The Capacity of a Mercury Electrode in Presence of Multivalent Cations

By *M. Vorsina* and *A. Frumkin*

M. Proskurnin and M. Vorsina[1] have developed a method for measuring the capacity of a mercury electrode by means of low frequency alternating current (one period per second) which, as shown by Vorsina and Frumkin[2], may be effectively applied at concentrations equal to 10^{-3} or 10^{-4}. Even at higher concentrations capacity measurements allow of a more detailed study of the relations between potential and surface conditions than is accessible, for instance, from electrocapillary data[3]. At lower concentrations the advantages of direct capacity measurements over other methods of investigation are particularly striking. It appeared therefore interesting to extend capacity measurements to other objects and in this connection multivalent cations seemed to be most promising, very little being known of their behaviour at the mercury/solution interface. Numerous data are found in the literature on the reversal of a negative surface charge by multivalent cations, this reversal being apparent from the electrokinetic behaviour and the stability of colloids, emulsions and suspensions. However the question remains as yet unsolved whether we are dealing in this case with a specific adsorption of cations, such as $La^{\cdots}$ or $Th^{\cdots\cdot}$, in amounts exceeding the negative surface charge, or with the presence at the interface of a layer of the corresponding hydroxide $La(OH)_3$ or $Th(OH)_4$. Electrocapillary curves of different multivalent cations have been obtained by Stifman[4] in the Electrochemical Laboratory of the Moscow University at concentrations ranging from 0.005 N upwards. These measurements, however, failed to produce sufficiently convincing evidence of specific cation adsorption. In the present investigation the influence of $Ba^{\cdot\cdot}$, $La^{\cdots}$ and $Th^{\cdots\cdot}$-ions on the capacity of the mercury electrode at various potentials and concentrations was studied. In order to secure a sufficient conductivity of the system 10^{-3} and 10^{-2} N HCl solutions were used as initial solutions, increasing quantities of salts with multivalent cations being subsequently added.

[1] Proskurnin and Vorsina, C. R. Acad. Sci. URSS, **24**, 915 (1939).
[2] Vorsina and Frumkin, ibid., 918; Frumkin, Trans. Faraday Soc., **36**, 123 (1940).
[3] Borissova and Proskurnin, Acta Physicochimica URSS, **4**, 819 (1936); Grahame, J. Amer. Chem. Soc., **63**, 1207 (1941); Ksenofontov, Proskurnin and Gorodetzkaya, Acta Physicochimica URSS, **9**, 39 (1938).

Method of measurements

Fig. 1 shows a diagram of the apparatus and electrical arrangement used in our measurements. It is essentially the same as that described by Proskurnin and Vorsina[5], and we shall mention here only a few alterations made in a later stage of the investigation. In the initial arrangement the measuring cell contained, beside the mercury electrode, an auxiliary platinum wire-net electrode for the polarization with alternating current and direct current and for measurements of the potential variations due to the passage of alternating current. In this case the measured capacity consists of two capacities connected in series, the first one being the capacity of the double layer at the surface of the mercury, and the second one that of the platinum electrode surface.

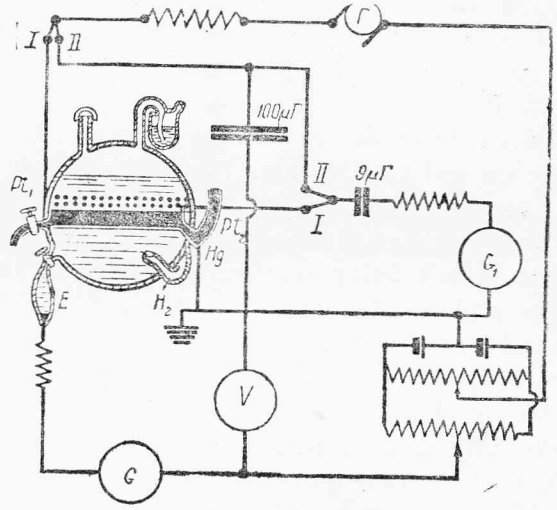


Fig. 1.

In order to exclude the influence of the latter, the surface of the platinum electrode must be made as large as possible. This may be attained, for instance, by covering it with platinum black,

[4] Stifman, Diss. Moscow University, 1939.
[5] loc. cit.

but platinum black saturated with hydrogen adsorbs a considerable amount of cations, thus vitiating the experimental results at low concentrations. Following a suggestion of M. Proskurnin[6] we preferred accordingly to introduce in the cell two platinum wire-net electrodes, one of them denoted by Pt_1 being used for the polarization with alternating current and direct current and the other one (Pt_2), placed at 1—1.2 mm. from the surface of the mercury, reserved to the measurement of the potential variations. Since the intensity of the current flowing in the measuring circuit, composed of a vibration galvanometer G_1 and a high resistance in series, was very low, the potential of the electrode Pt_2 remained practically constant. During the measurement the key was in position I; upon switching it to position II a standard capacity of 100 microfarads was introduced into the circuit for comparison with the unknown capacity.

Exclusion of the platinized electrodes decreases the adsorption effects, but at concentrations lower than $10^{-6}N$ adsorption on the walls of the vessel and on the surface of the platinum net is nevertheless quite noticeable. Our measurements were therefore limited to concentrations ranging from $10^{-5}N$ upwards. Each set of measurements was started with a solution of HCl or KCl, increasing quantities of salt being successively added to the initial solution. The space above the calomel electrode E, isolated by a stop cock and used for the determination of the potential of the mercury surface, contained the initial acid solution throughout the experiments. After each series of measurements the potential of this electrode was checked against a normal calomel electrode. All the potential values φ quoted in the present paper are referred to the latter electrode, unless mention be made of the contrary. A correction calculated according to Henderson's formula was made, when necessary, for the diffusion potential at the interface between the pure acid and the solution in the vessel containing additional salt.

The alternating component of the polarization $p_\sim$ which was directly measured in these experiments equals

$$p_\sim = \sqrt{\frac{i^2}{\omega^2 C^2} + r^2 i^2}$$

where i is the intensity of the alternating current flowing in the solution, ω—the circular frequency, C— the capacity in farads

[6] The authors are very much indebted to M. Proskurnin for valuable suggestions in the experimental part of the present research.

and r—the resistance of the solution between the surface of the mercury and the electrode Pt_2. In more dilute solutions the correction term comprising r is to be taken into account, the value of r being, with that aim, determined directly with a current of higher frequency.

The results of the experiments were substantially influenced by the quality of the water used for the solutions. If the conductivity water used was kept for some time in glass vessels, the negative branch of the curve showed a maximum characteristic for multivalent cations, a certain amount of the latter being, apparently, washed out of the glass.

