2},$$
(8)

ie all potentials are divided by $RT/F \approx 25 \text{ mV}$ while the coordinate and the film thickness are related to the Debye screening length in the solution, $(\epsilon RT/F)$ $8\pi F^2 c^{s}$)^{1/2}, combined with the ratio of the dielectric constants of the solution and the film, $\varepsilon/\varepsilon^f$. It should be noted that an analogous quantity, the screening length in the bulk film, depends strongly on the charging level and will be discussed below.

The set of differential equation and boundary conditions for the dimensionless potential $\psi(s)$ is

$$\frac{d^2\psi(s)}{ds^2} = (1/2)(N_a \exp[\psi(s)] - (N_k + N_e \exp\psi^m) \exp[-\psi(s)]) \quad (9)$$

$$\psi(s) = \psi^s \quad \text{at } s = 0 \tag{10}$$

$$\frac{\mathrm{d}\psi(s)}{\mathrm{d}s} = 2\,\sin(\psi^s/2) \quad \text{at } s = 0 \tag{11}$$

$$\psi(s) = \psi^{\mathsf{m}} \quad \text{at } s = s^{\mathsf{max}}$$
 (12)

It depends on the metal/solution potential drop, $\psi^{\rm m} = F \phi^{\rm m}/RT$, the film thickness, equation (8), and three combinations of parameters for each component of the system, proportional to the corresponding partition constants:

$$N_{e} = \left(\frac{\varepsilon^{f}}{\varepsilon}\right) \left(\frac{c_{e}^{0}}{c^{s}}\right) \exp\left(\frac{\Delta\mu_{e}^{0(mf)}}{RT}\right)$$
$$N_{a,k} = \left(\frac{\varepsilon^{f}}{\varepsilon}\right) \exp\left(\frac{-\Delta\mu_{a,k}^{0(fs)}}{RT}\right)$$
(13)

The potential drop inside the solution, ψ^s , is determined by solving these equations.

The ratios of local concentrations inside the film are expressed via these constants as well as the local potential value:

$$\frac{c_{a}}{c_{k}} = \left(\frac{N_{a}}{N_{k}}\right) \exp 2\psi(s), \quad \frac{c_{e}}{c_{k}} = \left(\frac{N_{e}}{N_{k}}\right) \exp \psi^{m} \quad (14)$$

RESULTS AND DISCUSSION

Analytical reasoning

A convenient starting point is the case of a sufficiently thick film where the electric fields of the charges inside the metal and the solution near the film surfaces are screened within two space-charge regions within the film well separated by the bulkfilm region. Then, the potential varies in the doublelayer regions while possessing a plateau in between. The local characteristics within this plateau may be found with the use of a thermodynamical consideration of the electronic and ionic equilibria with the media in contact[9], or immediately from equation (9) from the condition of the zero value of the derivative:

$$\psi^{f} = \left(\frac{1}{2}\right) \ln\left[\frac{(N_{k} + N_{e} \exp\psi^{m})}{N_{a}}\right]$$
(15)

$$c_{\mathbf{a}}^{\mathbf{f}} = c^{\mathbf{s}} \left(\frac{\varepsilon}{\varepsilon^{\mathbf{f}}} \right) [N_{\mathbf{a}}(N_{\mathbf{k}} + N_{\mathbf{e}} \exp \psi^{\mathbf{m}})]^{1/2}$$
(16)

$$\frac{c_{\mathbf{a}}^{\mathbf{f}}}{c_{\mathbf{k}}^{\mathbf{f}}} = 1 + \left(\frac{N_{\mathbf{e}}}{N_{\mathbf{k}}}\right) \exp\psi^{\mathbf{m}} \tag{17}$$

Equations (15) and (16) give expressions for the bulk-film potential $\psi^{\rm f}$ and anion concentration $c_{\rm a}^{\rm f}$. Then, cation $(c_{\rm k}^{\rm f})$ and electron $(c_{\rm e}^{\rm f})$ concentrations can be found with the use of equations (17) and (14), or the electroneutrality condition, $c_{\rm e}^{\rm f} = c_{\rm a}^{\rm f} - c_{\rm k}^{\rm f}$.

