# On an Experimental Verification of Stern's Double Layer Theory

By *O. Essin* and *B. Markov*

In his work on an experimental verification of Stern's double layer theory, Philpot[1], after a comparison of Gouy-Chapman's and Stern's equations, comes to the following conclusions. The Gouy-Chapman theory gives the exponential dependence of the density of the charge of a metallic surface $E$ upon the potential $\epsilon$ for any values of the latter. Stern's theory, on the contrary, leads to a linear relation between $E$ and $\epsilon$ for the limiting cases of large $\epsilon$ and concentrations $c$, and to an exponential relation for small $\epsilon$ and $c$. Furthermore, as Philpot emphasizes, from Stern's theory it follows that, at a fixed $E$ and large $\epsilon$, the potential may be expressed in terms of $c$ by the following equation:

$$\epsilon = \text{const.} \mp \frac{RT}{F} \ln c,$$

where the negative sign refers to $E > 0$, and the positive sign refers to $E < 0$. The conclusions thus arrived at from Stern's equations were experimentally corroborated by Philpot by using a mercury electrode in HCl and KCl solutions.

However, employing an analogous method of establishing the limiting dependences, it is easy to show that, from the Gouy-Chapman equation:

$$E = a\sqrt{c}\left\{\exp.\left(\frac{\epsilon F}{2RT}\right) - \exp.\left(-\frac{\epsilon F}{2RT}\right)\right\}, \qquad (1)$$

almost a linear relation results between $E$ and $\epsilon$ in the region of small values of $\epsilon$:

[1] J. Philpot, Phil. Mag., 13, 775 (1932).

$$E \simeq a\sqrt{c}\,\frac{F}{RT}\,\varepsilon$$

and an exponential relation for large values of $\varepsilon$:

$$E \simeq a\sqrt{c}\,\exp.\left(\pm\frac{\varepsilon F}{2RT}\right).$$

The rather complex experimental curves ($E$, $\varepsilon$), obtained by Philpot, do not always permit strict differentiation as to whether, roughly speaking, they consist of two linear segments connected by a logarithmic relation (Stern), or two logarithmic relations connected by a straigh line (Gouy-Chapman). In particular this refers, for example, to Fig. 7 of the original. Finally, from the Gouy-Chapman equation the same dependence of $\varepsilon$ upon $c$ (for large $\varepsilon$ and fixed $E$) follows as from the Stern theory. Indeed equation (1) in this case assumes the form:

$$\pm E \simeq \pm a\sqrt{c}\,\exp.\left(\pm\frac{\varepsilon F}{2RT}\right)$$

from which $\varepsilon = \text{const.} \mp \frac{RT}{F}\ln c$ (+ for $E < 0$ and — for $E > 0$).

Furthermore, as was pointed out by Frumkin[2], the deduction of the latter relation is, in general, not connected with a special form of the theory and may be arrived at from pure thermodynamical considerations.

We therefore believe that, along with investigations which set before themselves the aim of studying experimentally to what extent Stern's equation is capable of embracing the whole range of measurements of $\varepsilon$ as a function of $E$, an investigation is also necessary which would be devoted to an experimental verification of that which, being new in principle, has been introduced by Stern into the theory of the double layer. Along with the introduction of a finite ionic radius, the attempt to quantitatively account for the specific adsorption of ions is also basically new. This attempt, as Stern himself points out, is quite approximate, requiring further development.

One of the more characteristic conclusions which distinguish Stern's theory from the theory of Helmholtz and Gouy-Chapman is the possibility of the formation of a jump in the electrical poten-

[2] A. N. Frumkin, Erg. exak. Naturwiss., 7, 247 (1928).

tial (with respect to the solution) on a surface having a charge of $E=0$. This jump is caused not by the interchange of ions between the phases (Nernst's mechanism), but only by the different adsorption potentials ($\Phi_+$ and $\Phi_-$) of the cation and anion of the solution. For an experimental check of this part of Stern's theory, it is expedient, therefore, to eliminate the interchange of ions between the metal and the solution, which complicates the picture, and to study, for example, the change in potential of the maximum of the electrocapillary curve ($E=0$) with respect to the concentration of capillary-active ions in the solution. These conditions, evidently, will be closest to the picture proposed by Stern, since the potential, conditioned by the adsorption of dipoles[3] of the solvent, may be assumed here to be almost constant (the small concentration of ions in the solution and in the adsorbed layer in comparison with the concentration of the molecules of the solvent). On the other hand, a contact potential[4] is completely absent, since the electrode being studied and the comparison electrode are both mercury electrodes.

