Effects of Solvent and Solute Interactions on Double Layer Properties and Electrode Kinetics

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Local Order and Hydrogen Bonding in a Molecular Model for Adsorbed Solvent, with and without Adsorption of a Neutral Polymer Species

ROLANDO GUIDELLI

Institute of Analytical Chemistry, Florence University, Florence, Italy

With few exceptions [1–4], orientational models for solvent adsorption do not include consideration of solute adsorption and hence can only be compared with experimental curves of the inner-layer differential capacity for the solvent under conditions in which solute adsorption is regarded as negligible. More generally, however, any consistent orientational model for solvent adsorption, once generalized through the inclusion of solute adsorption, should also be able to account for the adsorption behaviour of solute species. The implications of the 0th (random) approximation in the statistical mechanical treatment of an adsorbed monolayer consisting of 'up' and 'down' solvent molecules, with and without the further presence of the polymer molecules of a neutral solute adsorbed in a single orientation, are briefly examined.

The different size of solute and solvent particles is accounted for *via* Flory–Huggins statistics. Certain inconsistencies in previous work on the subject are thus evidenced. It is concluded that the role played by local order in affecting the inner-layer properties cannot be disregarded. The above model of adsorbed monolayer is therefore reexamined taking local order into account *via* the quasi-chemical approximation. It is thus shown that an increase in attractive lateral interactions between adsorbed solvent molecules causes the single hump in the curve of the inner-layer capacity *versus* the charge density on the metal to split into two distinct humps. This may explain the presence of two humps in the differential capacity curves of certain highly polar organic solvents [5, 6]. Moreover, it is shown that a Frumkin isotherm behaviour over a wide range of surface coverages is to be expected, provided that solvent–solvent lateral interactions are more attractive than solvent–surfactant and surfactant–surfactant lateral interactions. Noting that the adsorption of several bulky organic molecules from aqueous solutions actually satisfies the Frumkin isotherm, appreciable hydrogen bonding between adsorbed water molecules must be inferred.

To account for the effect of hydrogen bonding both on differential capacity curves and on the adsorption isotherms of neutral surfactants, a general statistical mechanical treatment of the adsorbed monolayer is developed, in which solvent molecules are allowed to be adsorbed in an unspecified number of orientations, certain contiguous pairs of these orientations giving rise to hydrogen bonds. Local order and difference in size between solvent and solute particles are both accounted for. On the basis of quite general considerations it is shown that the maximum in the entropy of the adsorbed monolayer occurs at the same charge density at which the surface potential $\Delta\chi$ is zero, independent of any detailed model of the adsorbed monolayer. This prediction agrees with the experimental behaviour of the mercury-water interphase in the absence of solute adsorption [7, 8].

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Specificity of Hydration of Individual Ions in Relation to their Adsorption at Electrodes

B. E. CONWAY

Chemistry Department, University of Ottawa, Ottawa, Ont., Canada

In the aqueous medium, H-bonding structural equilibria play a major role in the hydration of ions and in their adsorption behaviour at electrodes. Not only energy but entropy factors in adsorption are consequently important and lead to specificity in ion hydration interactions and ion adsorption.

Specificity of ion–water interactions is reflected in the way such properties as the partial molar entropies, heat capacities and compressibilities of ions in aqueous solutions depend on ionic radii. Also, ion specificity arises in such spectroscopic properties as the ^1H nmr chemical shift and the changes in overtone stretching and bending infrared band frequencies in water caused by the presence of ions. These properties, derived for individual ions, will be examined in relation to specificity of adsorption of ions at electrodes, especially Hg and Pt.

At the former metal, hydration effects in ion adsorption can be investigated in studies of the adsorption of alkylammonium ions in the series $R_n\overset{+}{N}_{4-n}$ where $1 \leqslant n \leqslant 4$. Here the hydration of the N^+ centre is controlled by steric effects associated with varying coordination of the N-atom by R groups (R = Me or Et). When n = 4, at the tetraalkylammonium type of ion, hydrophobic adsorption effects arise and the unusual dependence of standard free entropy of adsorption of the cation on coverage can be accounted for in terms of hydration co-sphere sharing effects in the two-dimensional interphase at the Hg electrode. $\Delta H/\Delta S$ compensation effects in adsorption at Hg from aqueous medium indicate the importance of water structure effects in the interphase.

Generally, it is found that the dependence of thermodynamic and spectroscopic properties on ionic size or charge density for cations is quite different from that for anions. This effect is connected with the different orientation of OH bonds and lone-pair electrons in water molecules at anions in comparison with cations. At the former, better H-bonding in hydration shells with the remainder of the solvent can arise for reasons connected with H_2O dipole orientation.

In the case of Pt, interesting information on the state of adsorbed ions such as Cl^-, Br^-, I^-, $CF_3SO_3^-$ and PF_6^- can be derived from their competitive adsorption behaviour *vis à vis* chemisorbed H and OH or O species. In particular, information on lateral interactions and the electrosorption valence can be derived.

Role of Specifically Adsorbed Electrochemically Inert Species in the Electrode Kinetics

V. S. KRYLOV

Institute of Electrochemistry, Academy of Sciences, Moscow, U.S.S.R.

The problem of decoding the physico-chemical mechanism of interaction between the elementary act of an electrochemical reaction and the adsorption phenomena at a metal–solution interface is of major importance because it directly concerns the interpretation of electrochemical kinetics data and the proper mathematical description of the effect of the electric double layer on electrode processes. In connection with the latter aspect the fundamental problem arises, namely, the problem of adequate statistico-mechanical approaching the transition from the description of the elementary act of an electrochemical process occurring at the interface in the presence of electroinactive specifically adsorbed species, ions or dipole molecules, to the description of the resulting heterogeneous process the rate of which is experimentally measurable. The advances made in recent years in interpretation of the data on the kinetics of electrode processes involving the specific adsorption of ionic and dipole solution components relate mainly to substantiation of the role of the discreteness effects. The local electric field acting near the interface on discrete particles possessing electric charge or dipole moment differs, due to polarization of the interface by these particles, from the average field described by the macroscopic equations of electrodynamics with a continuous charge and dipole moment distribution. The characteristic relaxation times of 'the electrostatic image' forces, *i.e.* the redistribution times of free and bound charges at the interface due to its polarization by discrete particles present in solution, are of the order to 10^{-15}–10^{-14} sec. The characteristic times of many types of electrochemical reactions, however, are comparable with the fluctuation reorientation time of dipole molecules of the solvent in the solvation shells of reactants ($\sim 10^{-11}$ sec), *i.e.* they are by three–four orders of magnitude higher than the relaxation times of 'the electrostatic self-image' forces. For this reason, the discrete nature of charges and dipole moments should affect the probability of the elementary act of an electrochemical process. Moreover, the local electric field associated with the discreteness effect can influence the rate of electrochemical processes by changing the concentration of reactants and reaction products inside the layer adjacent to the electrode.

In the present paper the problem of statistico-mechanical averaging the probability of the elementary act of an irreversible electron transfer reaction occurring on a metal–solution interface in the presence of specifically adsorbed electrochemically inert ions or dipole molecules is discussed in detail. The analytical expressions are derived for the polarization curve of the interface in cases of localization of the reactants both inside and outside the compact part of the electric double layer. Within the framework of the theory presented the available experimental data on electrochemical kinetics complicated by the specific adsorption of