In a completely discharged state corresponding to high negative potential of the metal, these relations are reduced to the Donnan formulae:

$$\psi^{\rm f} = (1/2) \ln\left(\frac{N_{\rm k}}{N_{\rm a}}\right) = \frac{\Delta\mu_{\rm a}^{\rm O(fs)} - \Delta\mu_{\rm k}^{\rm O(fs)}}{2RT} \qquad (18)$$
$$c^{\rm f} = c_{\rm s}^{\rm f} = c_{\rm s}^{\rm f}.$$

$$c_{\mathbf{a}} = c_{\mathbf{k}} = c^{s},$$

$$c_{\mathbf{k}} = c^{s} \left(\frac{\varepsilon}{\varepsilon^{f}}\right) (N_{\mathbf{a}} N_{\mathbf{k}})^{1/2} = c^{s} \exp\left[\frac{-(\Delta \mu_{\mathbf{a}}^{0(\mathbf{f}s)} + \Delta \mu_{\mathbf{k}}^{0(\mathbf{f}s)})}{2RT}\right]$$
(19)

Then, all concentrations at a non-zero electronic charge can be expressed through the ionic concentration inside the film in the reduced state c*, eg,

$$c_{\rm a}^{\rm f} = c \ast \left[1 + \left(\frac{N_{\rm e}}{N_{\rm k}} \right) \exp \psi^{\rm m} \right]^{1/2}$$
(20)

Such a plateau in the potential profile inside the film exists at any non-zero values of the partition constants for the charge carriers, N_a as well as N_e and/or N_k , if the film is sufficiently thick. For a certain thickness L the bulk-film region should appear if L is much greater than the screening length within this plateau, L_d^f .

$$L \gg L_{\rm d}^{\rm f}, \quad L_{\rm D}^{\rm f} = \left(\frac{\varepsilon^{\rm f} RT}{8\pi F^2 c_{\rm a}^{\rm f}}\right)^{1/2}$$
 (21)

The film screening length depends on the metal potential via the anion concentration, equations (20) or (16). The ratio of the film and solution screening lengths can be written as

$$\frac{L_{\rm D}^{\rm f}}{L_{\rm D}^{\rm s}} = \left(\frac{\varepsilon^{\rm f}}{\varepsilon}\right) [N_{\rm a}(N_{\rm k} + N_{\rm e} \exp \psi^{\rm m})]^{-1/4} \qquad (22)$$

Then the criterion of the plateau existence inside the film, condition (21), can be rewritten for the dimensionless thickness of the film, s^{max} , equation (8):

$$s^{\max} \ge [N_{a}(N_{k} + N_{e} \exp \psi^{m})]^{-1/4}$$
 (23)

In the opposite limiting case of a sufficiently thin film,

$$L \ll L_d^{\mathrm{f}}, \quad ie \ s^{\mathrm{max}} \ll [N_{\mathrm{a}}(N_{\mathrm{k}} + N_{\mathrm{e}} \exp \psi^{\mathrm{m}})]^{-1/4}$$
(24)

the usual three-phase description does not hold any more, and the overall potential drop is distributed within the whole extension of the film.

Another relation determining the shape of the potential profile compares the electronic and co-ion concentrations inside the film. According to equation (13) their ratio is constant throughout the film at any polarization being only dependent on the metal potential and the parameters of the species, N_e and N_k . The electronic concentration in the reduced state is known to be very low[1, 3]. Therefore, the further analysis of this paper will be restricted to the case where the ionic species are dominant in that

potential range compared to the electronic ones. A shift of the electrode potential to the anodic direction leads to an exponential increase of the electronic contribution, and two limiting cases should be expected: 1) co-ion concentration is much greater than the electronic one within the whole polarization interval, which means inequality (25),

$$N_k \gg N_e \exp \psi^m$$
 (25)

to be retained up to the maximum metal potential, $\psi^{m} = \psi^{max}$, or, 2) an opposite inequality is valid at sufficiently high anodic potentials,

$$N_{\mathbf{k}} \ll N_{\mathbf{e}} \exp \psi^{\mathbf{m}}$$
 (26)

ie a gradual transition from the anion-cation system to the electron-counterion one must occur at intermediate potentials.

Thus, one can expect several qualitatively different states of the system depending mostly on its electronic and ionic parameters, as well as on the polarization range.

