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## CHEMISORPTION THEORY FOR CHARGED SPECIES AT ELECTRODES IN THE MODEL OF AN ENERGETICALLY HOMOGENEOUS SURFACE<sup>\*)</sup>

By

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### Abstract

Charge distribution along a "homogeneous" interface in presence of specifically adsorbed ions is discussed. Dependence of the pair potential of adions interaction on the distance between adions is analyzed. A new theory of ionic adsorption at homogeneous interfaces is proposed on the basis of this analysis. An original method for interpretation of experimental adsorption data is derived which has enabled us to give a proper explanation of experimental results for a number of systems, in particular for which the Grahame-Parsons theory turned out to be inapplicable.

Basic information on the ionic adsorption characteristics in electrochemical systems is obtained by capacitance measurements. At present the well-known Grahame-Parsons theory<sup>1)</sup> is usually used for interpretation of those data. It is based on the virial adsorption isotherm with a correction for the potential drop within the diffuse layer

$$\ln mc = \ln \sigma_1 - a + f\sigma/K_{12} + f\varphi_2(\sigma + \sigma_1) + 2B\sigma_1. \quad (1)$$

This approach gives Eq. (2) for the potential difference across the whole double layer within the rational scale

$$\varphi = \varphi_2(\sigma + \sigma_1) + \frac{\sigma}{K_{02}} + \frac{\sigma_1}{K_{12}}. \quad (2)$$

Thus, the Grahame-Parsons theory introduces 4 phenomenological characteristics, namely: a nonelectrostatic contribution to the one-particle energy of ionic adsorption ( $a$ ), capacity of the outer part of the Helmholtz layer ( $K_{12}$ ),

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the so-called attraction constant  $B$  (or the factor of charge discreteness  $\lambda = 2K_{12}Bf^{-1}$ ) as well as the total capacity of the compact layer ( $K_{02}$ ) which is treated as a fitting parameter even in the mixed electrolyte method. The electrode charge,  $\sigma$ , is used as an electrical variable. The effects of charge discreteness in the diffuse layer are neglected in the course of deriving the isotherm<sup>1)</sup> and the outer Helmholtz plane (OHP) is considered as being equipotential. The Grahame-Parsons approach is based on rather a crude model of the interfacial structure: point charges imitating adions are localized inside a compact layer which dielectric properties are constant across its section, this layer being in contact with an ideal metal (Fig. 1). Good or satisfactory agreement between the results of this theory and experimental data was observed for many electrochemical systems. But remarkable discrepancies have been found in a number of cases, see review articles<sup>2)</sup>. One of the possible reasons of these discrepancies may be the fact that basic physical concepts of the Grahame-Parsons theory are not adequate to describe the real situation at not very high coverages of an electrode surface by adions. In this case the total electrode charge,  $\sigma$ , consists of a component,  $\sigma_0$ , uniformly smeared along the surface and of the sum of electronic countercharges localized near corresponding adions (Fig. 1). A similar nonuniform charge distribution along the interface is also characteristic for the ionic plasma in the diffuse layer. As a result, the OHP is essentially nonequipotential.

A consistent derivation of the adsorption isotherm can be carried out only if the dependence of the pair potential of adions interaction,  $U$ , on the distance between adions,  $R$ , is analyzed in detail. In this report a very