After the apparatus had been filled, the solutions were purified by cathodic polarization of the mercury surface applied during a considerable length of time, the surface of the mercury in the apparatus being thereafter renewed. All the measurements were carried out in an atmosphere of hydrogen.

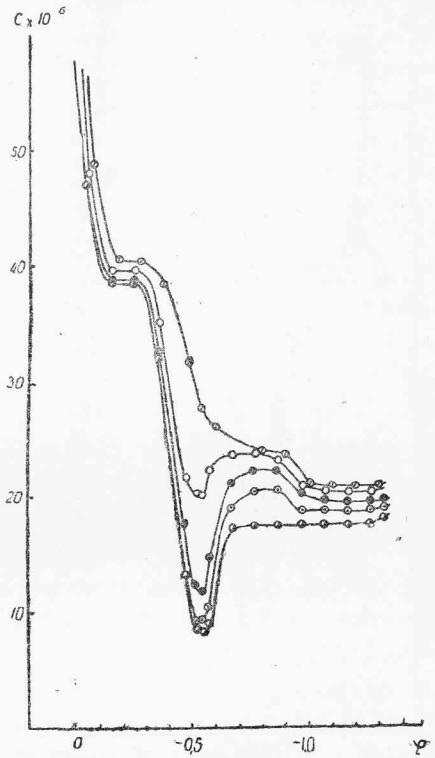
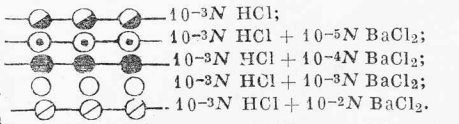


Fig. 2. Relation between capacity and potential in $10^{-3}N$ HCl + $BaCl_2$ solutions.

Experimental data

Curves representing the relation between the potential and the capacity in a 10^{-3} N HCl solution with varying additions of $BaCl_2$, $LaCl_3$ and $ThCl_4$ are given in Figs. 2, 3 and 4. From these curves the following conclusions may be drawn.



On addition of multivalent cations the minimum value on the capacity curve in HCl *viz.* $C_{min} = 8 \times 10^{-6}$ corresponding to $\varphi_{min} = -0.51$ increases and, in the case of $La^{\cdots}$ and $Th^{\cdots\cdot}$ is somewhat shifted towards less negative potentials, as seen from

Table 1. The addition of $LaCl_3$ to $10^{-2}N$ HCl gives similar results, but in this case the initial value of C_{min} is higher and its change under the influence of multivalent cations affects the course of the curve in a lesser degree.

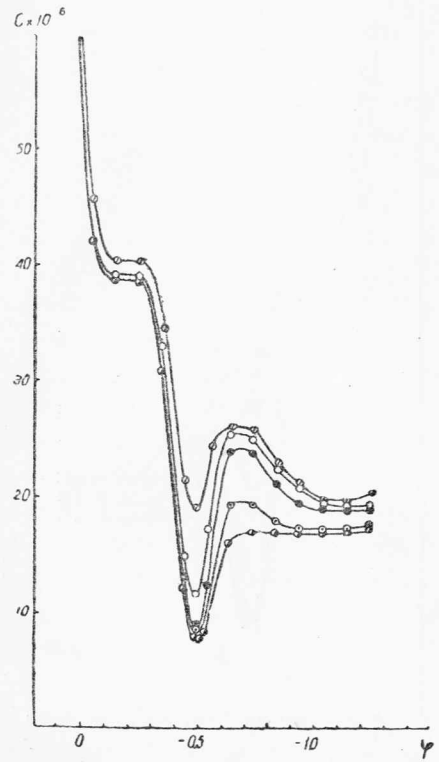


Fig. 3. Relation between capacity and potential in $10^{-3}N$ HCl+$LaCl_3$ solutions.

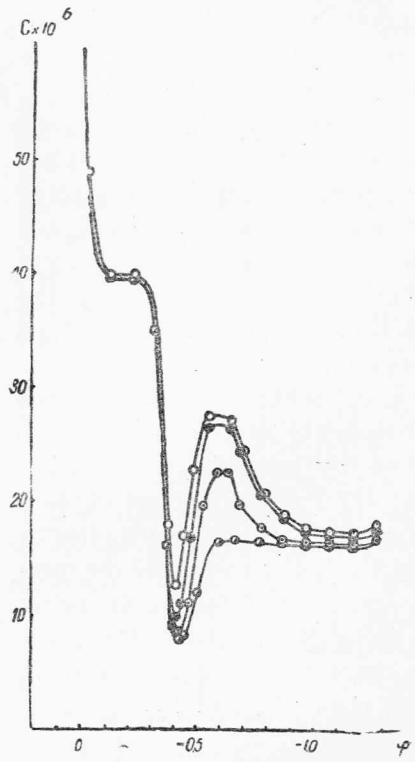


Fig. 4. Relation between capacity and potential in $10^{-3}N$ HCl+$ThCl_4$ solution.

- $10^{-3}N$ HCl;
- $10^{-3}N$ HCl + $10^{-5}N$ $LaCl_3$;
- $10^{-3}N$ HCl + $10^{-4}N$ $LaCl_3$;
- $10^{-3}N$ HCl + $10^{-3}N$ $LaCl_3$;
- $10^{-3}N$ HCl + $10^{-2}N$ $LaCl_3$.

- $10^{-3}N$ HCl;
- $10^{-3}N$ HCl + $10^{-5}N$ $ThCl_4$;
- $10^{-3}N$ HCl + $10^{-4}N$ $ThCl_4$;
- $10^{-3}N$ HCl + $10^{-3}N$ $ThCl_4$.

The change in the anodic branch, *i. e.* in the part of the initial capacity curve corresponding to positive surface charges ε, is not important and comprises only a region in the neighbourhood of the minimum; at less negative φ values no influence of the cations is observed and an increase in the capacity appears only upon addition

Table 1

Solution	$C_{min}\times10^6$	φ min	$C_{min}\times10^6$ calc. after eq. (5) and (6)	$C_{max}\times10^6$
$10^{-3}N$HCl	8.0	—0.51	5.5	
$+10^{-5}N$$ThCl_4$	8.6	—0.51		23.0
$+10^{-4}N$$ThCl_4$	10.2	—0.50	5.8	27.0
$+10^{-3}N$$ThCl_4$	12.9	—0.49	7.2	27.8
$+10^{-5}N$$LaCl_3$	8.2	—0.51		19.7
$+10^{-4}N$$LaCl_3$	9.0	—0.505		24.4
$+10^{-3}N$$LaCl_3$	11.6	—0.50		25.6
$+10^{-2}N$$LaCl_3$	19.0	—0.50	11.7	26.1
$+10^{-4}N$$BaCl_2$	9.3	—0.50		20.4
$+10^{-3}N$$BaCl_2$	11.6	—0.51		22.1
$+10^{-2}N$$BaCl_2$	20.2	—0.51		23.5
$10^{-2}N$HCl	14.7	—0.545	10.5	
$+10^{-5}N$$LaCl_3$	16.0			21.2
$+10^{-4}N$$LaCl_3$	16.9	—0.54		23.1
$+10^{-3}N$$LaCl_3$	17.3	—0.54		23.8
$+10^{-2}N$$LaCl_3$	19.3	—0.53		23.9

of considerable amounts of salts, being due to the increase in the total ion concentration of the solution.