Numerical analysis

Equation (9) has been integrated numerically for various values of the metal potential, adjusted to the boundary conditions (10)–(12), while keeping other parameters, $N_{a,k,e}$ and s^{max} constant. In practice, some test value was chosen for the potential at the film/solution interface ψ^s , equations (10) and (11), as a starting point at s = 0 to integrate up to the metal surface. Then, this value was corrected to approach the given metal potential ψ^m , this procedure being repeated to self-consistency.

This paper demonstrates some results for relatively thin films, $s^{max} = 10$. It should be noted that in view of definition (8) this means

$$L = 10L_{\rm D}^{\rm s} \varepsilon^{\rm f} / \varepsilon \tag{27}$$

ie the corresponding thickness, L, is determined by both the bulk-solution screening length, L_d^s , and the ratio of the dielectric constants, L being 10 nm for a 0.1 M aqueous solution if the dielectric constants are identical.

The metal potential was varied in the same interval, from $-90 \,\mathrm{mV}$ to $90 \,\mathrm{mV}$, since its variation in another interval may practically be simulated by the corresponding change of the partition constants, $N_{\mathrm{e,k,a}}$. The values of these partition constants are pointed in the legends of the figures.

"Membrane" system

At the zero value of the electronic parameter, $N_e = 0$, both ionic components are present inside the film in equal amounts at any electrode potential so that the model corresponds to a thin layer of an ion-exchange membrane (without fixed charges) at the metal surface. If the bulk-film ionic concentration c_* , equation (19), is not especially low so that condition (21) [ie (23)] is fulfilled, the metal field is screened within a space-charge region near the metal/film interface while another interface, with the solution, remains unpolarized. Figure 1 illustrates potential profiles for such a system.

In the case of equal resolvation energies for cations and anions, ie $\Delta \mu_a^{O(fs)} = \Delta \mu_k^{O(fs)}$ in equation



Fig. 1. Profiles of the potential $\phi(s)$ across the polymer film located between the metal electrode and the solution. "Membrane" state of the film at all metal polarizations: dominance of ionic species in the polymer phase within the whole range of oxidation levels. Comparison of a purely ionic system with that containing a low electronic concentration: $N_e = 0$ (a); 0.01 (b). For high negative potentials curves a and b are coincident (1', 2', 3'). Metal/solution potential drop: $\phi_m = -90 \text{ mV}$ (1', 2', 3'). Metal/solution potential drop: $\phi_m = -90 \text{ mV}$ (1', 2', 3'), $\phi_m = 90 \text{ mV}$ (1, 2, 3). No Donnan potential drop for the reduced state, $N_k =$ $N_a = 1$ (1', 1a, 1b), negative Donnan potential due to ions, $N_k = 0.1$, $N_a = 1$ (2', 2a, 2b), positive Donnan potential due to ions, $N_k = 1$, $N_a = 0.1$ (3', 3a, 3b).

(3), both ionic parameters in equation (13) are identical $(N_a = N_k)$. As expected, variation of the electrode polarization leads merely to double-layer formation at the metal/film interface while the bulk-film potential ψ^{f} remains unchanged, being zero according to equation (18) (lines 1' and 1a).

The addition of a low concentration of electronic species [satisfying the condition (25)] results in a minor shift of the plateau value inside the film at the most positive potentials (line 2b) while curve 2' for negative potentials is not affected at all.

A difference of the resolvation energies for anions and cations (which means $N_a \neq N_k$) leads to a nonzero potential at the bulk-film plateau; see equation (18), due to the Donnan effect but this potential drop at the film/solution interface is constant (at $N_e = 0$), or almost constant (at small values of N_e), upon variation of the electrode polarization being determined by the ionic equilibrium with the solution (lines 2', 2a, 2b, or 3', 3a, 3b).

Electron-counterion system

Let the ionic concentration in the reduced state again be high enough [condition (21) or (23)] to realize the metal-field screening at the interface. Then, the profiles at high negative potentials are practically identical to those for the membrane system with the same values of the ionic partition constants (compare line 1 in Fig. 2a and line 1' in Fig. 1). However, a greater value of the electronic parameter [satisfying condition (26)] results in a crucial modification of the potential profile at a more positive polarization, relative to the "membrane" case; compare Figs 2a and 1.



The potential distribution possesses again a plateau region inside the film but its plateau value is changed considerably by variation of the electrode potential, *ie* both interfaces are essentially polarizable (lines 2, 3, 4 in Fig. 2a).