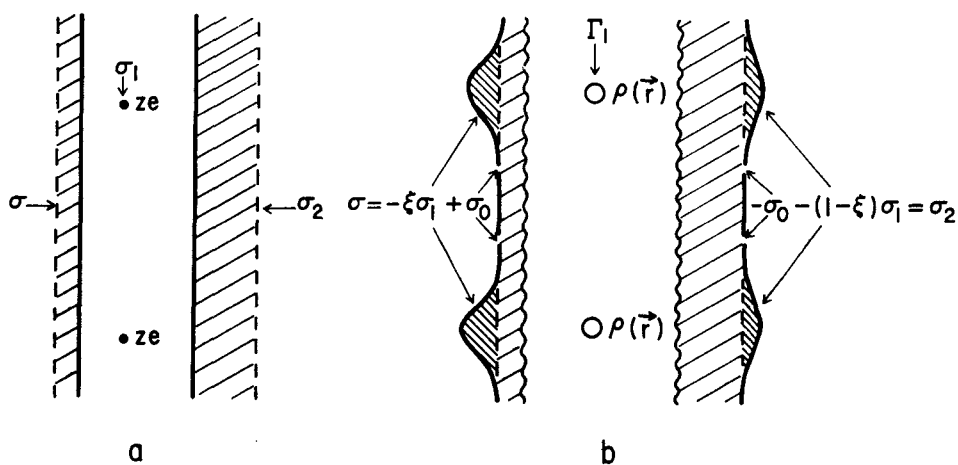


Fig. 1. Models of the interfacial structure in the Grahame-Parsons treatment (a) and in the new theory (b).

*Chemisorption Theory for Charged Species at Electrodes*

general model for the interfacial structure is considered. The following 6 factors were properly taken into consideration: 1) electric field penetration into the metal, 2) a spatial structure of the solvent and its possible variation near the electrode surface, 3) penetration of the electronic cloud of the metal into the adjacent solvent layer and possible chemisorption of solvent molecules, 4) a finite size of adions, 5) a partial transfer of the ionic charge into the electrode in the course of adsorption, 6) electric field screening by the ionic plasma of the diffuse layer, with account for the nonlinear effects. Our analysis carried out in Refs (3) within such a general model showed that the relation obtained by the "method of images",  $U(R) \simeq (ze)^2 \frac{2a^2}{\epsilon R^3}$  which is popular in electrochemical literature is absolutely inapplicable. As an illustration, the real form of this function at medium and large distances between adions at PZC is given below

$$U(R) \simeq (ze)^2 A^2 \frac{2}{\epsilon R} \exp(-R/L_D), \quad (3)$$

$$U(R) \simeq (ze)^2 A^2 \frac{2\epsilon L_{02}^2}{R^3} \left(1 + \frac{R}{L_D}\right) \exp(-R/L_D). \quad (4)$$

Even apart from the exponential terms related to the screening of the interaction by the diffuse layer ions, one can see that even the exponent is different in Eq. (3):  $U \sim R^{-1}$  instead of  $R^{-3}$ . At large distances between adions "the inverse cubic law" is really valid, but the coefficient differs drastically from the traditional one: *e. g.* for aqueous solutions it is some hundred times greater. The analytical expressions obtained for  $U(R)$  are used for deriving a new adsorption isotherm at homogeneous electrochemical interfaces.

At not very high coverages of the electrode surface the electrochemical potential of an adion is the sum of an entropy term, the one-particle adsorption energy and the contribution of the interionic interaction, with account for all screening factors

$$\mu_{\text{ads}} = RT \ln F\Gamma_1 + E_{\text{ads}} + W_{\text{int}}. \quad (5)$$

The latter term is a linear function of the surface coverage,  $\Gamma_1$ . In its turn,  $E_{\text{ads}}$  is equal to the sum of a nonelectrostatic contribution, the energy of ionic transfer within the field of the double layer and the energy of image forces. As a result, the adsorption isotherm has the following form

$$\ln mc/F\Gamma_1 = -a(\sigma_0) + zf\varphi_1(\sigma_0, c) + W'_{\text{im}}(\sigma_0, c)/RT + 2v(\sigma_0, c) F\Gamma_1. \quad (6)$$

It should be emphasized that this relation contains functions not of the total

electrode charge,  $\sigma$ , but only of its uniformly smeared component,  $\sigma_0$ , which is immediately related to the electrode potential:  $E - E_{\sigma=0} \equiv \varphi = \sigma_0 / K(\sigma_0, c)$ , where  $K$  is the integral double layer capacity in a surface-inactive electrolyte solution. Thus, it is the electrode potential that should be chosen as an electrical variable. Then, the coefficient  $v$  is the "true" attraction constant since it can be immediately expressed through the pair potential of adions interaction,

$$v = \frac{N}{F} \pi \int_0^\infty R dR \left\{ 1 - \exp \left[ - \frac{1}{kT} U(R) \right] \right\} \quad (7)$$

