

ELECTROCHEMISTRY OF SILVER IODIDE¹
THE CAPACITY OF THE DOUBLE LAYER AT THE SILVER
IODIDE-WATER INTERFACE

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I. INTRODUCTION

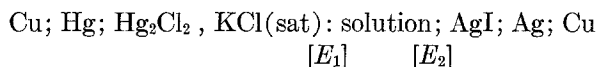
Extensive and accurate data on the properties of the electrical double layer on mercury have been collected by several investigators (e.g., by Grahame (1) and by Frumkin (2)). Data on other double layers are much more scanty. It is the purpose of the present paper to extend the existing data on silver iodide (Verwey (3), Verwey and Kruyt (4), De Bruijn (5), van Laar (6), Mackor (7)) particularly by using a greater variety of counter ions and co-ions.

Silver iodide has an important advantage over mercury as a subject for study of electrochemical properties of interfaces, in that the properties of colloidal AgI (e.g., stability, electrophoresis) are well known and are available for comparison with electrochemical data. It has the disadvantage (compared to mercury) that the range over which the interfacial potential difference can be varied is much less (ca. 450 mv. as compared to 2400 mv.).

II. EXPERIMENTAL PART

a). Outline of Method

The first aim of the experiments was the determination of the surface charge (σ) as a function of the potential difference across the interface. The galvanic cell:



¹ Based on the doctor's thesis of J. Lyklema, "Adsorptie van Tegenionen" (Adsorption of Gegenions), Utrecht, 1957.

² The second author expresses his gratitude to the Petroleum Research Fund for supporting his stay at the University of Southern California, Los Angeles 7, California, in 1959-1960 during which this paper was written.

was used for this purpose. The e.m.f. of this cell, E_{cell} , reflects any changes in the properties of the solution through E_1 and E_2 . When the concentrations in the solution are not too high E_1 can be kept virtually constant (see below), in which case

$$dE_{\text{cell}} = dE_2. \quad [1]$$

The changes in the solution involved variations in the concentrations of the potential-determining (Ag^+ , I^-) ions and in the concentrations and natures of indifferent ions. The ionic strength of the solution was kept constant during the process first mentioned.

The surface charge is defined through

$$\sigma = F(\Gamma_{\text{Ag}^+} - \Gamma_{\text{I}^-}), \quad [2]$$

in which Γ_{Ag^+} and Γ_{I^-} represent the number of equivalents of silver and iodide ions, respectively, adsorbed per square centimeter. These quantities can be found from a simple material balance when the concentrations of Ag^+ or I^- ions are known; these in turn can be evaluated directly from E_{cell} .

The surface charge, defined by [2], is the thermodynamic analog of the electrical charge on the mercury interface in surface electrochemical investigations. It is identical with the true surface charge provided Ag^+ and I^- are the only specifically adsorbed ions.

It should be kept in mind that calibrations have to be carried out for each type and concentration of electrolyte in order to allow for variations in the liquid junction potential, E_1 , and in the activity coefficients of the potential-determining ions.

In order to increase the available adsorbing surface the solution contained a suspension of finely divided silver iodide, which must be in equilibrium with the silver iodide of the electrode.

It is customary and advantageous to choose the zero point of charge (z.p.c.) as the reference point for E_2 and σ ; $E_2 - E_2(\text{z.p.c.})$ will be called ψ , the double layer potential. The z.p.c. can be determined by several independent methods. For silver iodide in dilute solutions of monovalent electrolytes at 25°C., van Laar (6) found it to be located at

$$-\log C_{\text{I}^-} = P_{\text{I}^-} = 10.56. \quad [3]$$

From $d\sigma$ and dE_2 the differential capacity of the double layer C is found through

$$C = \frac{d\sigma}{dE_2}. \quad [4]$$

b). *Essential Parts of the Experimental Setup*

The actual measurements consist in determinations of E_{cell} after addition of successive small amounts of a silver or an iodide salt solution. As

