

Excess nonspecific Coulomb ion adsorption at the metal electrode/electrolyte solution interface: Role of the surface layer

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Excess ion adsorption Γ induced by the polarization image forces in the system of a metal electrode/symmetric electrolyte solution separated by an insulating interlayer has been calculated. The adopted theoretical scheme involves the Coulomb Green's function in a three-layer system with sharp interfaces and specular reflection at them. The influence of the spatial dispersion of the dielectric permittivities $\varepsilon_i(\mathbf{k})$ in all the three media on the image force energy W_{im} and the adsorption Γ has been analyzed, where \mathbf{k} is the wave vector. A comparison with the classical model, where $\varepsilon_i = \text{const}$, has been carried out. It has been shown that both the Debye-Hückel ion screening and the spatial dispersion of the solvent contribution $\varepsilon_{\text{sol}}(\mathbf{k})$ to the overall dielectric function $\varepsilon_{\text{el}}(\mathbf{k})$ of the electrolyte solution lead to the qualitative difference with the results for the classical model. In particular, in a wide range of ion concentrations n_0 a thin interlayer $L \geq 5-10 \text{ \AA}$ effectively screens out the attractive influence of the metallic electrode, so that the net Coulomb adsorption may become repulsive. The approach and the results obtained qualitatively describe two physically different situations. Specifically, the introduced interlayer corresponds either to the dense near-electrode (inner) electrolyte layer or to the intentionally deposited control coating of arbitrary thickness.

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I. INTRODUCTION

The influence of image-force energies at the interfaces between two plasmalike media, such as metals and electrolyte solutions, has been the subject of widespread investigations for rather a long period [1], although the role of polarization phenomena is sometimes underestimated [2]. One should keep in mind that even the well-known simplest, quoted in textbooks, classical expression for this kind of electrostatic energy, which describes the case of constant dielectric permittivities ε_i 's on either side of the common interface, hides its complicated quantum-mechanical background [3,4]. When the spatial dispersion of the dielectric permittivities $\varepsilon(\mathbf{k})$'s is accounted for, a further level of complexity arises [5,6]. Here \mathbf{k} is the wave vector. The variety of model $\varepsilon(\mathbf{k})$ dependences for solvents as hosts for embedded ions describe rich physics and chemistry both in the bulk of electrolyte solutions [7–18] and near their interfaces [19–25] with other plasmalike media.

All this diversity goes back to the Inkson basic interpolation formula

$$\varepsilon_I(\mathbf{k}) = \varepsilon_* + \frac{\varepsilon_0 - \varepsilon_*}{1 + \frac{\varepsilon_0}{\varepsilon_*} \Lambda^2 k^2}, \quad (1)$$

which was first developed for semiconductors [26] and takes into account the peculiarities of a test charge \bar{e} screening by their bound electrons. Here, ε_0 is the macroscopic (long-wavelength) static dielectric constant, ε_* the short-wavelength one, and Λ the correlation length of bound electrons. In the solvent, the constitutive entities are solvent

molecules, but the character of screening is very similar to that by valence electrons in semiconductors. The parameter Λ has now the meaning of the solvent intermolecular correlation length.

At the same time, the dissolved ions give rise to the Debye-Hückel contribution

$$\varepsilon_{DH}(\mathbf{k}) = \frac{\varepsilon_0 \kappa^2}{k^2}, \quad (2)$$

where κ is the relevant inverse screening radius, so that the overall dielectric function becomes

$$\varepsilon(\mathbf{k}) = \varepsilon_I(\mathbf{k}) + \varepsilon_{DH}(\mathbf{k}). \quad (3)$$

Hereafter, for simplicity, we consider only a 1:1 electrolyte solution, so that κ equals $(8\pi n_0 e^2 / k_B T \varepsilon_0)^{1/2}$, n_0 is the bulk concentration of each kind of ions, e the elementary charge, T the absolute temperature, and k_B the Boltzmann constant.

The dielectric mismatch at the boundary between a metallic (or semiconducting) electrode and an electrolyte solution may result in the nonmonotonic spatial profile of the image-force energy W_{im} in the solution both when the latter is treated as a plasmalike Debye-Hückel medium [5,27,28] or described by Eq. (3) [20,29]. Moreover, such a behavior of the image forces leads to the nonmonotonic concentration dependence of the excess electrostatic nonspecific adsorption $\Gamma(n_0)$ and the corresponding excess surface tension $\Delta\sigma(n_0)$ at the point of zero charge [20,27–31]. At the vacuum/electrolyte solution interface, on the contrary, the respective concentration dependences $\Gamma(n_0)$ and $\Delta\sigma(n_0)$ are monotonic [32].

The results cited above were obtained using the abrupt interface model and assuming the specular quasiparticle reflection at the medium interfaces [33–35]. In actual truth, however, the metal electrons spill out over the positive back-

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