The most marked effects are observed on the cathodic branch, *i. e.* at negative values of ε. Even small additions of multivalent cations bring about an abrupt rise of C leading to a maximum on the C, φ curve. The values of C_{max} are listed in Table 1. This effect depends in a high degree upon the valency of the cations. Thus C_{max} attains the value 23×10^{-6} at concentrations equal to $10^{-5}N$ for $ThCl_4$, $10^{-4.5}N$ for $LaCl_3$ and $10^{-2.4}N$ for $BaCl_2$ (interpolated values). At still more negative values of φ, $\frac{\partial\varepsilon}{\partial\varphi}$ having passed through a maximum falls again but remains on a higher level than that observed in the initial HCl solution. For instance, in this part of the curve in 10^{-3} N HCl, $C=17.2\times10^{-6}$ and in presence of $10^{-3}N$ $Ba^{\cdot\cdot}$, $La^{\cdot\cdot\cdot}$ or $Th^{\cdot\cdot\cdot\cdot}$ it ranges from 18.6 to 19.6×10^{-6}. Finally, at the highest cathodic polarizations a new rise of the capacity curve is observed. As already discussed in the cited paper of Borissova and Proskurnin, this effect is quite real in neutral solutions. In acid ones it is vitiated by electrolysis occurring at these potentials with evolution of hydrogen on the mercury. In the arrangement described there

always was a possibility of traces of platinum from the wire-net electrodes getting on the mercury, thus decreasing the overvoltage and facilitating the evolution of hydrogen. Under the conditions of our experiments this must bring about an apparent increase of the capacity. This part of the curve was therefore left out of consideration in the present research.

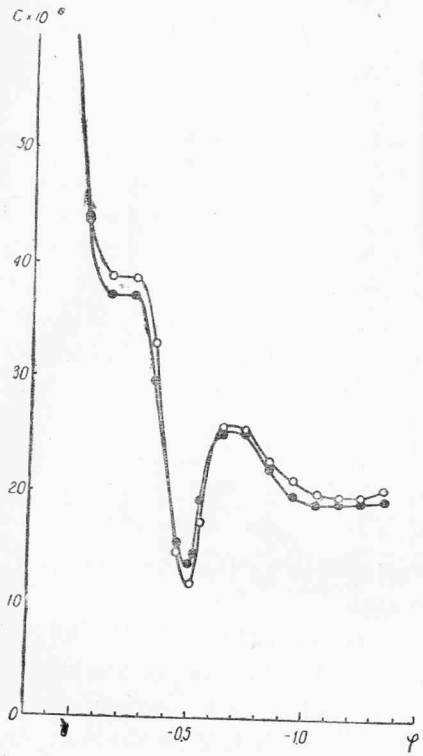


Fig. 5. Relation between capacity and potential in HCl and KCl solutions in presence of $LaCl_3$.

○ ○ ○ — $10^{-3}N$ HCl + $10^{-3}N$ $LaCl_3$;
● ● ● — $10^{-3}N$ KCl + $10^{-3}N$ $LaCl_3$.

As seen from Table 1 there is but little difference between the maximum values of C in solutions containing $LaCl_3$ at the same concentration and HCl at $10^{-2}N$ and $10^{-3}N$. It may be hence inferred that the particle adsorbed on the negative branch is not the hydroxide $La(OH)_3$ but the $La^{\cdots}$-ion. In order to prove this conclusion, additional measurements were carried out in $10^{-3}N$ solutions of KCl+$LaCl_3$. Curves corresponding to $10^{-3}N$ HCl + 10^{-3} $LaCl_3$ and $10^{-3}N$ KCl + $10^{-3}N$ $LaCl_3$ are represented in Fig. 5. As may be observed, the agreement is very close. The independence of the observed effect from the concentration of hydrogen ions, when the latter is varied in such wide limits, proves that the adsorption of hydroxide does not play any rôle in the examined effect.

Comparison with the Stern double layer theory. Calculation of the charge and of the ψ_1-potential

As shown by Vorsina and Frumkin[1] the curves of the differential capacity $C = \frac{\partial \varepsilon}{\partial \varphi}$ obtained in HCl and KCl solutions on the whole closely approach curves calculated according to the Stern theory,

assuming the capacity of the Helmholtz layer for the anodic branch to be 38×10^{-6}, and for the cathodic one -20×10^{-6}. The observed minimum value of the capacity C_{min}, however, considerably exceeds the calculated one[7].

It appeared of interest to extend this comparison to solutions containing multivalent cations. In calculating the dependence between $\frac{\partial \varepsilon}{\partial \varphi}$ and φ the equations of the Stern theory were used in the simplified form already applied by one of the authors[8] in a previous communication, *i. e.* without taking into account the specific adsorption and the covering of the surface with ions, and assuming the cation radii to be equal and the number of places in the Helmholtz layer to be determined by its thickness d which is taken equal to the diameter of a water molecule. The capacity of the Helmholtz layer, both for the positive and the negative branches, was assumed to be equal to 19×10^{-6}. As already mentioned, this value gives no satisfactory approximation for the positive branch. The interest, however, is centred chiefly on the negative branch. Calculations for solutions with multivalent ions being already very cumbersome, no attempt was made to take into consideration the variation of the capacity of the Helmholtz layer with the potential as it was done for a univalent electrolyte in the previous paper, referred to above. Under these conditions we obtain from the Stern double layer theory for solutions of the above mentioned composition the following expressions, where φ_a is the electrode potential measured from the potential of the zero charge point in absence of specific adsorption ($\varphi_a = \varphi + 0.50$), ε—the charge per unit surface of the electrode in coulombs per cm.^{2}, ε_1 and ε_2—the charges of the rigid and diffuse parts of the double layer, ψ_1—the potential at the distance of one ionic radius from the surface of the electrode, x—a dimensionless quantity equal to $\frac{\psi_1 F}{RT}$, c_1 and c_2—the respective concentrations of the univalent and multivalent cations in gram-equivalent per cm.^{3}, ν—the valency of the multivalent cation, and c_3—the concentration of the anion equal to $c_1 + c_2$:

$$\varepsilon = K(\varphi_a - \psi_1), \qquad (1)$$

[7] Vorsina and Frumkin, loc. cit., Frumkin, loc. cit.
[8] Frumkin, Z. physikal. Chem. (A), **164**, 421 (1933).