Since, however, Stern's theory disregards the forces of interaction[3] between the adsorbed ions in the sense that it does not take into consideration the violation of the random distribution of the ions parallel to the surface of separation under the action of these forces, a certain deviation from experiment may be expected in advance[5].

Let us now consider what form, in accordance with Stern's theory, the dependence of the potential maximum of the electrocapillary curve upon the concentration of the capillary-active ion in the solution should have in the simplest case — when the adsorption potential of one of the kinds of ions is considerably less than for the other kind (*i. e.*, in an aqueous solution of KJ, where it can be assumed that $\Phi_- \ll \Phi_+ = 0$). In this case, *i. e.*, for $E=0$ and $\Phi_+ \to 0$, Stern's equation may be written in the following form:

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[3] A. N. Frumkin, Reports of the Karpov Institute, 4. 64 (1925).

[4] See, for example, A. N. Frumkin a. A. Gorodetzkaja, Z. physik. Chem., 136, 451 (1928).

[5] See A. N. Frumkin, Uspechi Chimii, 4, 938 (1935). In this paper there are also pointed out other substantial shortcomings of Stern's theory.

$$Fz\left\{\frac{1}{2+\frac{1}{c}\exp.\left(\frac{\Phi_- - F\varepsilon}{RT}\right)} - \frac{1}{2+\frac{1}{c}\exp.\left(\frac{F\varepsilon}{RT}\right)}\right\} = \left.\begin{matrix} \\ \\ \end{matrix}\right\}_{\varepsilon=\zeta} = a\sqrt{c}\left\{\exp.\left(-\frac{F\varepsilon}{2RT}\right) - \exp.\left(\frac{F\varepsilon}{2RT}\right)\right\} \quad (2)$$

Further, assuming a low degree of surface covering[6] and sufficiently negative values of $\varepsilon$, we obtain

$$\frac{Fz}{a}\sqrt{c}\left\{\exp.\left(\frac{-\Phi_- + F\varepsilon}{RT}\right) - \exp.\left(-\frac{F\varepsilon}{RT}\right)\right\} = \exp.\left(-\frac{F\varepsilon}{2RT}\right). \quad (3)$$

As an analysis of this equation shows, it leads in the best case, *i. e.*, employing simplifications most favorable for the final result, to the relation

$$\varepsilon \simeq \alpha - \beta \ln c$$

in which the coefficient $\beta \leqslant \frac{RT}{F}$. As will be evident from what follows, the relation observed experimentally gives $\beta > \frac{RT}{F}$.

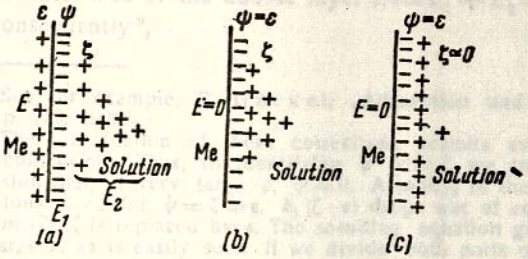


Fig. 1. A schematic diagram of the double layer.

Let us introduce two corrections into equation (2). The first of these, proposed by Stern[7], consists in the fact that we no longer identify potentials of the first ($\psi$) and second ($\zeta$) ionic layers (see Fig. 1*a* and 1*b*). The second correction amounts to the following: The fact that the adsorption of an anion decreases the number

[6] See, for example, A. N. Frumkin, Z. physik. Chem., **164**, 121 (1933).