unlike a similar characteristics,  $B$ , in the Grahame-Parsons theory. Analytical expressions were obtained for the dependences of the quantities,  $v$ ,  $\varphi_1$  and  $W'_{im}$  on the electrode potential. They all contain the same parameter,  $\Delta = \frac{\int \rho(x) L_{ox} dx}{zeL_{02}}$ , which is determined both by the dielectric properties of the metal/solvent system,  $\varepsilon(\vec{I}, \vec{I}')$ , and the charge distribution within the adion,  $\rho(\vec{I}')$ . In particular,  $\Delta$  is influenced by the partial transfer of the ionic charge into the electrode. On the whole, the final expressions for the adsorption isotherm contain only two parameters,  $\Delta$  and  $a$ , compared to 4 parameters in the Grahame-Parsons theory. Those two quantities,  $\Delta$  and  $a$ , can be either calculated on the basis of concrete quantum-mechanical models, or treated as phenomenological parameters to find them at comparison with experimental data.

For an illustration, graphs in various coordinates were plotted with using the new adsorption isotherm. Values of the parameters were taken to be typical for the adsorption of cesium and haloid ions at the mercury electrode from aqueous solutions. The attraction constant,  $v$ , depends on the electrode potential mainly due to variation of the screening properties of the diffuse layer. Therefore it has a maximum near PZC of a surface-inactive electrolyte solution (Fig. 2). Its variation in the decinormal solution is relatively small. On the other hand, a pronounced maximum should be observed at  $c=0.001$  N. For each fixed electrode potential ( $E$  or  $\sigma_0$ ) the plot in "virial" coordinates ( $\ln mc/FT_1, FT_1$ ) should be a straight line, the lines for different potentials being not parallel (Figs. 3, 4). The latter effect is almost unnoticeable at  $c=0.1$  N (Fig. 3). At the same time, this nonparallelism manifests itself drastically in the millimolar solution (Fig. 4). The following figures show plots in the Grahame-Parsons coordinates, *i. e.* for a set of fixed electrode charges,  $\sigma$ , positive, zero and negative. Values of the charge are shown in the figures near each curve (in  $\mu\text{C}/\text{cm}^2$ ) as well as the electrolyte concentrations. The plots for 0.1 N in virial coordinates, with no correction

*Chemisorption Theory for Charged Species at Electrodes*

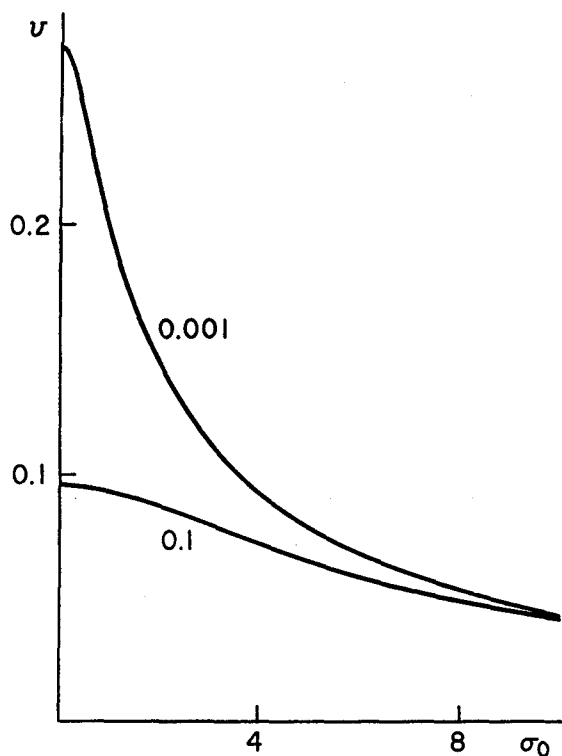


Fig. 2. Dependence of the attraction constant,  $v$ , on the  $\sigma_0$  charge for 0.1 N and 0.001 N solutions of a mixed electrolyte.

