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Influence of the Anion on the Capacity of a Mercury Electrode in Dilute Solutions

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We have shown in our preceding paper¹ that measurements of the capacity of a mercury electrode in dilute solutions of multi-valent cations allow of observing some hitherto unknown adsorption phenomena. In connection with these results it appeared promising to extend these measurements to solutions of salts with different anions. Although this part of the investigation could not be performed with sufficient completeness, some of the results obtained present undoubted interest. The experimental method was the same as in the cited investigation. In order to destroy organic admixtures, all the salts used were heated to 450—500°, KBr and KI in an atmosphere of hydrogen. Hydrogen bromide solutions were prepared from gaseous HBr and NaOH solutions by decomposition of sodium amalgam prepared electrolytically. The results of the measurements are represented in Figs. 1, 2, 3, 4 and 5 and in Table 1, where values of the minimum capacity $C_{\min}$ and of the corresponding electrode potential $\varphi_{\min}$ referred to a normal calomel electrode are given.

The last column contains the values of the minimum capacity, calculated according to the Stern theory without taking into account the specific adsorption.

From equation (6) of our preceding paper we have for $\left(\frac{\partial \varepsilon}{\partial x}\right)_{\min}$ in the case of a uni-univalent electrolyte:

$$\left(\frac{\partial \varepsilon}{\partial x}\right)_{\min} = 2cdF + \left(\frac{RTD}{2\pi}\right)^{1/2} c^{1/2}$$

and, similarly, for a uni-bivalent electrolyte:

$$\left(\frac{\partial \varepsilon}{\partial x}\right)_{\min} = 3cdF + \left(\frac{3}{2}\right)^{1/2} \left(\frac{RTD}{2\pi}\right)^{1/2} c^{1/2},$$

¹ Vorsina and Frumkin, Acta Physicochimica URSS, **18**, 242 (1943).

Table 1

Solution	$C_{\min} \times 10^6$	$\varphi_{\min}$	$C_{\min} \times 10^6$ calculated according to equation (1)
$2 \times 10^{-4} N$ NaOH	4.3	-0.49	2.9 (3×10^{-6})
$10^{-3} N$ NaOH	7.2	-0.465	5.5 (5.9×10^{-6})
$10^{-2} N$ NaOH	15.3	-0.465	11.0 (11.7×10^{-6})
$10^{-3} N$ Na ₂ SO ₄	7.4	-0.475	6.3
$10^{-2} N$ Na ₂ SO ₄	13.8	-0.50	12.0
$10^{-4} N$ H ₂ SO ₄	4.2	-0.50	2.5
$10^{-3} N$ H ₂ SO ₄	8.1	-0.50	
$10^{-2} N$ H ₂ SO ₄	14.4	-0.50	
$10^{-3} N$ KCl	7.9	-0.51	
$10^{-2} N$ KCl	14.7	-0.52	
$10^{-4} N$ HCl	3.9	-0.51	2.1 (2.15×10^{-6})
$10^{-3} N$ HCl	7.9	-0.51	
$10^{-3} N$ KBr	11.9	-0.56	
$10^{-4} N$ HBr	5.3	-0.51	
$10^{-2} N$ HBr	11.4	-0.56	
$10^{-5} N$ KI + $10^{-3} N$ HCl . .	15.4	-0.56	

hence, according to equation (5) from the same paper:

$$C_{\min} = \frac{K \left(\frac{\partial \varepsilon}{\partial x} \right)_{\min}}{\left(\frac{\partial \varepsilon}{\partial x} \right)_{\min} + \frac{RT}{F} K} \quad (1)$$

by means of which taking $K = 19 \times 10^{-6}$ the calculated values for $C_{\min}$ given in Table 1 were obtained. It will be seen that the observed values for $C_{\min}$ are always higher than the calculated ones, $C_{\min}$ increasing with increasing adsorbability of the anion. Thus, at the concentration $10^{-3} N$, $C_{\min}$ equals 7.2×10^{-6} in NaOH, 7.9×10^{-6} in KCl and 11.9×10^{-6} in KBr. At $c = 10^{-4} N$, $C_{\min} = 3.9 \times 10^{-6}$ in HCl and 5.3×10^{-6} in HBr. At the concentration $10^{-2} N$ in presence of Br⁻-ions the capacity curves show no minimum at all and in presence of I⁻-ions (Fig. 5) the minimum disappears already at $10^{-4} N$.