$$\varepsilon = -\varepsilon_1 - \varepsilon_2, \tag{2}$$

$$\varepsilon_1 = dF\,(c_1 e^{-x} + c_2 e^{-\nu x} - c_3 e^{x});$$

$$\varepsilon_2 = \pm \left(\frac{RTD}{2\pi}\right)^{1/2} \left[c_1\,(e^{-x}-1) + \frac{c_2}{\nu}\,(e^{-\nu x}-1) + c_3\,(e^{x}-1) \right]^{1/2}. \tag{3}$$

The sign of the value ε_2 is opposite to that of x. From equation (1) we obtain

$$\varphi_a = \frac{\varepsilon}{K} + \psi_1 = \frac{\varepsilon}{K} + \frac{RT}{F}x, \tag{4}$$

$$\frac{\partial \varepsilon}{\partial \varphi_a} = \frac{K\frac{\partial \varepsilon}{\partial x}}{\frac{\partial \varepsilon}{\partial x} + \frac{RT}{F}K}. \tag{5}$$

From equations (2) and (3) there follows:

$$\frac{\partial \varepsilon}{\partial x} = -\frac{\partial \varepsilon_1}{\partial x} - \frac{\partial \varepsilon_2}{\partial x} = dF\,(c_1 e^{-x} + \nu c_2 e^{-\nu x} + c_3 e^{x}) \pm \left(\frac{RTD}{2\pi}\right)(c_1 e^{-x} + c_2 e^{-\nu x} - c_3 e^{x}) \left[c_1\,(e^{-x}-1) + \frac{c_2}{\nu}\,(e^{-\nu x}-1) + c_3\,(e^{x}-1) \right]^{-1/2} \tag{6}$$

where $d = 3.1 \times 10^{-8}$ cm, $K = 19 \times 10^{-6}$ farads per cm.^{2} and $T = 291°$.

Substituting a set of x values into equations (4), (5) and (6) we obtain the corresponding values for $\frac{\partial \varepsilon}{\partial \varphi_a}$ and φ_a and may thus construct the C, φ_a curve. The results of these calculations for $c_1 = 10^{-6}$, $c_2 = 10^{-7}$ and 10^{-6} and $\nu = 4$ corresponding to $10^{-3}N$ HCl + $+10^{-4}N$ and $10^{-3}N$ $ThCl_4$ solutions are shown graphically in Fig. 6. It may be seen that in contradistinction to the observed ones, the calculated curves have no maxima. The effect of the multivalent cation is manifested only by a steeper slope of the curve on passing from zero to negative values of φ_a. The absence of a maximum on the calculated C, φ curve is independent of the choice of c_1 and c_2. An examination of the course of curves $-\frac{\partial \varepsilon_1}{\partial x}$ and $-\frac{\partial \varepsilon_2}{\partial x}$ shows that neither of them has a maximum in the region of negative values of φ_a and according to equations (5) and (6) the same obtains for $\frac{\partial \varepsilon}{\partial \varphi_a}$. This also appears from the following reasoning. With increase of the absolute value of φ_a $\frac{\partial \varepsilon}{\partial \varphi_a}$ approaches the limiting value K. Therefore, if a maximum is to appear on the $\frac{\partial \varepsilon}{\partial \varphi_a}$, φ_a curve, $\frac{\varepsilon}{\partial \varphi_a}$ must equal K at some finite value of φ_a. As seen from equation

(5) this is however only possible when $\frac{\partial \varepsilon}{\partial x} = \infty$. Thus, the existence of a maximum on the capacity curve in presence of multivalent cations cannot be deduced from the assumptions of the Stern theory. This statement is in no way affected by the introduction of a specific adsorption energy for the cations independent from the electric field, as it is done by Stern in his paper. We shall consider this question in more detail in a paper to be published shortly.

The last assumption moreover does not conform, as will be shown presently, with the position of the minimum on the observed $\frac{\partial \varepsilon}{\partial \varphi_a}$ curves. As seen from Table 1 the value of φ_{min} is but little affected by the addition of multivalent cations. The minimum of the capacity curve is somewhat shifted towards more positive potentials, the value of the shift, however, does not exceed 0.025. A similar and even larger shift of φ_{min}, as compared with values of the potential corresponding to $\varepsilon = 0$, appears on the $\frac{\partial \varepsilon}{\partial \varphi_a}$, φ_a curves calculated according to Stern on the above mentioned assumptions and is due to the asymmetry of these curves, caused by the unequal valency of the anion and the cation. For the $10^{-3}N$ HCl + $10^{-4}N$ $ThCl_4$ solution the calculated shift of φ_{min} equals 0.01 V, for $10^{-3}N$ HCl + $10^{-2}N$ $LaCl_3$ — 0.05 V.

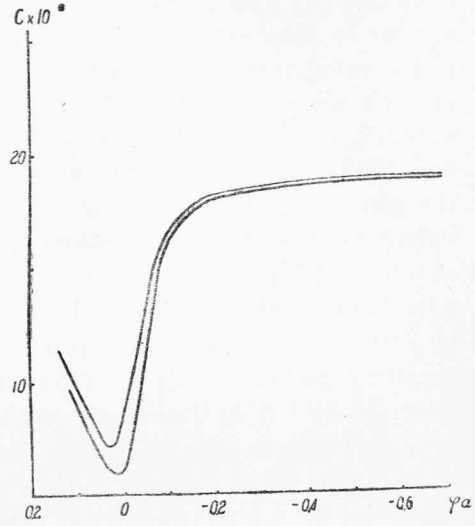


Fig. 6. Relation between capacity and electrode potential calculated according to the Stern theory.

Lower curve — $10^{-3}N$ HCl + $10^{-4}N$ $ThCl_4$.
Upper curve — $10^{-3}N$HCl + $10^{-3}N$ $ThCl_4$.

Thus, the observed shift of the capacity minimum does not exceed that calculated on the assumption of the absence of specific adsorption of the cation. Hence, it may be concluded that no appreciable shift of the zero charge point ($\varepsilon = 0$) occurs in dilute solutions of multivalent cations. The position of the zero point cannot, how-

ever, be directly determined from capacity curves. It should be expected that a specific adsorption of the cation will bring about a shift of the zero charge point towards positive φ values and simultaneously an additional shift of φ_{min} in the same direction (see the next paper of this series). The absence of an appreciable shift of the zero charge point in presence of multivalent cations at higher concentrations may be also deduced from Stifman's [9] electrocapillary measurements mentioned above. In 0.1 N solutions, where the potential of the maximum of the electrocapillary curve corresponding to the zero charge point can be determined with sufficient accuracy, the values $\varphi_0 = -0.49, -0.51, -0.495$ were obtained for $AlCl_3$, $La(ClO_4)_3$ and $ThCl_4$ respectively. From all these data it may be concluded that the zero charge point in dilute solutions of the chlorides of multivalent cations at concentrations c_1 and c_2 not exceeding $10^{-3}N$ lies at 0.5 V within 0.01 V. This corresponds to an approximately equal adsorbability of the anion and the cation. This value, which could be determined more accurately by means of high precision electrocapillary measurements in dilute solutions, shall be recurred to later. In 10^{-3} N HCl solutions without $La^{\cdots}$ and $Th^{\cdots\cdot}$ this point lies, probably, nearer to $\varphi = -0.51$.