[7] O. Stern, Z. Elektrochem., **30**, 513 (1924).

of free positions for the adsorption of cations and *vice versa*, is taken into account by Stern, as a first approximation, by the introduction of 2 instead of 1 into the isotherm for each kind of ions taken separately. It is more correct, of course, to employ directly an equation of the adsorption isotherm of two kinds of particles[8]. Making use of these corrections, Stern's equations assume the following form:

$$\left.\begin{aligned} E = k_0(\varepsilon - \psi) = Fz\left\{\frac{(\omega_1 - \omega_2)\,c}{1 + (\omega_1 + \omega_2)\,c}\right\} + \\ + a\sqrt{c}\left\{\exp.\left(\frac{F\zeta}{2RT}\right) - \exp.\left(\frac{-F\zeta}{2RT}\right)\right\} \\ E_2 = k_1(\varrho - \zeta), \end{aligned}\right\} \quad (4)$$

where

$$\left.\begin{aligned} \omega_1 = b_1 \exp.\left(\frac{-\Phi_- + F\psi}{RT}\right) \\ \omega_2 = b_2 \exp.\left(\frac{-\Phi_+ - F\psi}{RT}\right). \end{aligned}\right\} \quad (5)$$

For the case which we examined (Fig. 1b), the change of the metallic face of the double layer $E = E_1 + E_2 = 0$, *i. e.*, $\psi = \varepsilon$, and consequently[9],

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[8] See, for example, E. Hückel, „Adsorption und Kapillarkondensation", p. 219, 1928.

[9] The introduction of these corrections permits avoiding some erroneous conlcusions. Thus, in identifying $\psi$ with $\zeta$, we arrive at the absurd conclusion that, at very large $c$, $\psi = 0$. Actually, in the absence of these corrections, *i. e.*, for $\psi = \zeta = \varepsilon$, $k_1(\zeta - \varepsilon)$ drops out of equation (6); and in equation (7), $\zeta$ is replaced by $\varepsilon$. The resulting equation gives $\psi = \varepsilon = 0$ for very large $c$, as is easily seen if we divide both parts of the equation by $\sqrt{c}$ and place $c \to \infty$. We arrive at the same result if we take for the charge density in the adsorbed layer ($E_1$) the non-corrected expression of Stern (without the second correction). Generally speaking, at very large concentrations, where $\zeta \to 0$, $\psi = \varepsilon$ may be quite a significant magnitude. Actually, dividing all three parts of equation (6) and (7) by $\sqrt{c}$ and assuming that $c \to \infty$, we obtain $\zeta \to 0$, while $\varepsilon = \psi \neq 0$.

Furthermore, equation (6), especially without the introduction of the second correction, is completely analogous to the equation emloyed by Stern to explain the existence of a maximum or a minimum in the curve of the change in the electrokinetic potential with the concentration of the solution with the only distinction that the rôle of $\zeta$ is played here by $\varepsilon$. As shown by an analysis of equation (6), *i. e.*, an equation in which the mutual adsorption of two kinds of ions is taken into account more exactly, it does not give either a maximum or a minimum for the curve ($\varepsilon$, $c$). Actually, from equation (6) it follows, firstly, that $\varepsilon$ cannot be equal to $\pm\infty$

$$Fz\left\{\frac{(\omega_1 - \omega_2)\,c}{1 + (\omega_1 + \omega_2)\,c}\right\} = k_1(\zeta - \varepsilon) = \tag{6}$$

$$= a\sqrt{c}\left\{\exp.\left(\frac{-F\zeta}{2RT}\right) - \exp.\left(\frac{F\zeta}{2RT}\right)\right\}. \tag{7}$$

An analysis of equations (6) and (7) shows that in this case it is impossible to obtain the relation

$$\varepsilon = \alpha - \beta \ln c$$

with the coefficient $\beta > \frac{RT}{F}$.

The slow change in $\varepsilon$ with $c$, following from the common and corrected equations of Stern and not corresponding to the experimentally observed change (see below), is explained by an increase (together with $|\varepsilon|$) of the adsorption of ions of opposite sign (in our case cations). For example, the increase in the concentration of $J'$ ions in the solution increases their adsorption and makes the potential $\varepsilon$ more electronegative. The latter circumstance (together with an increase in $c$) facilitates the adsorption of $K^+$ ions, which leads to a retarding of the increase of the charge density in the adsorption layer and, in the end, to a less sharp change in $\varepsilon$ with $c$.