The discrepancies between the calculated and the observed values of $C_{\min}$ are least of all for electrolytes which, like NaOH,

do not decrease, or, like Na₂SO₄, even increase the interfacial tension at the mercury solution boundary at the zero charge point. This discrepancy may be still somewhat lowered, if in calculating

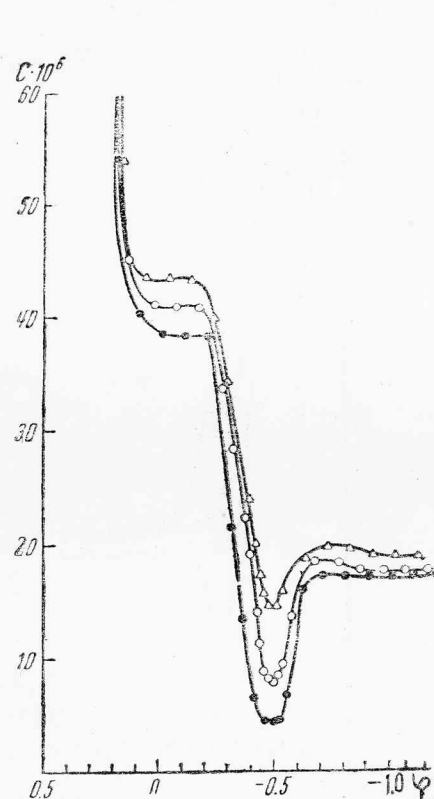


Fig. 1. Relation between capacity and potential in H₂SO₄ solutions.

●—●—● 10⁻⁴ N H₂SO₄;
○—○—○ 10⁻³ N H₂SO₄;
Δ—Δ—Δ 10⁻² N H₂SO₄.

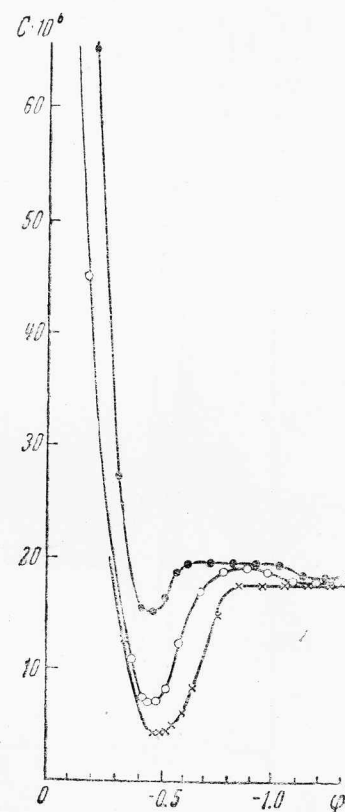


Fig. 2. Relation between capacity and potential in NaOH solutions.

×—×—× 2 · 10⁻⁴ N NaOH;
○—○—○ 10⁻³ N NaOH;
●—●—● 10⁻² N NaOH

$C_{\min}$ we do not take $K = 19 \times 10^{-6}$ but assume that the capacity of the Helmholtz layer is higher in presence of anions than in presence of cations.

This has already been done in the first part of this investigation², where, consequently, modified equations of the Stern theory were deriv-

² Vorsina and Frumkin, C. R. Acad. Sci. URSS, **24**, 918 (1939).

ed and numerical calculations for $K_1 = 38 \times 10^{-6}$ and $K_2 = 20 \times 10^{-8}$ performed, these values corresponding to the positively and negatively charged surface respectively. The values of $C_{\min}$ obtained

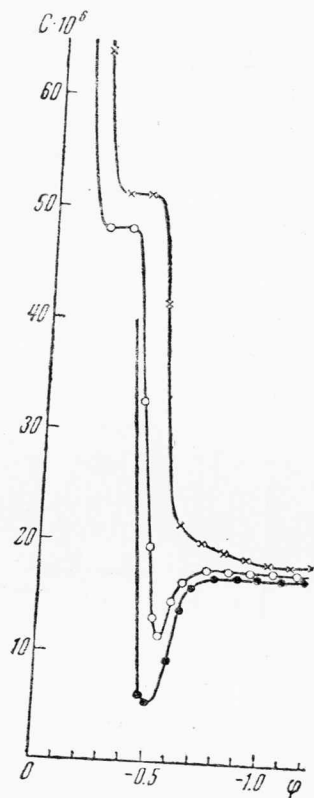


Fig. 3. Relation between capacity and potential in HBr solutions.