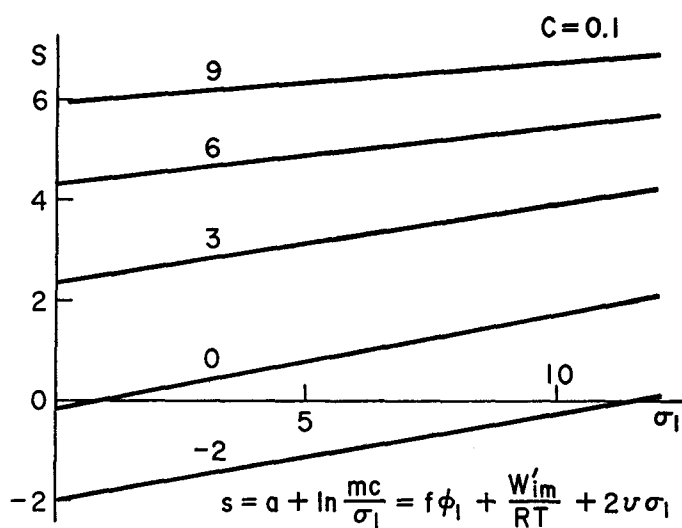


Fig. 3. Plots in "virial" coordinates ( $\ln mc/FF_1 + a, FF_1$ ) at various electrode potentials, *i. e.*  $\sigma_0$  charges (the latter are given near each plot),  $c=0.1$  N.

M. A. VOROTYNTSEV

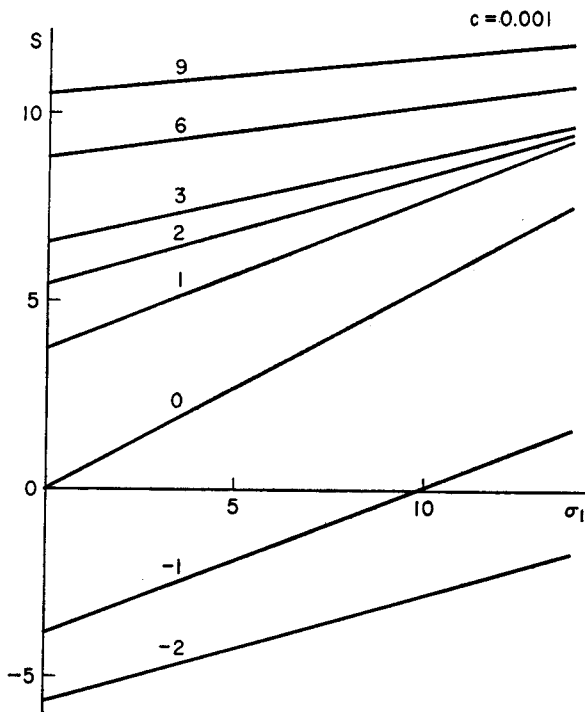


Fig. 4. See Fig. 3,  $c=0.001$  N.

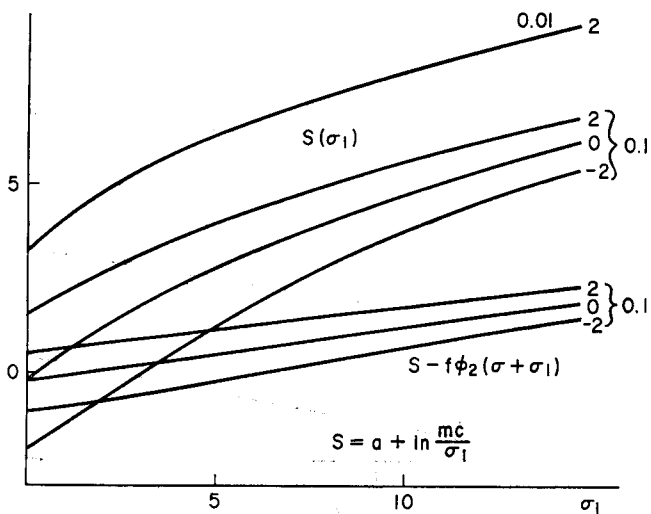


Fig. 5. Graphs at various electrode charges,  $\sigma$  (their values are given near each graph). The dependences of  $\ln mc/FG_1+a$  or  $\ln mc/FG_1+a+f\phi_2$  on the charge of specific adsorption,  $\sigma_1$ , at  $c=0.1$  N and  $c=0.01$  N.