Let us finally examine the limiting case, artificially removing the decreasing effect of the adsorption of the cations on the increase in $\varepsilon$, *i. e.*, let us suppose that the electrostatic attraction of the cation to the surface of the metal (adsorption), due to the presence of $\varepsilon$, is insignificant in comparison with the action of the specific forces of adsorption on the anions. In other words, we assume, together with our previous assumption $\Phi_- \ll \Phi_+ = 0$, that $|\varepsilon| \ll |\Phi_-|$.

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for $0 \leq c \leq \infty$; and, secondly, that, writing it in an implicit form, $f(\varepsilon, c) = 0$, and taking $\frac{d\varepsilon}{dc} = -\frac{\partial f}{\partial c} \Big/ \frac{\partial f}{\partial \varepsilon}$, we find that, for finite values of $\varepsilon$ and $c$, neither $\frac{\partial f}{\partial c}$ may be equal to zero nor $\frac{\partial f}{\partial \varepsilon}$ may be equal to infinity. For $c = \infty$, we only get the equation of the asymptote. From this it follows directly that the explanation of the maximum or minimum of the electrokinetic potential, given by Stern, is based on a misunderstanding or on the discarding of an expression of the type (7), *i. e.*, $E_2$ for the diffuse part of the double layer. In this connection Bickermann's attempt (Z. physik. Chem., 171, 209, 1934) to explain the maximum in the rate of cataphoresis, without assuming the presence of a maximum for the electrokinetic potential and basing itself only on the diffuse theory of the structure of the double layer, is interesting.

Furthermore, placing $\zeta = 0$ [10] we arrive at the structure of the double layer which is pictured in Fig. 1c. This permits us, on the basis of picture (1c), to obtain equation (8):

$$k_1 \varepsilon = \frac{Fz}{1 + \frac{1}{c} \exp. \left( \frac{\Phi_- - F\varepsilon}{RT} \right)}, \tag{8}$$

which gives $\varepsilon_\infty = \frac{Fz}{k_1}$ for $c \to \infty$, from which

$$\varepsilon = \frac{\Phi_-}{F} - \frac{RT}{F} \ln \left( \frac{\varepsilon_\infty}{\varepsilon} - 1 \right) c;$$

and finally, for a small surface concentration, *i. e.*, for $\frac{\varepsilon_\infty}{\varepsilon} \gg 1$ we have [11]

$$\left. \begin{aligned} \varepsilon &= \frac{\Phi_-}{F} - \frac{RT}{F} \ln \varepsilon_\infty - \frac{RT}{F} \ln \frac{c}{\varepsilon} \\ \varepsilon &= \text{const.} - \frac{RT}{F} \ln \frac{c}{\varepsilon}. \end{aligned} \right\} \tag{9}$$

Inasmuch as we did not find a sufficient number of experimental data in the literature to test equation (9), we carried out potential measurements of the maximum of the electrocapillary curves for various concentrations of an aqueous solution of KJ. The apparatus which was used (represented diagrammatically in Fig. 2) was analogous to the one employed by Gouy and Frumkin. Polarization of the mercury meniscus was accomplished with the aid of two resistance boxes connected to a two-volt battery the potential of which was controlled in the usual manner (by comparison with a standard cell). The position of the mercury meniscus in the capillary was fixed by adjusting it to the hair in the ocular of a microscope. A reading of the height of the mercury

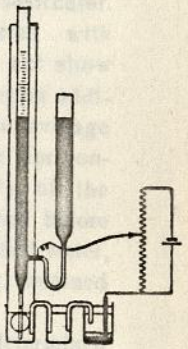

Fig. 2. A diagram of the apparatus.

[10] See, however, the work of Levina a. Sarinsky, J. Phys. Chem. (Russ.), **10**. 586 (1937).

[11] Upon rough simplification, an equation of the type of (9) may be obtained from (6) if we eliminate the second correction from it. Upon accepting the above assumptions, it is written:

$$k_1 \varepsilon = Fzc \left\{ \exp. \left( \frac{-\Phi_- + F\varepsilon}{RT} \right) - \exp. \left( -\frac{F\varepsilon}{RT} \right) \right\}.$$

Since $\Phi_- \ll 0$ and $|\varepsilon| \ll |\Phi_-|$, the second exponent may be discarded, which leads to an equation of the type of (9). This conclusion is possible for a small degree of surface covering and for sufficiently small $c$.

