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Abstract

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STATISTICAL THEORY OF THE DOUBLE LAYER AT THE METAL-SOLUTION INTERFACE

The electric double layer at the metal–solution interface plays a very substantial role in electrochemical and colloidal processes. The basic theoretical ideas concerning the structure of the diffuse double layer at the metal–solution interface were formulated in the works of Gouy, Chapman, and Stern ([1]). In ([2–4]) attempts were made to further improve the theory of the double layer by taking into account a number of factors not reflected in the above-mentioned works.

Although the Gouy–Stern theory describes, to a good approximation, the properties of the double layer over a sufficiently wide range of potentials and concentrations, the neglect of interionic interaction, characteristic of this theory, leads in a number of specific cases to disagreement between it and experiment ([5–8]). This applies in particular to experimental data concerning nonequilibrium processes occurring in the double layer.

One of the possible causes producing the indicated discrepancy between theory and experiment may be, as was emphasized by A. N. Frumkin ([9]), the neglect of the discrete nature of ionic layers. Attempts at a theoretical development of the idea of the discrete structure of charge in the double layer were undertaken in the works of Esin and Shikhov, Ershler, and Grahame ([2–4]).

A consistently statistical treatment of other aspects of the problem of allowing for interionic interaction in the theory of the double layer also appears very essential. The theory of the diffuse double layer is based on the assumption of the one-dimensional character of the layer. This means that the field potential in the electric double layer is considered to depend only on the distance from the surface of the metal. It is clear, however, that in reality interionic interaction must lead to the existence of some correlation in the spatial arrangement of ions in planes parallel to the surface of the metallic electrode. On the other hand, the Gouy–Stern theory proves applicable at such concentrations of the solution when, it would seem, the assumptions on which it is based cannot be valid. Finally, it should be pointed out that the absence of the effect of positive adsorption of ions on the metal surface near the point of zero charge cannot be interpreted from the point of view of Gouy' s theory.

Thus, although the theory of the double layer is widely and successfully used in electrochemistry and colloid chemistry, its statistical foundations and limits of applicability cannot in essence be regarded as clarified.

In the present work we make an attempt to construct a consistent statistical theory of the double layer at the interface between metal and electrolyte.

The method of correlation functions, developed by Bogolyubov ([10,11]) and by Born and Green ([12]), underlies the indicated generalization of the theory. In describing the interface between two phases it is necessary to generalize this method to the case of pri-

absence of an external field. At high concentrations of the solution, the calculation of the thermodynamic characteristics of the diffuse double layer can in principle be carried out on the basis of the "superpositional approximation" [10]. However, the mathematical difficulties thereby become quite considerable.

Therefore, a consistent construction of the theory of the electric double layer is possible when a small parameter is present in the initial equations. In the case of not too large volume concentrations of the solution, it proves possible to take as the expansion parameter the dimensionless quantity $\varepsilon = v/r_d^3$, where v is the specific volume and r_d is a characteristic length depending on the temperature and concentration of the solution. By the method of configuration space [10,11], unary and binary distribution functions of the first and second approximations in the parameter ε were found.

Since we cannot present the cumbersome calculations here [12], we shall confine ourselves only to a summary of the results.

The first approximation leads to the ordinary Gouy theory of the double layer. In this approximation (the self-consistent-field approximation), the centers of the ions are located in the external field independently of one another, and the mean field does not depend on their mutual arrangement in planes parallel to the interface.

This approximation is obtained from the Gibbs distribution on the basis of two conditions: the smallness of the solution concentration $N \ll N_0$, where N_0 is the number of solvent molecules, and the absence of correlation between the positions of ions.

The indicated circumstances make it possible to decide unambiguously the question of the self-consistency of the Poisson–Boltzmann equation in the theory of the double layer. The latter, in contrast to the analogous equation of the theory of Gronwall, La Mer, and Sandved for a bulk solution [13], is self-consistent. The physical premises underlying the approximation under consideration also make it possible to indicate the limits of applicability of the commonly used theory of the diffuse double layer.

The developed general theory of the double layer, being consistently statistical, also makes it possible in principle to take into account the effect of ion correlation

for an arbitrary law of interaction between them. This effect is described by the second and subsequent approximations in the parameter δ.

Near the point of zero charge, the calculations are substantially simplified owing to the presence of a second small parameter $\delta = e\varphi_0/kT$ (φ_0 is the electrode potential).

Allowance for correlation in the arrangement of ions is of fundamental importance in the region close to the electrode surface ($x \ll \frac{1}{\varkappa}$, where $1/\varkappa$ is the effective thickness of the double layer). In calculating the correlation, one must take into account the requirement that the metal surface be equipotential, for example by introducing image forces. It is also necessary to take into account the finite size of the ions, which limits their approach to the metal surface. To simplify the calculations, we assumed that ions of both kinds have the same radii. Expansion of the first- and second-order correlation functions in a series in powers of the small parameters of the theory—the quantities ε and δ—made it possible to calculate the correlation functions determining the probability of the mutual arrangement of ions, the distribution of the mean concentrations and of the mean charge density, and the potential of the self-consistent field in the double layer in the second approximation (i.e., to calculate corrections to the Gouy theory of the diffuse double layer). It turned out that the correction to the characteristic of the double layer directly measured in experiment—its capacitance in a symmetric electrolyte—is exactly equal to zero. In an asymmetric electrolyte it differs from zero, but is very small. This calculation made it possible to understand why the Gouy theory is confirmed by experiment with a high degree of accuracy, despite the fact that the concentrations in the double layer are not as small as is assumed in that theory.

In the work, the adsorption of ions at the electrode near the point of zero charge was also calculated. In the Gouy approximation, the positive effect of adsorption is absent, since the numbers of ions repelled from and attracted to the metal surface are, on average, identical.

In the next approximation it is necessary to take image forces into account. As it turns out, the latter play a very significant role here, preventing the accumulation near the metal surface of ions of any one sign.

As a result of the calculations it was shown that, in the second approximation as well, the numbers of repelled and attracted ions are, on average, equal to one another. Therefore the effect of positive adsorption due to electrical forces near the zero point is extremely small. The small effect of negative adsorption observed experimentally is apparently connected with forces of a nonelectrical character.

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Note: Figure translations are in progress. See original paper for figures.