*Chemisorption Theory for Charged Species at Electrodes*

for the diffuse layer contribution, become straightened and practically parallel to one another at large charges of specific adsorption,  $\sigma_1 = F\Gamma_1$  (Fig. 5). At low surface coverages these plots are curved. The curvature is larger in the case of adsorption at the oppositely charged surface. If in accordance with the Grahame-Parsons approach a correction is introduced for the potential drop within the diffuse layer the plots become much straighter, though even in this case a small S-shaped bend is retained in the region of the diffuse layer recharge (Fig. 5). Decrease of the total electrolyte concentration in the case of adsorption at a like-charged surface does not change the shape of the curves (Fig. 5). At the same time, in the case of adsorption at an oppositely charged surface, passing from the decinormal to millinormal solution results in a very sharp deviation from the linear dependence (Fig. 6). This deviation even increases if the correction for the diffuse layer contribution is subtracted (Fig. 7). Thus, the new theory predicts existence of such non linearities, first of all in the case of ionic adsorption at an oppositely charged surface for a low ionic strength of the solution. Evidently, these results differ from the predictions of the Grahame-Parsons theory which expects linear plots in these coordinates. It is the anomalies of such kind, probably, that have been observed experimentally for a number of real sys-

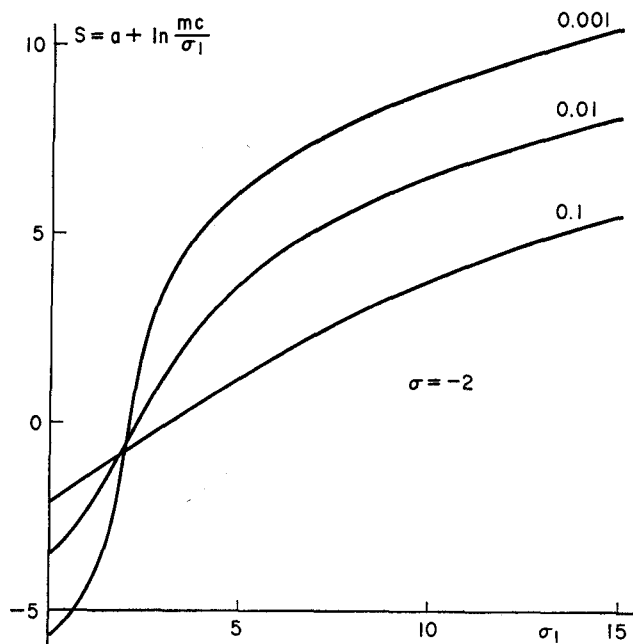


Fig. 6. See Fig. 5,  $\sigma = -2 \mu\text{C}/\text{cm}^2$ ,  $c = 0.1 \text{ N}$ ,  $0.01 \text{ N}$  and  $0.001 \text{ N}$ .

M. A. VOROTYNTSEV

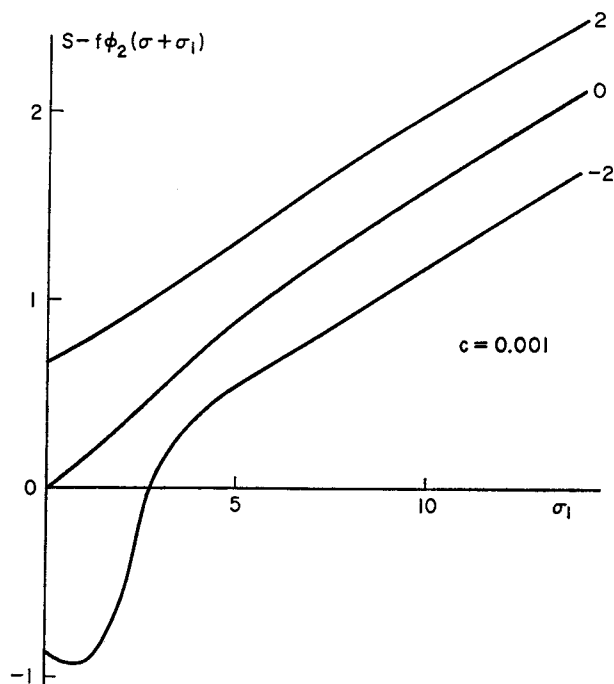


Fig. 7. Dependence of  $\ln mc/\sigma_1 + a + f\phi_2$  on the charge of specific adsorption,  $\sigma_1$ , in 0.001 N at various values of the electrode charge,  $\sigma = 2, 0$  and  $-2 \mu\text{C}/\text{cm}^2$ .