●—●—● 10⁻⁴ N HBr;
○—○—○ 10⁻³ N HBr;
×—×—× 10⁻² N HBr.

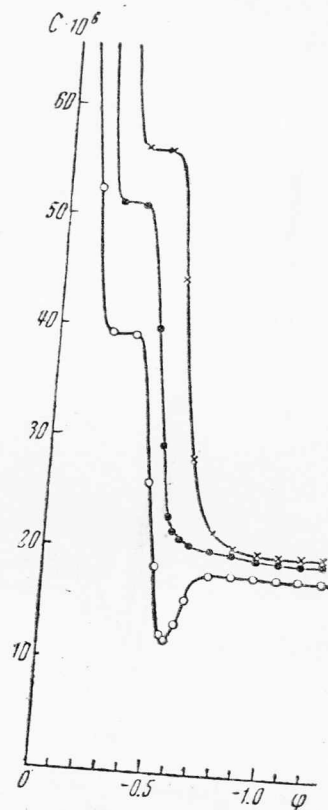


Fig. 4. Relation between capacity and potential in KBr solutions.

○—○—○ 10⁻³ N KBr;
●—●—● 10⁻² N KBr;
×—×—× 10⁻¹ N KBr.

in this way are given in brackets in the last column in Table 1. It may be seen however that even with this correction the observed values of $C_{\min}$ are still higher than the calculated ones. As will be shown later the specific adsorption of ions must result in an increase of the minimum capacity. The increased capacity observed in the case of electrolytes causing a rise of interfacial tension, such as Na_2SO_4 , suggests that, beside the negative adsorption in the layer

immediately adjacent to the surface of the metal, there exists at greater distances a definite positive specific adsorption, which leads to a rise of concentration of the ions as compared with values that should arise under the influence of the electric field alone.

The position of the point of minimum capacity on the abscissae is similarly influenced by the adsorbability of the anion, as can be seen from the values of $\varphi_{\min}$ in Table 1. In solutions of electrolytes with anions showing no specific adsorption on the surface of mercury (OH^- , SO_4^{2-}) at a concentration equalling $10^{-3}N$, values of $\varphi_{\min}$ are observed lying between -0.47 and -0.50 ; in $10^{-3}N$ KCl $\varphi_{\min} = -0.51$, and in $10^{-3}N$ KBr $\varphi_{\min} = -0.56$. In the case of KI the shift of $\varphi_{\min}$ to -0.56 is observed already at $10^{-5}N$. It would be most interesting to compare the observed values of $\varphi_{\min}$ with the position of the zero charge point φ_0 in the same solutions, but although the determination of the latter value is quite possible even at considerable dilutions, no corresponding experimental data for sufficiently dilute solutions are actually available. From electrocapillary measurements in $1N$ solutions we have for $\text{KOH} - 0.47$, $\text{K}_2\text{SO}_4 - 0.48$, $\text{H}_2\text{SO}_4 - 0.51$, $\text{KCl} - 0.56$, $\text{KBr} - 0.65$ and for $\text{KI} - 0.82$. At $c = 0.01N$ the corresponding values are for $\text{NaCl} - 0.52$, $\text{NaBr} - 0.58$ and $\text{KI} - 0.66$ ³.

