THE PROBLEM OF THE STRUCTURE OF THE DENSE PART OF THE DOUBLE LAYER

L. I. Krishtalik

UDC 541.13

Over the last few years papers on the theory of the double electric layer have often developed the view that the cations closest to the electrode are separated from the metal by a layer of water not more than one molecule thick (see, for example, the survey in [1]). The basic arguments in favor of this idea are, first of all, data on negative adsorption of electrolytes, and, second, certain considerations relating to the practical nondependence of the electrode's capacitance on the nature of the cation in the negative charge region. From the data on negative adsorption of the electrolyte the thickness of the layer free of ions has been worked out as 3-4 Å, which is in opposition to the view of direct contact between cations and electrode.* The almost identical capacitance of the double layer for a variety of cations seems to invalidate the possibility of their direct contact with the metal, for in such a case the thickness of the double layer (and therefore the capacitance inversely porportional to it, as well) would alter considerably during variation in the cation radius (for example, from Na^+ to Cs^+—1.7 times).

It was demostrated by us earlier that the above evaluation of the thickness of the layer did not correspond to the distance of maximum approach by the ions to the metal, but was an effective value obtained by replacing the true smooth distribution of the ionic concentration by a step-by-step condition [2]. Hence the true distance between the ion centers closest to the electrode and its surface ought to be much smaller than the evaluation given above. It is not difficult to determine it on the basis of adsorption data without knowing the dependence of salt concentration on distance from the electrode.

The aim of this brief communication is pricipally to discuss the second, valid argument put forward against the model of ions in direct contact with the metal. The view that the model leads, as a first approximation, to inverse proportionality of the capacitance to the radius of the cations is based on the assumption of an identical dielectric permeability of the layer of condensor, equivalent to the dense part of the double layer, for all cations. As such, investigators usually take the corresponding characteristic of water in a state of greater or lesser dielectic saturation. This assumption, however, is in general invalid.

Indeed, the lines of force of the field do not only pass through the water molecules, but also, if it can be called so, through the "body" of the cation itself. Here, since the field is most intense close to the charges, the basic contribution to the overall picture is made by the dielectric properties of the ions themselves, and not the water (as shown schematically in the figure). As we know, in a series of like ions an increase in size is accompanied by an increase in polarizability, that is to say, an increase in the effective dielectric permeability. This effect should result in greater capacitance, i.e., it goes against any increase in thickness of the double layer. Hence, generaly speaking, there is no reason to expect in advance any great change in capacitance when the radius of the cations alters.

In order to assess how much the effect of increase in the ions' polarizability is able to compensate the growth of the double layer, we made the following approximate calculation. Considering the ions as like dielectric globules, we calculated their dielectric permeability from the polarizability of the gas ions and [3] their radius, using the Clausius-Mosotti equation. As the radius of the gas ions we took radii calculated by the Thomas-Fermi

---

*This thickness relates to the distance between the plane of the ion centers and the Gibbs plane of zero adsorption of water. The latter coincides at the limit (for an infinitely dilute solution) with the plane of arrangement of the centers of the closest water molecules to the electrode, but in solutions of finite concentration during negative adsorption of the dissolved material it is shifted slightly toward the electrode. In any case, the distance from the center of the ions to the "electron" surface of the metal is greater than the quantity given above by a distance of the order of a water molecule radius.

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 2, No. 12, pp. 1483-1485, December, 1966. Original article submitted July 4, 1966.

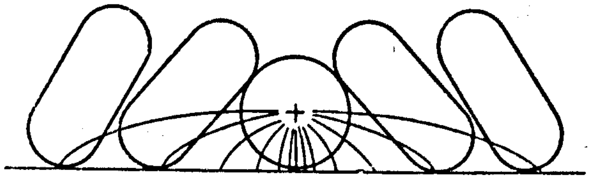

Fig. 1

method [4]. The dielectric permeability obtained was used to calculate the capacitance of the double layer, the thickness of which was taken as equal to the crystal radius of the cation (Goldschmidt's radii with corrections after Belov and Bokii [3]). As a result we obtained the following values of the capacitance(in $\mu F/cm^2$): 10.5 for Na^+; 10.75 for K^+, 10.5 for Rb^+; 12.1 for Cs^+; 13.7 for Mg^{2+}; 15.2 for Ca^{2+}; and 15.5 for Sr^{2+}. Qualitatively similar results were obtained for another, physically less valid, selection of data, for example, when calculating the dielectric permeability of gas ions from their crystal radii, or when using the not very reliable values of polarizability of the ions in the crystal or the solution.

The thoeretical values of the capacitance given above are close in order of magnitude to the experimental ones, although slightly below them. This fact should not be a surprise since the calculation was made for a very rough model, both as regards the evaluation of the dielectric permeability of the ions as well as in the sense that no allowance was made for the effect of water between the ions, or the possibility of a more complex structure of the double-layer. At the same time, further refinement of the model is hardly justified; if we are to remain within the bounds of classical concepts a quantitative theory of close interaction between ions, metal,and solution should be a quantum-mechanical one.

The main conclusion to be drawn from the calculations given above is that the effect of an increase in the dielectric permeability as the size of the ions grows is large enough to compensate the influence of the ion radius on the thickness of the double layer—in a number of alkaline, and, accordingly, alakali earth cations we do not observe an great reduction in capacitance.

We do not claim for a moment that the cations not in direct contact with the surface of the metal do not make any contribution to the capacitance of the electrode. Evidently the true picture is rather complex, and even given a nondiffuse structure of the double layer some way from the metal, at small distances from the electrode the ions may be distributed according to a law depending strongly on nonCoulomb close interaction forces. That such distribution exists follows directly from the fact of negative adsorption of the electrolyte at a zero charge potential.

As a result the capacitance of the dense double layer is influenced by both the behavior of the ions directly adjoining the electrode, as well as by the ions some way away from it, for example, a distance of the order of one or two water molecule diameters, though for the moment it is not possible to evaluate the relative role played by either. From this standpoint the outer plate of the Helmholtz double layer should be more correctly regarded as a region several angstrom units thick, and not the plane of location of the ion charges. It is possible that variation in structure in this narrow region is responsible for such effects as the slow rise in capacitance as the negative charge of the surface increases.

I am happy to express my graditude to Academician A. N. Frumkin for his valuable comments during discussion of this paper.

LITERATURE CITED

1. M. A. V. Devanathan, B. V. K. S. R. A. Tilak, Chem Rev., 65, 635 (1965).
2. L. I. Krishtalik, Élektrokhimiya, 2, 1351 (1966).
3. Chemistry handbook [in Russian], Vol. 1, Goskhimizdat, Moscow-Leningrad (1962).
4. P. Gambosh, Statistical theory of the atom and its applicability [in Russian], Foreign Lit. Press.,Moscow (1951).