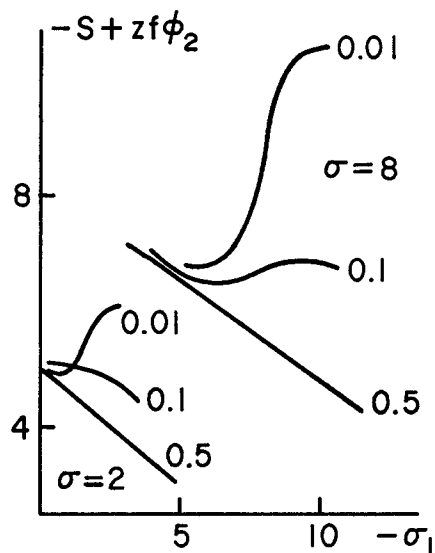
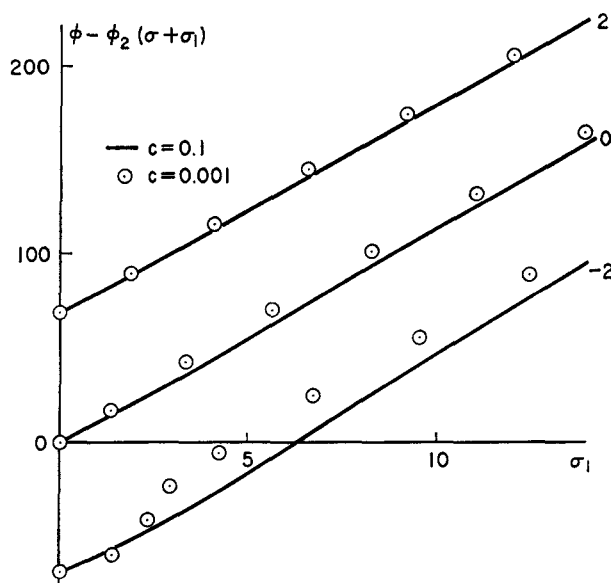


Fig. 8. Experimental results (4) for the dependence of  $\ln mc/\sigma_1 + a + f\phi_2$  on  $\sigma_1$  at  $\sigma = 2 \mu\text{C}/\text{cm}^2$  and  $\sigma = 8 \mu\text{C}/\text{cm}^2$  in 0.5, 0.1 and 0.01 N solutions for the  $\text{Bi}/\text{C}_2\text{H}_5\text{OH} - \text{LiCl} - \text{LiClO}_4$  contact.

*Chemisorption Theory for Charged Species at Electrodes*

tems, in particular at adsorption of various haloid anions at the Bi electrode from aqueous and alcohol solutions (Fig. 8). Really, passing to more diluted solutions results in sharp deviations from straight lines which take place at rather low charges of specific adsorption. Fig. 9 shows the results of calculation in another Grahame-Parsons coordinate system, for the dependence of the potential drop within the Helmholtz layer on  $\sigma_1$ . In these coordinates the curves are much closer to straight lines and the plots for different electrolyte concentrations are practically coincident almost everywhere. Some slight anomalies can be expected only at small values of  $\sigma_1$  in the case of adsorption at an oppositely charged surface. These predictions of the theory are also in a qualitative agreement with experimental data, for example for chloride anion adsorption at Hg from aqueous solutions (see Ref. 1b. It should be kept in mind that the experimental curves are related to the binary electrolyte and Fig. 9 to the mixed one). It is interesting to note that Grahame and Parsons who found these deviations from their theory wrote in their paper (1b) that they could not propose any explanation for them.