Comparison of $\varphi_{\min}$ and φ_0 shows that a change in the nature

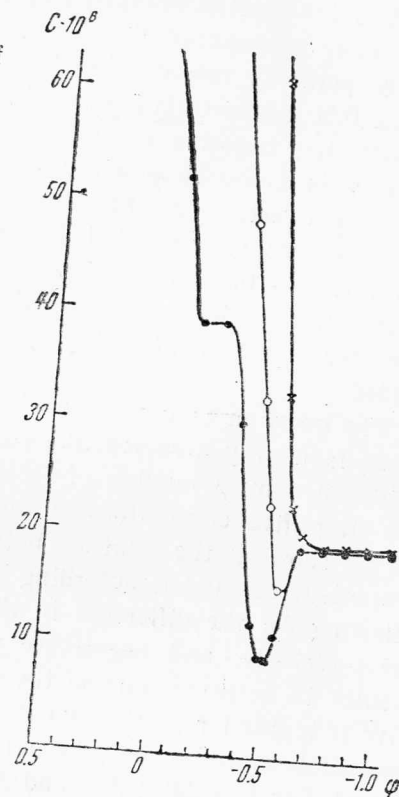


Fig. 5. Relation between capacity and potential in $10^{-3}N$ HCl + KI solutions.

●—●—● 10⁻³ N HCl;
○—○—○ 10⁻³ N HCl + 10⁻⁵ N KI;
×—×—× 10⁻³ N HCl + 10⁻⁴ N KI.

³ The data for $c = 0.01N$ are taken from a paper by Essin and Shikhov, J. Phys. Chem. (Russ.), 17, 236 (1943).

of the anion causes a change of both values in the same direction. As far as one may judge from values obtained in KBr and NaBr solutions, which were unfortunately of different concentration, the effect of the specific adsorption of the anion on $\varphi_{\min}$ appears somewhat more pronounced than on φ_0 . If the assumption that the zero charge point of mercury in absence of specific adsorption lies at $\varphi_0 = -0.50$ is correct, it is somewhat disconcerting that both $\varphi_{\min}$ and φ_0 have less negative values in NaOH, Na_2SO_4 , and K_2SO_4 solutions. This could be possibly accounted for by assuming in these solutions a certain specific adsorption of the cations exceeding that of the anions or else that in absence of specific adsorption φ_0 lies not at -0.50 , but at somewhat less negative values of the potential. In order to solve definitely this problem, more accurate measurements of both φ_0 and $\varphi_{\min}$ in dilute solutions are needed.

The question as to the position of the minimum on the capacity curve is notably involved, the values of both $\varphi_{\min}$ and $C_{\min}$ being determined by a number of factors, even if we limit ourselves to the simplified conceptions of the Stern theory. In our first paper curves showing the relation between capacity and potential were presented, calculated according to the modified Stern theory and allowing for the difference in the capacity of the Helmholtz layer for positively and negatively charged surfaces. This discrepancy results in an asymmetry of the capacity curve, and, since the capacity is higher for positively charged surfaces, $\varphi_{\min}$ is shifted towards potentials corresponding to a negative charge of the surface of the metal. For $K_1 = 38 \times 10^{-6}$ and $K_2 = 20 \times 10^{-6}$ the following magnitude of the $\varphi_{\min}$ shift with respect to the zero charge point were calculated: $c = 10^{-4}N - 0.01$, $c = 10^{-3}N - 0.02$, $c = 10^{-2}N - 0.05$. In the second paper an examination of phenomena observed in multivalent cation solutions showed that an increase of the valency of one of the ions similarly brings about a shift of the capacity minimum towards potentials at which the adsorption of this ion is lowered. This effect is however not large, even for electrolytes of the ThCl_4 type. Undoubtedly, the position of the capacity minimum and the value of minimum capacity are much more influenced by the specific adsorbability of one of the ions. The reason for this becomes apparent from an examination of the equations of the Stern theory, although it gives only a very rough approximation in the case of

specific anion adsorption⁴. In the case of specific anion adsorption and with a low degree of covering of the surface, we obtain for the value of the surface charge for an electrolyte with univalent cation [see in our preceding communication equations (2) and (3)]:

$$\varepsilon = -\varepsilon_1 - \varepsilon_2, \quad (2)$$

$$\varepsilon_1 = dFc(e^{-x} - e^{v_a x + \Phi_-/RT}), \quad (3)$$

$$\varepsilon_2 = \pm \left(\frac{RTD}{2\pi} \right)^{1/2} c^{1/2} \left[(e^{-x} - 1) + \frac{1}{v_a} (e^{v_a x} - 1) \right]^{1/2}, \quad (4)$$

where c is the concentration of the electrolyte in g.-eq. per cm^3 , v_a —the valency of the anion, and Φ_- —its work of adsorption. In the case of a univalent anion the expression for the charge of the diffuse layer takes as well known the particularly simple form

$$\varepsilon_2 = \left(\frac{RTD}{2\pi} \right)^{1/2} c^{1/2} (e^{-x/2} - e^{x/2}). \quad (4a)$$