column was made with an accuracy approaching 0,05 mm. This was attained by employing a microscope which had a small magnification. All measurements were carried out at 18° C with reference to a saturated calomel electrode (the surface area of the mercury in the latter was equal to about 15 cm.²). The mercury employed was cleaned by filtration, by repeated washing in an Ostwald apparatus with a 5% solution of $Hg_2(NO_3)_2$ acidulated with $HNO_3$, and finally by distillation under vacuum. Chemically pure KJ was dried at 110—120° C to drive off traces of iodine and moisture and was cooled in a desiccator. The solutions prepared with bi-distilled water did not show noticeable coloration upon addition of sulphuric acid (of average concentration) to them (for control). The glass parts of the apparatus were washed before using, first with distilled water, and then with the solution being investigated. The data obtained are collected in Table 1.

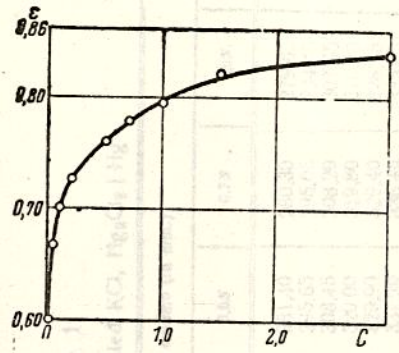


Fig. 3. A curve showing the potential as a function of the concentration.

The values of the potential of the maximum were determined graphically according to Pashen's method (method of an average line). The values of ε found in this manner are given in Table 2 and pictured in Fig. 3 as a function of $c$.

To test equation (9), on the abscissae of Fig. 4 are plotted values of $\lg \frac{c}{\varepsilon}$ or $\lg (cf/\varepsilon)$, where $f$ is the average activity coefficient[12]; and on the ordinates are plotted values of ε. Furthermore, on the same graph are included three point for KJ taken from the work of Gouy[13]. As is seen from Fig. 4, equation (9) more or less satisfactorily describes the experimental data. However, the slope of the straight line obtained amounts to about 0,1 instead of the required 0,058.

[12] Landolt, II. Ergänzungsband, part 2, p. 1121.
[13] Gouy, Ann. Physique, (9), 6, 25 (1916).

## Table 1

$t = 18°$ C. Hg | KJ || saturated KCl, $Hg_2Cl_2$ | Hg

Height of the mercury column (in mm.)

| Volts \ Conc. | 0,01*N* | 0,05*N* | 0,1*N* | 0,2*N* | 0,5*N* | 0,7*N* | 1,0*N* | 1,5*N* | 3,0*N* |
|---|---|---|---|---|---|---|---|---|---|
| 1,40 | 293,65 | 287,60 | 286,20 | 283,10 | 281,40 | 280,30 | 279,65 | 278,90 | 277,30 |
| 1,30 | 305,70 | 301,45 | 300,35 | 297,25 | 295,65 | 295,05 | 294,45 | 293,70 | 292,20 |
| 1,20 | 317,40 | 313,60 | 312,05 | 309,55 | 308,45 | 308,20 | 307,65 | 306 95 | 304,95 |
| 1,10 | 327 40 | 324,40 | 326,20 | 321,30 | 320 00 | 319,80 | 318 90 | 318,40 | 315,50 |
| 1,00 | 336,10 | 333,85 | 332,85 | 331,10 | 329,90 | 329,40 | 328,75 | 327,60 | 324,35 |
| 0,90 | 343,80 | 342,05 | 341,15 | 339,20 | 337,20 | 336,40 | 335,05 | 333,25 | 329,00 |
| 0,88 | — | — | — | — | — | — | — | — | 329,40 |
| 0,86 | 346,45 | 345,05 | 343,85 | 342,15 | 339,30 | 338.40 | 336,55 | 334,75 | 329,75 |
| 0,84 | 347,55 | 346,00 | 345,10 | 343,15 | 339,90 | 339,00 | 337.10 | 334,85 | 329,75 |
| 0,82 | 348,75 | 347,05 | 345,90 | 344,00 | 340,45 | 339,60 | 337,50 | 335 00 | 329,75 |
| 0,80 | 349,95 | 348,05 | 346,95 | 344.75 | 341 05 | 339,90 | 337,50 | 334 90 | 329,10 |
| 0,78 | 351,05 | 349,20 | 347,85 | 345,25 | 341,25 | 339,90 | 337.50 | 334,60 | |
| 0,76 | 351,75 | 350,15 | 348,45 | 345,85 | 341.25 | 339,90 | 337,35 | 334.30 | |
| 0,74 | 352,70 | 350,80 | 349,10 | 345,95 | 341,25 | 339,80 | 337,00 | 333,70 | |
| 0,72 | 353 65 | 351,25 | 349,15 | 345,95 | 340,85 | 339,00 | 336,25 | 332,20 | |
| 0,70 | 353,95 | 351,75 | 349,15 | 345,85 | 340,30 | 338,50 | 335,40 | 331,90 | |
| 0,68 | 354,70 | 351,85 | 349,15 | 345,65 | 339,50 | 337,60 | 334,45 | | |
| 0,66 | 355,10 | 351,85 | 349,05 | 344 85 | 338,30 | — | 333,20 | | |
| 0,64 | 355,25 | 351,60 | 348,45 | 344,20 | — | — | — | | |
| 0,62 | 355,50 | 351,25 | 347,80 | | | | | | |
| 0,60 | 355,50 | 350,55 | 346 90 | | | | | | |
| 0,58 | 355,50 | 349,85 | 345,55 | | | | | | |
| 0,56 | 355,35 | 348,55 | | | | | | | |
| 0,54 | 354,85 | | | | | | | | |
| 0,52 | 353,95 | | | | | | | | |
| 0,50 | 353,05 | | | | | | | | |