In Table 1 some values of C_{min} are also confronted with values calculated according to the Stern theory. It may be seen from a comparison of column 2 and 4 that the increase of C_{min} due to the addition of $LaCl_3$ and $ThCl_4$ is considerably higher than the calculated one, this effect being observed at such concentrations of the added salt, where the influence of the Cl′-ions cannot yet be observed. In going over to negative surface charges of the electrode, a marked qualitative divergence is observed between the calculated and the observed C, φ curves. Its character will be made particularly clear by calculating ε and ψ_1 from the observed values of $\frac{\partial \varepsilon}{\partial \varphi}$. The value of ε was calculated according to equation

$$\varepsilon = \int_{\varphi_0}^{\varphi} \frac{\partial \varepsilon}{\partial \varphi} d\varphi \qquad (7)$$

where φ_0 is the value of φ at which $\varepsilon = 0$, it being assumed that, as already mentioned above, $\varphi_0 = -0.51$ for the initial HCl solution and $\varphi_0 = -0.50$ for solutions containing multivalent cations.

[9] Loc. cit.

An error in the determination of the position of the zero charge-point amounting to 0.01 V will cause an error in $\varepsilon \sim 10^{-7}$ coulombs/cm.^{2},

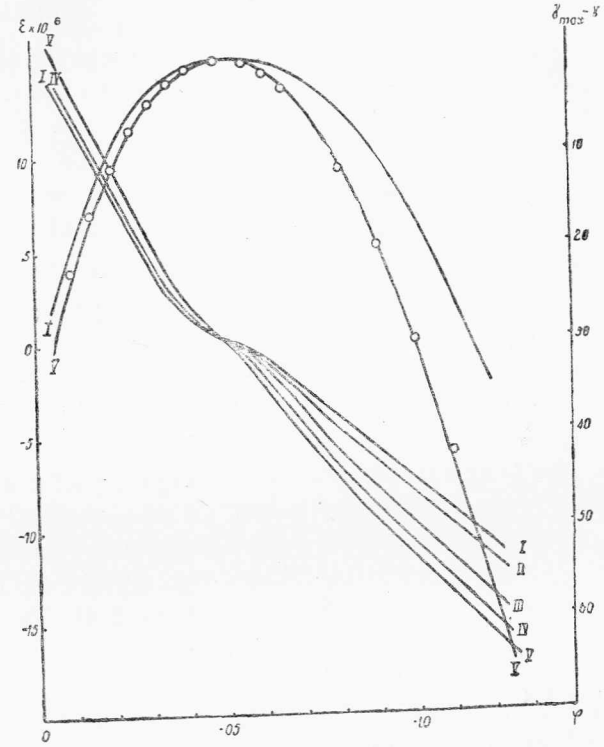


Fig. 7. Dependence of charge on electrode potential and electrocapillary curves calculated from capacity values in 10^{-3} N HCl+$LaCl_3$ solutions.

I — $10^{-3}N$ HCl; II — $10^{-3}N$ HCl + $10^{-5}N$ $LaCl_3$; III — $10^{-3}N$ HCl + $10^{-4}N$ $LaCl_3$; IV — $10^{-3}N$ HCl + $10^{-3}N$ $LaCl_3$; V — $10^{-3}N$ HCl + $10^{-2}N$ $LaCl_3$.

○ ○ ○ —experimental data for the electrocapillary curve in a $10^{-2}N$ $AlCl_3$ solution from measurements by Stifman.

i. e. of the order of 1 percent in the part of the curve under examination. A series of ε, φ curves for 10^{-3} N HCl solutions with increasing amounts of $LaCl_3$ is represented in Fig. 7. These curves clearly show the gradual disappearance, on addition of multivalent cations, of the medium part with a lesser slope which is characteristic for the diffuse structure of the double

layer and has already been described by Philpot[10]. For a detailed examination of the relation between the charge and the potential, curves representing the value $C_i = \frac{\varepsilon}{\varphi - \varphi_0}$ plotted against φ should be used preferably to the ε, φ curves. The value C_i may be designated as integral capacity in contradistinction to the differential capacity $C = \frac{\partial \varepsilon}{\partial \varphi}$ which is determined experimentally.

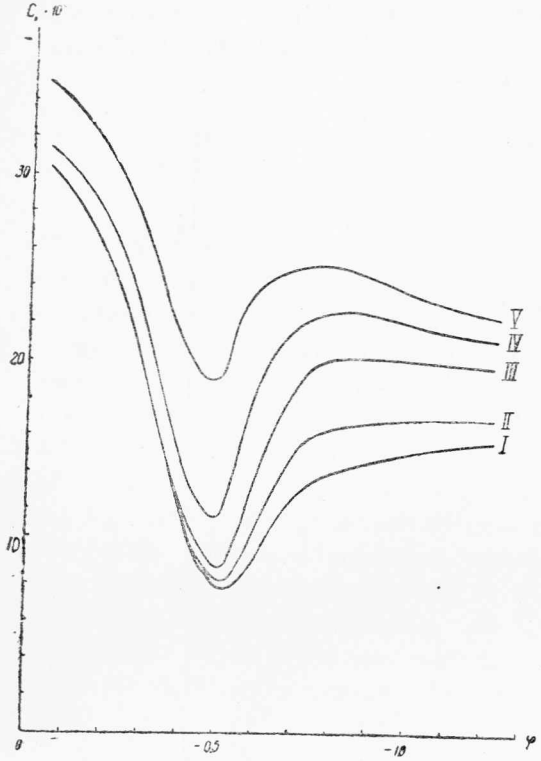


Fig. 8. Pelation between integral capacity and electrode potential in $10^{-3}N$ CHI+$LaCl_3$ solutions.
I — $10^{-3}N$ HCl; *II* — $10^{-3}N$ HCl + $10^{-5}N$ $LaCl_3$; *III* — $10^{-3}N$ HCl + $10^{-4}N$ $LaCl_3$; *IV* — $10^{-3}N$ HCl + $10^{-3}N$ $LaCl_3$; *V* — $10^{-3}N$ HCl + $10^{-2}N$ $LaCl_3$.