Within the range of the metal potentials satisfying condition (26) the electronic concentration inside the film is much greater than the co-ion one so that the system should be referred to as an "electroncounterion" one. Equation (15) shows that the variation of both interfacial potential drops represents about one half of the overall polarization[6].

A similar transition from the membrane type of profile to the electron-counterion one, in accordance with inequalities (25) and (26), is observed at nonequal values of the ionic resolvation energies (Fig. 2b, c) although the shape of the potential profile can be more complicated since the above change of profile type is combined with the Donnan effect.

Figure 3 illustrates again the above tendencies as a function of the electronic parameter, N_e , at two fixed values of the metal potential. There is no effect of the electronic properties in the profile at high negative potentials where the system contains mostly ionic components. On the other hand there is a gradual transition between the membrane and electron-counterion types of profile at high positive potentials. The plateau value of the potential is strongly dependent on the electronic parameter, N_e in the latter case; see equation (15).

"Insulating" system

At sufficiently low values of the ionic partition constants satisfying condition (24) the concentrations of all mobile charge species at high negative potentials are too low to produce electronic-field screening inside the film. As a result, the metal/solution potential drop is distributed within the whole layer, with no tendency to form a plateau inside it. For a system



Fig. 2. Transformation of the potential distribution from the membrane type into the "electron-counterion" one on sweeping the polarization in the positive direction, $\phi_m = -90 \text{ mV}$ (1); -30 mV (2); 30 mV (3); 90 mV (4); (a) equal resolvation energies of cations and anions in the film ($N_k = N_s = 1$), $N_c = 1$; (b) different values of the ionic resolvation energies, $N_k = 0.1$, $N_s = 1$, $N_c = 0.1$; (c) see Fig. 2b, $N_k = 1$, $N_a = 0.1$, $N_c = 0.1$.

Fig. 3. Transformation of the potential distribution from the membrane type into the "electron-counterion" one at changing the electronic parameter, N_e , due to the change of the standard electronic potential of the polymer phase, or the bulk electrolyte concentration c^s , $N_e = 0$ (a); 0.01 (b); 0.1 (c); 1 (d). There is no marked effect of the electronic charge at negative polarizations (1) and a strong shift of the plateau value at positive ones (2a, b, c, d). $N_k = N_a = 1$.



Fig. 4. Potential profiles at low ionic partition constants $(N_k = 0.01, N_a = 0.01)$ for various metal potentials: $\phi_m = -90 \text{ mV} (1)$; -30 mV (2); 30 mV (3); 90 mV (4): (a) purely "insulating" system, $N_e = 0$; (b) transformation from the "insulating" type into the "semiconductor" one (the region of the "electron-counterion" behaviour corresponds to even more positive potentials), $N_e = 1$.



Fig. 5. Potential profiles at intermediate values of the partition constants, $N_k = 0.1$, $N_a = 0.1$, $N_e = 0.1$. $\phi_m = -90 \text{ mV} (1)$; -30 mV (2); 30 mV (3); 90 mV (4).

without electrons (Fig. 4a), similar linear profiles of the potential are observed for the whole potential range, except for the most negative or positive metal charges where non-linear effects lead to a decrease of the screening length inside the film compared to its value at *pzc*, L_d^f , defined by equation (21). Thus, the potential profile of such a system is identical to that of a metal electrode coated with an insulating film.

At small values of the electronic parameter N_e , such a shape of the profile is retained. However, the electronic concentration in typical conducting polymers at high charging levels reaches several mol/[3, 5]. This means that at sufficiently large values of N_e screening of the field occurs inside the film. Then sweeping the electrode potential in the positive direction results in a gradual transformation of the profile from the insulating type to the electron-counterion one (Fig. 4b).

"Semiconductor" system

Figures 2 and 4b demonstrate that the profile is modified to the electron-counterion type at sufficiently high positive potentials independent of whether it corresponds to the membrane or insulating type. However, in the latter case one can notice an intermediate regime where the profile possesses a plateau inside the film (determined also by electrons and anions) but most of the film/solution interfacial potential drop is localized inside the film while the interfacial potential, ψ^{s} , in equation (10) is rather small (Fig. 4b). Since such profiles appear at the interface between the solution and an inorganic semiconductor such a behaviour is related below to this system although their other properties are quite different (another interfacial boundary, two kinds of mobile charge carriers inside the film etc.).