It follows from the expressions for ε_1 and ε_2 that for Φ_- differing from zero, the minima of $-\frac{\partial \varepsilon_1}{\partial x}$ and $-\frac{\partial \varepsilon_2}{\partial x}$ correspond to different values of x ; for $v_a = 1$ the minimum of $-\frac{\partial \varepsilon_1}{\partial x}$ corresponds to $x = -\frac{\Phi_-}{2RT}$, and that of $-\frac{\partial \varepsilon_2}{\partial x}$ to $x = 0$. Moreover, since both values increase rapidly with increase of their distance from the minimum, the minimum value of $\frac{\partial \varepsilon}{\partial x}$, according to equation (2), exceeds considerably the sum of the minimum values of $-\frac{\partial \varepsilon_1}{\partial x}$ and $-\frac{\partial \varepsilon_2}{\partial x}$.

Since the law of decrease with increasing distance from the interface of the forces giving rise to the specific adsorption of ions is different from that of the electric field in the double layer, this conclusion must hold for any concept of the double layer structure. In the case of specific anion adsorption the smoothing of the minimum is still increased by the increase of capacity due to the substitution of anions for cations, so that at higher concentrations of surface-active anions the minimum disappears altogether. From

⁴ Essin and Shikhov, loc. cit.; Essin and Markov, J. Phys. Chem. (Russ.), **13**, 318 (1939); Whitney and Grahame, J. Chem. Phys., **9**, 827 (1941).

equations (2), (3) and (4a) the value of $x_{\min}$ corresponding to $\left(\frac{\partial \varepsilon}{\partial x}\right)_{\min}$ may be determined and, consequently, that of $C_{\min}$

$$dFc(e^{-x_{\min}} - e^{x_{\min} + \Phi_-/RT}) + \left(\frac{RTD}{2\pi}\right)^{1/2} c^{1/2} \times \frac{1}{4} (e^{-x_{\min}/2} - e^{x_{\min}/2}) = 0. \quad (5)$$

It follows from (5) that the value of $x_{\min}$ coincides with the value of x at which, in a solution with a concentration 16 times as large as that of the solution considered, the value of ε becomes zero. Thus

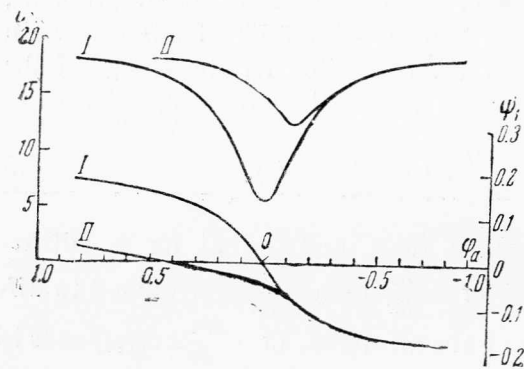


Fig. 6. Influence of specific adsorption of the anion on the capacity and the ψ_1 potential, according to the Stern theory ($K = 19 \times 10^{-6}$, $c = 10^{-6}$ g.-eq. per cm^3).

I—capacity and ψ_1 potential in absence of specific anion adsorption; II—the same quantities for $\Phi_- = 8RT$.

than the zero charge point, i. e. that the shift of this point, brought about by specific adsorption, must be more pronounced than that of the zero charge point.