The value $\frac{\varepsilon}{\varphi - \varphi_0}$ may be considered as the capacity of a condenser, whose potential and charge equal respectively the potential drop due to the ions of the double layer and the total charge of these ions. This interpretation, is, however, justified only if the potential drop in the double layer vanishes at $\varepsilon = 0$, *i. e.* in absence of specific adsorption effects, or in other words, when $\varphi - \varphi_0$ coincides with φ_a, as it is practically observed in the considered cases.

A series of $\frac{\varepsilon}{\varphi - \varphi_0}$, $(\varphi - \varphi_0)$ curves for higher concentrations have been calculated by Grahame[11]. Fig. 8 shows curves of the

[10] Philpot, Phil. Mag., **13**, 775 (1932).
[11] Grahame, J. Amer. Chem. Soc., **63**, 1207 (1941); Grahame, however, applies this method of calculation also to electrolytes with surface active ions such as NaI. The examination of his curves clearly shows that in this case the calculated value of the integral capacity has no physical meaning.

integral capacity for 10^{-3} *N* HCl and 10^{-3} *N* HCl with $LaCl_3$. It may be observed from Fig. 8 that in passing from the differential to the integral capacity the maximum on the negative branch does not disappear. Since $\varepsilon = C_i(\varphi - \varphi_0)$, we have $\frac{\partial \varepsilon}{\partial \varphi} = C_i + \frac{\partial C_i}{\partial \varphi}(\varphi - \varphi_0)$ and the existence of a maximum in $\frac{\partial \varepsilon}{\partial \varphi}$ is not necessarily dependent on the existence of a maximum of C_i, but may be brought about by an abrupt change in C_i in a definite interval of φ values. It is well known that such maxima of $\frac{\partial \varepsilon}{\partial \varphi}$ are observed, for example, in solutions containing adsorbable organic substances. It follows from the above said that maxima obtained in presence of multivalent cations do not belong to this group. The physical meaning of these maxima becomes much clearer if the value of ψ_1 is calculated from the observed C,φ curves by means of equation (1). This equation is valid under assumptions which are more general than is the case for the other equations of the Stern theory, the only condition imposed being that of a proportionality between the charge and the mean potential drop in the Helmholtz part of the double layer. Provided the examination of the curve is limited to the part in which the rigid layer contains only cations (practically only cations with several charges), and the potential drop is not yet high enough to bring about a noticeable deformation of the latter, this assumption may be justified to a considerable extent. As to ψ_1 it may be calculated according to the equation

$$\psi_1 = \varphi_a - \frac{\varepsilon}{K} = \frac{K\varphi_a - \varepsilon}{K} \qquad (8)$$

or graphically, as shown by one of the authors in a previous publication[12].

In carrying out this calculation two possible sources of error are to be borne in mind, due to the inaccuracy in the determination of the zero charge point and of the value K. The first one is of no great consequence since an error in φ_0 of order 0.01 with $\left(\frac{\partial \varepsilon}{\partial \varphi}\right)_{\min} \sim 10 \times 10^{-6}$ leads to an error in ψ_1 of order 0.005. The choice of the K values involves far greater difficulties. In solutions which do not contain multivalent cations an increase in cathodic polarization is accompanied by a rise of the value C, owing to the decrease in the

[12] Frumkin, Trans. Faraday Soc., **36**, 123 (1940).

diffuseness of the double layer. In presence of multivalent cations a decrease of C is observed at sufficiently high cathodic polarizations. As seen from the course of the C_i,φ curves this is related to the gradual disappearence of the disturbance of the double layer structure causing an increase of the capacity. In both cases the magnitude of the capacity must approach the value K, but from different sides. In the examined solutions the experimental values of C at high cathodic polarizations lie within the limits $16.5-20.5\times10^{-6}$, depending on the concentration of multivalent cations, a distinct scattering, due doubtless to experimental errors, having to be considered. The majority of the values lies within the limits $17-19.8\times10^{-6}$, and K must be taken within the same limits. For subsequent calculations the value $K=19\times10^{-6}$ was selected as being in better accord with the conclusions derived from the theory of overvoltage[13]. In this case, however, the possible error will be not less than 5 %, which, according to equation (8), may lead to an error in the evaluation of ψ_1 equal to 0.025 for $\varepsilon=10^{-5}$, and to 0.05 for $\varepsilon=2\times10^{-5}$. As seen from equation (8), if the values $\frac{\partial\varepsilon}{\partial\varphi}$ and K become close to each other even the course of the change of ψ_1 with the potential cannot be reliably determined. It is therefore expedient to limit the application of equation (8) to an interval of negative values of φ_a not exceeding $0.4-0.5$ V. This equation cannot either be used for positive φ_a values because of the considerable difference between the K values for positive and negative surface charges. Fig. 9 shows ψ_1,φ curves calculated for $10^{-3}N$ HCl with addition of various $LaCl_3$ amounts. As may be observed, at not too low concentrations of $La^{\cdots}$ the course of these curves is very different from that of the initial HCl solution. From a definite φ value ψ_1 no longer becomes more negative with further cathodic polarization; after having passed through a minimum it begins to increase and passes from negative values to positive ones. Calculations show that the course of the ψ_1,φ curves is the same for other K values within the mentioned limits, notwithstanding some difference in the absolute values. In contradistinction to what should be expected from the Stern theory in the case of specific adsorption of the cation, when the work of adsorption is independent from the electric field, positive ψ_1 values are observed

[13] Frumkin, Acta Physicochimica URSS, 18, 23 (1943).

not at a zero charge, but at considerable negative charges of the surface.

The adsorption process bringing about the charge reversal of the surface takes place only if the cation is attracted by the electric field of the electrode surface. Owing to this character of the relation between the value of this additional adsorption and the potential, the value of ψ_1 becomes zero twice within a considerable interval of multivalent ions concentrations, firstly, near the point $\varphi=-0.5$ and, secondly, at considerably more negative φ values for instance $\varphi=-0.72$ in a $10^{-3}N$ HCl + $10^{-4}N$ $LaCl_3$ solution.

However, the increase of the negative surface charge above a certain limit is also followed by a relative decrease of the described effect. As seen from Fig. 9 after reaching a certain limit the value of ψ_1 no longer increases with $|\varphi-\varphi_0|$ and even diminishes, causing thereby a decrease of the integral capacity.