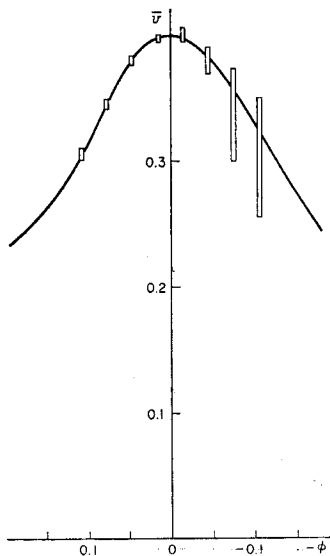
At present experimental data for several real systems have been analyzed on the basis of the new theory. In all those cases an agreement with the predictions of the theory was found. As an illustration, an important example, iodide anion adsorption at Bi from aqueous 0.01 N solutions, is con-



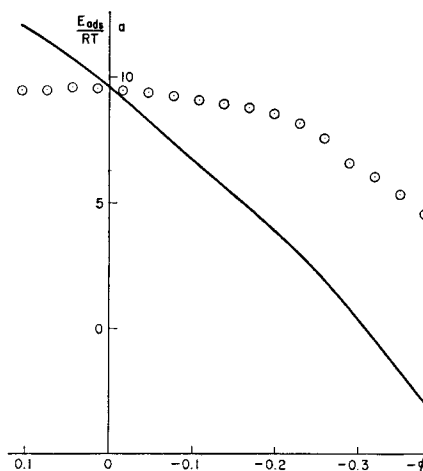
**Fig. 9.** Dependence of the potential drop within the Helmholtz layer,  $\phi - \phi_2$ , on  $\sigma_1$  in 0.1 N and 0.001 N solutions at  $\sigma = 2, 0$  and  $-2 \mu\text{C}/\text{cm}^2$ .

sidered below. As it has been mentioned above (Fig. 8), for this system the Grahame-Parsons model proved to be quite inapplicable in diluted solutions. For this reason Damaskin and Palm<sup>4)</sup> brought up a new physical hypothesis that cations are drawn into the Helmholtz layer by the field of specifically adsorbed iodide ions. As a result, to explain these experimental data they had to introduce several additional fitting characteristics, apart from the four usual parameters of the Grahame-Parsons approach. We were able to give<sup>6)</sup> and adequate interpretation of the same experimental data on the basis of the new theory without introducing any additional complications, *i. e.* with using only two parameters,  $\Delta$  and  $a$ .

First of all the value of  $\Delta$  was found by comparison of the theoretical expressions for the attraction constant,  $v$ , with the corresponding experimental data. Fig. 10 demonstrates that the theoretical curve agrees with all experimental points, within their dispersion, the  $\Delta$  value being potential independent,  $\Delta=0.71$ . Such agreement is observed, in particular, at positive surface charges where the accuracy of experimental data is very high, of the order of 1%. Thus found value of  $\Delta$  parameter was used for calculating the



**Fig. 10.** Comparison of the theoretical (solid line) and experimental (points) results for the potential dependence of the attraction constant,  $v(\varphi)$ , for the contact, Bi/H<sub>2</sub>O-KF-KI,  $c = 0.01$  N.



**Fig. 11.** Potential dependence of the one-particle adsorption energy,  $E_{ads}$  (solid line), and its nonelectrostatic component,  $a$  (points), see Fig. 10.

*Chemisorption Theory for Charged Species at Electrodes*

electrostatic contribution to the one-particle adsorption energy. It should be stressed that an independent adjusting parameter is introduced for this purpose in the Grahame-Parsons theory. At the same time, no additional fitting characteristics is used in the new theory. Therefore, such examination was much stricter for the new theory. However, this testing also gave quite satisfactory results. Fig. 11 shows the dependence of the total one-particle adsorption energy on the electrode potential, within the rational scale. After subtracting the electrostatic contribution from this quantity, with using the  $\Delta$  value found above, the dependence of the nonelectrostatic contribution,  $a$ , on the electrode potential was obtained (points in Fig. 11). As it should be expected, the energy,  $a$ , is practically constant near PZC. At large negative surface charges the binding energy of the iodide anion with the electrode is decreasing.

Thus, the new theory of ionic adsorption enabled us to derive an original method<sup>6</sup> for interpretation of experimental data. An application of this method has resulted in an explanation for a number of experimental results observed earlier, including those for the systems for which the Grahame-Parsons approach proved to be inapplicable. It should be emphasized once again that the proposed theory is based on a model for the interfacial structure which is much more adequate to describe the real situation than that of the Grahame-Parsons approach. At the same time, the consistent derivation of the ionic adsorption isotherm on the basis of principles of the statistical mechanics enabled us to diminish remarkably the number of phenomenological parameters used for interpretation of experimental data.

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