Fig. 6 shows the dependence of $c = \frac{\partial \varepsilon}{\partial \varphi_a}$ on φ_a , i. e. on the electrode potential measured from the zero charge point in absence of specific adsorption, calculated by means of equations (2), (3) and (4a) and the relationship

$$\varphi_a = \frac{\varepsilon}{K} + \frac{RT}{F} x, \quad (6)$$

assuming $\nu_a = 1$, $K = 19 \times 10^{-6}$, $c = 10^{-6}$ g.-eq. per cm^3 , $\Phi_- = 8RT$ (upper curve) and for comparison $\Phi_- = 0$ (lower curve). The value $(\varphi_a)_{\min}$ for $\Phi_- = 8RT$ equals -0.12 , which in Table 1 corresponds to

the value $x_{\min}$ is more negative than that, which corresponds to the zero charge point in the same solution, and at the minimum of capacity the charge is negative, and, consequently, $\varphi_a < \psi_1$ [see equation (1) of the preceding paper]. Since, further, in the zero charge point $\varphi_a = \psi_1$, it follows from the above said that the capacity minimum lies at a more negative potential φ_a

$\varphi_{\min} = -0.62$. For this case, as shown by the calculation, the zero charge point lies at $\varphi_a = -0.065$. Thus, the shift of the latter point is actually less than the shift of the capacity minimum. $C_{\min}$ equals 12.4×10^{-6} instead of 5.5×10^{-6} , a value which is obtained in absence of specific adsorption ($\Phi_- = 0$). Fig. 6 shows also the ψ_1 potentials in relation to φ for both values of Φ_- . As should be expected, the specific adsorption of the anion brings about a shift of the ψ_1 potential towards more negative values as compared with the case of non-active electrolytes, the zero point for ψ_1 thus being shifted towards positive φ_a values. For $\Phi_- = 8RT$, $\psi_1 = 0$ corresponds to $\varphi_a = 0.47$. Speaking in terms of colloid chemistry this point may be called the isoelectric point of the metal, and the zero charge point—the isoionic point. In the case of specific adsorption the isoionic and isoelectric points of the metal thus become shifted in opposite directions as referred to the zero value of φ_a . The curves in Fig. 6 present a clear picture of the effect of the specific adsorption on the course of $\frac{\partial \varepsilon}{\partial \varphi}$; for comparison with experimental data it would be more expedient to take into account simultaneously the effect of specific adsorption and of the change in the capacity of the Helmholtz layer, due to the substitution of anions for cations. Following the way indicated in our previous paper, the value of K in equation (6) is to be considered as a function of x determined by the relation (for $\nu_a = 1$):

$$K = (K_1 e^{x + \Phi_-/RT} + K_2 e^{-x}) : (e^{x + \Phi_-/RT} + e^{-x}). \quad (7)$$

Equations (6), (7), (2), (3) and (4a) together with the relationship

$$\frac{\partial \varepsilon}{\partial \varphi_a} = \frac{\partial \varepsilon}{\partial x} \cdot \frac{\partial \varphi_a}{\partial x}$$

permit to express φ_a and $\frac{\partial \varepsilon}{\partial \varphi_a}$ through x and, consequently, to determine the relationship between $\frac{\partial \varepsilon}{\partial \varphi_a}$ and φ_a for this somewhat more complicated case.

For SO_4^{2-} , Cl^- and Br^- anions delays are observed on the positive branches of the curves, in a certain measure similar to the horizontal parts on the negative branches. As it may be seen from the curves for KCl presented in our first paper, an increase in concentration results in the appearance of a maximum and a minimum

instead of the delay on the C, φ curve. The experimental data are however too scarce to allow of expressing a definite opinion on the corresponding adsorption processes.

Summary

1. The magnitude of the minimum value of the differential capacity and of the corresponding value of the potential in dilute solutions depend on the adsorbability of the anion. The increase of the latter is followed by an increase of the minimum capacity, and the position of the minimum is shifted towards more negative potentials. In presence of strongly adsorbed anions (I') at not too low concentrations, the minimum on the capacity curve disappears altogether.

2. The values of minimum capacity observed in electrolyte solutions, which do not lower the interfacial tension at the mercury/solution boundary and in which the specific adsorption of anions is, consequently, least marked (NaOH , Na_2SO_4), still considerably exceed the values calculated from the double layer theory.

3. A qualitative interpretation of the effect of specific adsorption of anions on the magnitude and position of the capacity minimum may be given on the basis of the Stern double layer theory.

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