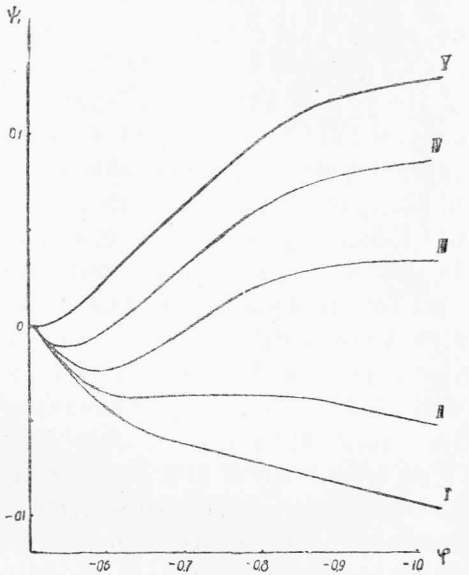


Fig. 9. ψ_1-potentials calculated from capacity measurements in relation to electrode potentials in $10^{-3}N$ HCl + $LaCl_3$ solutions.

I — $10^{-3}N$ HCl;
II — $10^{-3}N$ HCl + $10^{-5}N$ $LaCl_3$;
III — $10^{-3}N$ HCl + $10^{-4}N$ $LaCl_3$;
IV — $10^{-3}N$ HCl + $10^{-3}N$ $LaCl_3$;
V — $10^{-3}N$ HCl + $10^{-2}N$ $LaCl_3$.

Since the course of the C, φ curves at considerable negative potentials shows no appreciable change in the value of the capacity of the Helmholtz layer in presence of multivalent cations, the occurrence of values of the integral capacity exceeding $19-20\times10^{-6}$ as well as that of positive ψ_1 values, may be accounted for only in assuming the existence in the double layer of two potential drops of opposite signs: metal surface /cation layer and cation layer/solution. In order to render this picture quantitatively more precise, the values of the cation and anion adsorption Γ_c and Γ_a at the surface of the electrode in moles per cm² should be determined in addition

to ε, these three values being obviously related by the expression $\varepsilon=(n_a\Gamma_a-n_c\Gamma_c)\,F$. The values Γ_c and Γ_a may be determined from the relation between surface tension and concentration, sufficiently accurate determinations of this kind at low concentrations presenting however some difficulties. The determination of Γ_c and, consequently, that of Γ_a exclusively by means of electrical measurements is only possible on introducing auxiliary assumptions on the nature of the part of the double layer turned towards the solution. If we suppose the Cl′-ions to be disposed in the energetically most advantageous positions, the double layer will be composed in the case of $LaCl_3$ of a layer of La‴-ions adjacent to the mercury surface and of Cl′-ions adjoining some of the La‴-ions in points located at the farthest distance from the surface of the metal. The capacity of the part formed by La‴- and Cl′-ions may be considered as resulting from the connection in series of two condensers having respectively the capacities 19×10^{-6} and 38×10^{-6} which are observed for normal Helmholtz layers at the surface of mercury in the case of La‴ -and Cl′-ions; on this assumption it will equal $12.7\times$ $\times10^{-6}$. In a $10^{-3}N$ $HCl+10^{-3}N$ $LaCl_3$ solution at $\varphi_a=-0.5$, $\psi_1=$ $=0.085$, $\varepsilon=-11.1\times10^{-6}$. With this picture of the double layer structure there results $\Gamma_aF=0.085\times12.7\times10^{-6}=1.08\times10^{-6}$ and $\Gamma_cF={}^1/_3\times12.18\times10^{-6}=4.06\times10^{-6}$. Consequently, the total adsorption of ions $\Gamma_a+\Gamma_c$ equals $\frac{1}{F}\times5.14\times10^{-6}$. With the same potential drop and a non-diffuse double layer of normal structure we should have obtained $\varepsilon=-0.5\times19\times10^{-6}=-9.5\times10^{-6}$ and $\Gamma_a+\Gamma_c=\Gamma_c=\frac{1}{F}\times3.16\times10^{-6}$. From the viewpoint of the theory of electrocapillary phenomena the ratio $\frac{\Gamma_a+\Gamma_c}{n_c\Gamma_c-n_a\Gamma_a}$ is of interest, since the product of this value into $\frac{RT}{F}\ln\frac{c'}{c''}$ equals the difference between the potentials of the electrode corresponding to the electrolyte concentrations c' and c'', the interfacial tension remaining constant. For a normal non-diffuse layer the value of this ratio in a $LaCl_3$ solution must equal 0.33 whereas for the above mentioned values of Γ_c and Γ_a it is 0.46. These conclusions may be checked by means of sufficiently accurate measurements of electrocapillary curves.

Available electrocapillary measurements may be compared only

with the results of measurements at relatively high concentrations of multivalent cations. In so doing our procedure differed from that generally adopted, *i. e.* instead of comparing the value of C with the second derivative $\frac{d^2\gamma}{d\varphi^2}$ [14], which requires an exceptionally high precision of electrocapillary measurements, we made the converse calculation of the electrocapillary curves from experimental values of C. As already mentioned above, we determined first the value of ε and then that of $\gamma_{max}-\gamma$ according to the equation

$$\gamma_{max}-\gamma=\int_{\varphi_0}^{\varphi}\varepsilon d\varphi$$

where γ_{max} is the interfacial tension in the maximum of the electrocapillary curve. Fig. 7 shows the electrocapillary curve of 10^{-2} N $LaCl_3+10^{-3}$ N HCl calculated in this way, together with the curve obtained by Stifman from direct measurements in a 10^{-2} N $AlCl_3$ solution. The agreement is very satisfactory. As was to be expected, the value of γ is not appreciably affected by the nature of the trivalent cation. An analogous agreement between the calculated and the measured electrocapillary curves was also observed in the case of 0.01 N $ThCl_4$. The electrocapillary curve for 10^{-3} N HCl calculated from capacity measurments is also given in the same figure. Comparison of the descending branches of the two curves in Fig. 7 shows the value of the interfacial tension in dilute solutions to be strongly influenced by the valency of the cation.

Structure of the double layer in presence of multivalent cations

From measurements of the capacity of a mercury electrode in dilute solutions in presence of multivalent cations the following conclusions may thus be drawn.

Multivalent cations are adsorbed on the negatively charged surface of the electrode in amounts exceeding the equivalent of the negative surface charge. This effect is most pronounced at medium values of the charge, corresponding to a potential drop in the double layer approximating -0.3 V, the relative value decreasing at higher potentials. The adsorption of multivalent cations does not cause

[14] Proskurnin and Frumkin, Trans. Faraday Soc., **31**, 110 (1935); Borissowa and Proskurnin, Acta Physicochimica URSS, **4**, 819 (1936); Grahame, J. Amer. Chem. Soc., **63**, 1207 (1941).

a marked shift of the zero charge point of the electrode. The value of the adsorption effect is practically independent from the concentration of the hydrogen ions in the solution. The surplus adsorption of cations (with respect to the charge of the surface) must be accompanied by a simultaneous adsorption of anions.