Table 2

| $c$ (concentr.) | 0,01$N$ | 0,05$N$ | 0,1$N$ | 0,2$N$ | 0,5$N$ | 0,7$N$ | 1,0$N$ | 1,5$N$ | 3,0$N$ |
|---|---|---|---|---|---|---|---|---|---|
| $\varepsilon$ potential maximum (in V) | —0,60 | —0,67 | —0,70 | —0,73 | —0,76 | —0,78 | —0,80 | —0,82 | —0,84 |

Furthermore equation (9) was tested using the data of Erdey-Gruz and Szarvas[14] for a mercury drop electrode the potential of which they consider equal to the potential of the maximum of

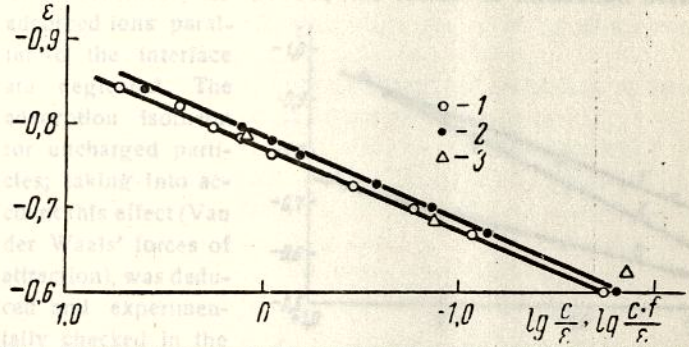


Fig. 4. Experimental curves constructed to verify equation (9) for a KJ solution:

1 — points for $\varepsilon \sim \lg\left(\frac{c}{\varepsilon}\right)$ } our data

2 — points for $\varepsilon \sim \lg\left(\frac{cf}{\varepsilon}\right)$ } our data

3 — points for $\varepsilon \sim \lg\left(\frac{cf}{\varepsilon}\right)$ Gouy's data.

the electrocapillary curve for a corresponding solution. The results are presented in Fig. 5, the points for concentrations of $c \leqslant 0{,}01\ N$ being rejected. As follows from Fig. 5, the slope for NaJ is also equal to 0,1, while for NaBr it is close to the required value (0,063 instead of 0,058).

It is necessary to note that, in accordance with the data of Erdey-Gruz and Szarvas for a mercury drop electrode, the deviation between the actual slope and $\frac{RT}{nF}$ usually becomes larger the sharper the capillary activity of the anion is expressed (*i. e.*, $S'' > J' > Br' > Cl'$, and the like). To a certain extent this, of course, may be accounted for by the decreased rôle of the adsorption of

[14] Erdey-Gruz a. Szarvas, Z. physik. Chem., 177, 277 (1936).

cations. However, the absolute values of the slopes cannot be justified by the latter. Such an increase in the actual slope over the value required by equation (9) can hardly be referred to those simplifications which were accepted in the initial premises of its deduction. Furthermore, these simplifications were deliberately chosen in such a manner as to obtain the largest possible slope.