At intermediate values of the ionic and electronic parameters one can see curves at negative potentials combining a double-layer region inside the film near the metal surface with a uniform-field region closer to the solution surface (Fig. 5). At high anodic potentials the profile is getting again typical features of the electron-counterion system.

CONCLUSIONS

The above analytical and numerical analysis has demonstrated the existence of several typical profiles of the potential across the film, the system being able to change the type of the profile upon varition of the electrode polarization. These conclusions are summarized in Fig. 6 presenting various possible variants of the potential distribution evolution depending on the ionic and electronic parameters (partition constants for the corresponding interfacial equilibria, $N_{a.k.e}$).

The profile in the reduced state depends mostly on the product of the ionic partition constants, $N_k N_a$, corresponding to the "membrane" type at sufficiently large values, or to the "insulating" one in the opposite limiting case. Upon increasing the charging level of the film, the profile retains "membrane" features, or transforms into the "electron-counterion" type, possibly via an intermediate "semiconductor" case.



ionic partition constants' product, Nk Na

Fig. 6. Schematic diagram of various types of the potential profile depending on the ionic screening properties in the reduced state and the electronic charge. Numbers at the arrows point to the corresponding figure.

One should keep in mind that this terminology is rather conventional and must not be considered in a straightforward manner. It only reflects some characteristic features of the equilibrium potential distribution and may be misleading if considering other properties of the system. For example, the term "insulating type" means no, or weak metal-field screening inside the film, and is not related immediately to the conductivity characteristics of the film. Analogously, one must be careful if using the term "semiconductor type" since the film contains both counterions and electronic species so that its interface with the metal is polarizable, unlike the metal/ inorganic semiconductor one. We have avoided calling the "electron-counterion" state of the film a "metallic" one since such terminology seems to be especially dangerous, eg in interpretation of the redox-reaction data[4, 5].

The potential distribution across the film cannot be measured directly at the moment (although one can imagine experimental studies of the electronic, or ionic, concentration profiles inside the layer, eg by means of an optical or scattering technique). However, one could distinguish between the various states of the system with the use of theoretical predictions for measurable characteristics.

As yet, most attention has been paid to such an analysis for the "membrane" and "electroncounterion" types for sufficiently high charging levels[6]. The most straightforward way is to compare the electronic and co-ion contents of the film. Available data[10-12] correspond mostly to the maximum charge of the film and testify in favour of the practical absence of co-ions at equilibrium conditions. The above two states are characterized also by different charging curves, electronic charge vs electrode potential. In particular, at relatively low charging degrees the expected slopes in semilogarithmic coordinates for these two states differ by a factor of 2, thus providing an easily verifiable condition if such curves are measured in really equilibrium conditions. Again, such data are in accordance with the "electron-counterion" state of the system[6].

Numerous studies have been devoted to kinetics of redox reactions of solute species which occur at the film/solution boundary. The "membrane" theory predicts no variation of this interfacial potential drop so that the reaction rate is affected solely by the concentration of electronic species inside the film which is known from independent measurements. Oppositely, in the "electron-counterion" case one can expect effects of both the electron charge and the varying potential drop at the interface. Therefore, a Tafel-like behaviour should be observed, both in the cathodic and anodic directions, similar to reactions at the bare metal electrode though with a more complicated expression for the transfer coefficient. Kinetic data for redox reactions taking place within the range of sufficiently high film charges have again been in conformity with the latter case[13, 14]. The reactions having an equilibrium potential within the interval where the film is reduced have demonstrated a considerable shift into the potential range of film charging[15]. Finally, reactions with a formal potential in the intermediate range have shown some features similar to those at an inorganic semiconductor electrode, eg the "kinetic limiting current"[15].

Another way to make a choice between the "membrane" and "insulating" states at very low charging degrees may probably be made on the basis of capacitance measurements in the corresponding polarization interval.

It should be kept in mind that all these results are obtained within the framework of a thermodynamic consideration and are immediately applicable for interpretation of quasi-equilibrium phenomena only. This condition is obviously violated in the course of cyclic-voltammetry measurements leading to considerable incorporation of co-ions inside the film[16–18] due to kinetic restrictions on the counter-ion removal from the film during the discharging process[7, 8].

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