Different effects have been recently reported which occur during electrolysis with a mercury cathode and bear evidence of the adsorption of anions by a negative surface in presence of multivalent cations. So for instance the reduction of anions on a mercury cathode is considerably facilitated (*i. e.* the reduction potential becomes less negative) in presence of multivalent cations. This effect was observed in the reduction of the anions NO_3', NO_2', BrO_3', IO_3'. Heyrovsky[15] and coworkers explained it on the assumption of complexes or ionic pairs of the type $La^{\cdots}$ $(NO_3)''_2$ being formed in these cases in the solutions, thus allowing the anion to be brought near to the negatively charged surface. They also considered the decrease in the negative values of the ζ-potential as a factor facilitating the adsorption of anions. According to Orlemann and Kolthoff complexes of the type $(BaIO_3)'$ are formed. As shown by one of the authors[16] the value of the cathodic polarization on anion discharge in presence of multivalent cations must decrease by $\frac{1+\alpha}{\alpha}\zeta'$, where ζ' is the potential in the point where the centre of the anion is located and α is comprised between 0 and 1. It was thereby assumed that in the vicinity of a multivalent cation ζ' may reach considerable positive values. Stifman[17] has shown that in presence of $Al^{\cdots}$- and $Th^{\cdots\cdot}$-ions a certain difference is observed between the values of interfacial tension in KI and KCl solutions on the descending branches of electrocapillary curves, the latter, as well known, coinciding in absence of such ions. Hence, it also follows that the formation of a double layer on the negatively charged surface in solutions containing multivalent cations is accompanied by an adsorption of anions. No such effect was however observed on direct investigation of the adsorptive behaviour of negative hydrogen charcoal

[15] Heyrovsky, Actualités scientifiques et industrielles, **90**, Paris, (1934); Tokuoka et Ruzicka, Coll. trav. chim. Tchecoslovaquie, **6**, 339 (1934); Orleman and Kolthoff, J. Amer. Chem. Soc., **64**, 1907 (1942).
[16] Froumkine, Actualités scientifiques et industrielles, Paris, (1936).
[17] Loc. cit.

in $ThCl_4$ solutions[18]. The cause of this discrepancy between values relating to negatively charged charcoal and mercury is yet not clear. The concepts of the double layer structure in solutions containing multivalent cations, which were developed in connection with the study of anion electroreduction may also be used to interpret some peculiarities in the relation between capacity and potential observed in these solutions.

We shall begin by assuming that the solutions contain ionic pairs of the type $La^{\cdots}$ Cl'. The adsorbability of such pairs on the uncharged surface will be but slight. They will be attracted by a negatively charged surface, most of the adsorbed pairs being orientated normally to the surface, the cation being turned towards the surface of the mercury and the anion towards the solution. This will result in positive ψ_1 values, and, consequently, in all the phenomena described in the first part of the present paper. At higher values of the negative charge of the surface these ionic pairs will be more and more displaced by $La^{\cdots}$-ions which have a higher positive charge, thus decreasing the capacity of the double layer. The concept of ionic pairs playing a part in the formation of the double layer thus affords an adequate interpretation of the basic peculiarities of the capacity curves. It fails, however, to account for the fact that the reversal of the charge of negative surfaces may be also observed by electrokinetic methods. This bears evidence of the presence of a certain surplus positive charge in the layer adjacent to the electrode, which may be separated from the corresponding negative charges in a tangential electric field. This would be impossible should all the anions in the double layer be bound with cations forming ionic pairs. It is, however, highly probable that the formation of ionic pairs is not indispensible for the occurrence of charge reversal and that the latter may be derived from more general concepts on the structure of the double layer.

As shown above this does not follow from the Stern theory of the double layer. Stern's theory, however, takes no account of the fact that the part of the double layer which is turned towards the solution consists of discrete ions. Although the theory formally takes into account the radii of the ions, they only contribute to determine the volume of that part of the double layer where the adsorption of the

[18] Piloyan, Krivorutschko u. Bach, Koll. Z., **64**, 287 (1933).

ions may occur, the actual calculation of the electric potential being made, as it were, on the assumption of the electric charges being distributed uniformely instead of being fixed on discrete particles. Consequently, the potential is considered as a function of the distance from the surface, and not as a function of the distance from separate ions. This circumstance has been repeatedly mentioned in the literature[19], but up to now there is no quantitative theory of the double layer accounting for its discrete structure. A few qualitative conclusions may, however, be drawn, which are of interest in solving the problem considered. Let us assume that the electrolyte in the

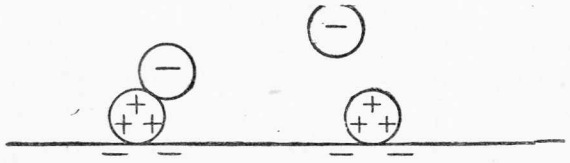


Fig. 10. Schematic picture of the double layer structure in presence of multivalent cations.

solution has a strongly asymmetrical structure, consisting, for instance, of positive cations with a large number of charges and of univalent anions. This being the case, the interaction between the electric fields of separate ions may be disregarded in first approximation and the double layer must have the structure represented in Fig. 10. One part of the lines of force starting from the positive charges will be terminated on the negative charges of the surface and another part—on the anions in the solution. Obviously, in this case the number of positive charges in the double layer exceeds that of the negative charges on the surface of the metal, thus giving rise to the phenomenon of charge reversal. However a total disregard of the interaction between the fields of separate ions does not either lead to exact results. Indeed, in this case the double layer could exist only if the work of cation adsorption were positive and independent from ε and from the mean value of the potential. Cations should be in particular also adsorbed at a surface on the average uncharged, *i. e.* at $\varepsilon=0$. It has however been shown in the present investigation that such

[19] *Cf.* Frumkin, Phys. ZS. d. Sowjetunion, 4, 256 (1933), where the discrete structure of the double layer is also considered in connection with the charge reversal. See also Essin and Shikhoff, J. Phys. Chem. (Russ.) (in press).

an adsorption does not occur or at any rate is very feeble. Thus the structure of the double layer in electrolyte solutions with multivalent cations must actually conform to a picture intermediate between that of Fig. 10 and that underlying the Stern theory, and must approach the former with increase of the valency of cations. At high values of the surface charge density the distance between the positive ions decreases, the structure of the double layer approximates that assumed in the Stern theory and the relative magnitude of the charge reversal effect must decrease.

Summary

The differential capacity of the surface of a mercury electrode in dilute solutions of $BaCl_2$, $LaCl_3$ and $ThCl_4$ has been measured. Throughout the examined cases capacity maxima were observed at potentials corresponding to not very high negative values of the surface charge. The magnitude of the surface charge, that of the potential at the distance of one ionic radius from the interface and the equivalent capacity of the electrode were calculated from experimental data. These calculations show that the presence of multivalent cations brings about a reversal of the negative charge of the electrode surface. Possible interpretations of this effect have been discussed from the viewpoint of the double layer theory.

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Received
March 2, 1943.