The most probable reason for the deviation of the slopes is, apparently, the condition that, in all our considerations, the same as in the theory of Stern, the forces of interaction between the adsorbed ions parallel to the interface are neglected. The adsorption isotherm for uncharged particles, taking into account this effect (Van der Waals' forces of attraction), was deduced and experimentally checked in the work of Frumkin already cited above [3].

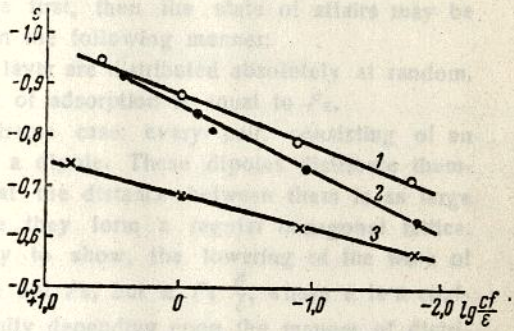


Fig. 5. Data from the work of Erdey-Gruz and Szervas: *1* — for NaJ; *2* — for NaCN; *3* — for NaBr.

But in the literature there are no investigations dealing with the analogous calculation for ionic adsorption [15]. In a private communication, Frumkin proposed the following explanation for the increased value of the slope (the authors of the present paper also uphold this explanation). The faster increase in the potential with the concentration than that which follows when one takes into account the electrical repulsion by the introduction of the term $F\varepsilon$, points to the fact that actually the action of the field on adsorption is less

[15] The state of affairs becomes at a first glance more complicated owing to the following circumstance. A calculation of the forces of mutual attraction (Van der Waals') between adsorbed, uncharged particles leads to a linear decrease in $\Phi$ with an increase in $\Gamma$. In our case of the preferential adsorption of ions of similar charge, an increase in $\Phi_-$ with $\Gamma_-$ (force of repulsion) could have been expected by analogy, *i. e.*, as a first approximation $\Phi_- = \Phi_-^0 + q\Gamma_-$, where $q > 0$. Since we assumed that $\Gamma_- \sim \varepsilon$, then the slope should have decreased:

$$\varepsilon \sim -\frac{RT}{F + qk_1} \ln c \,.$$

pronounced. Such a result may be expected if we take into consideration that the measured jump in the potential $\varepsilon$ is an average value of the potential over the whole surface. The work of adsorption depends upon the potential at that point at which the ion is present. As the result of mutual repulsion, other ions of the same sign which are present in the same plane will be farther from a chosen ion than they would be if the distribution were random; and the effect of their repulsion will be smaller.

If we make use of the picture of the double layer given in Fig. 1c, *i. e.*, all cations are present in the second layer and all anions are present in the first, then the state of affairs may be more exactly formulated in the following manner:

1) The ions in every layer are distributed absolutely at random. The lowering of the work of adsorption is equal to $F\varepsilon$.

2) The opposite extreme case: every pair, consisting of an anion and a cation, form a dipole. These dipoles distribute themselves in such a way that the distance between them is as large as possible — for example they form a regular hexagonal lattice. In this case, as it is easy to show, the lowering of the work of adsorption will already be not $F\varepsilon$, but $\alpha\ F\varepsilon\ \frac{d}{l}$, where $\alpha$ is a coefficient of the order of unity depending upon the manner of distribution of the dipoles, $d$ is the distance between the centers of a cation and an anion in one pair, and $l$ is the distance between pairs of ions along the plane. Since $d \ll l$, the lowering of the work may be much less than it is considered to be in Stern's theory, and this explains the results obtained.

Quantitative calculations, pointing out to what extent the picture of the double layer should approach (1) or (2), are difficult to carry out. In any case, it should lie somewhere between them.

Thus, evidently, it is somewhat premature to speak of a quantitative check of Stern's theory until that time when an adsorption isotherm will be given for ions, taking into account their forces of interaction in the adsorption layer.

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