it takes a long time before the adsorption equilibrium is established, particularly near the equivalence point, the establishment of one single adsorption isotherm may require several days, during which the liquid junction potential E_1 must be constant and reproducible. Errors resulting from the contamination of the solution by KCl from the salt bridge (and consequent precipitation of AgCl) must therefore be minimized. This was achieved by using a salt bridge as described previously by van Laar (8). In this salt bridge, in which the mixture of KNO_3 and NaNO_3 (8) is substituted by a saturated KCl solution, the KCl is discharged under a known excess pressure through a very narrow hole into the solution. In our case only 1.3×10^{-8} g.-equivalents of KCl per hour were introduced into about L/4 of the solution. In lengthy experiments a small correction for precipitated AgCl was inevitable. The adsorption capacity of the AgCl, however, was negligible.

The silver iodide electrodes were prepared electrolytically essentially after De Bruijn (5a). Their standard potentials remained constant within 0.1 mv. during a couple of titrations, and within 1 or 2 mv. for a year or longer.

The purest chemicals commercially available were used. In most cases they were of AnalaR quality. Whenever necessary they were recrystallized until the chloride impurity was small compared with the amount of chloride introduced by the salt bridge.

The e.m.f.'s were measured with a Philips pH-meter (type GM 4491) at 20°C. under standard conditions of stirring and an excess pressure of 1 atm. on the KCl. Readings were generally reproducible within 0.3 mv.

Recent unpublished experiments in our laboratory by R. S. Hansen and B. H. Bijsterbosch resulted in incompletely reversible adsorption isotherms of deviating shapes. Though the origin of these irregularities is not yet fully understood they have probably to do with impurities of the reagents. In order to confirm the reliability of the results described in this paper, E. J. van Tellinghen and D. van Wijngaarden conducted some experiments on AgI which was filtered off once after charging it negatively and once after charging it positively in the hope of discarding all charged impurities (surfactants, chloride, etc.). Though their isotherms still deviated slightly from the ones published here at the silver side of the z.p.c. in 10^{-3} KNO_3 solution, the 10^{-1} isotherms of this paper and especially the influence of the nature of the counter ion (Li, K, Rb) were confirmed within experimental error.

c). Surface Area and Aging

In order to transform the adsorption into a specific surface charge the specific surface area of the suspension must be known. None of the methods used, however, is felt to be entirely satisfactory. In the methods where the AgI precipitate has to be dried, as in the B.E.T. gas adsorption methods, the surface area might be changed irreversibly. In the "wet" methods, such as the methylene blue adsorption, the area per adsorbed molecule is

rather uncertain. The situation is further complicated by the decrease of the adsorption capacity on aging.

In the subsequent section a surface area of 5.76 m.²/gram is used. This value was found by an indirect method, namely, by measuring the differential capacity of AgI per gram at the z.p.c. in 10⁻³ M KF or NaF solution and by assuming that the differential capacity per square centimeter of AgI under these conditions is the same as that for Hg. The latter value is known from the work of Grahame (1). This assumption is based on the consideration that in dilute electrolyte solutions at the z.p.c. the total capacity per square centimeter should be governed chiefly by its diffuse part and this should be independent of the nature of the interface. The great similarity of capacities on AgI and mercury under these conditions near the z.p.c. provides some experimental justification for this assumption.

We have tried to check this surface area by means of some direct adsorption methods (Table I) but none of these methods is accurate enough to allow more than a confirmation of the order of magnitude.

In methods 2, 3, and 4 use was made of the molecular area of the adsorbed molecules on coal. The first value of method 5 was calculated with a molecular area of the methylene blue molecule of 197 Å.² (Graham, on coal (9)), the second one with 386 Å.² (v. d. Heuvel, on BaSO₄ (10)).

From a theoretical point of view the sixth method is outstandingly attractive. This method was previously used by Schofield (11) on clay suspensions. It is based on the expulsion of co-ions (e.g., SO₄²⁻ ions from a negatively charged surface). The relative concentration increment of repelled ions written as $\Delta c/\sqrt{c}$ is proportional to the surface area. The advantages of this method are: (a) it measures a surface area in the conditions of experimental interest (wet); (b) it measures what may be regarded as the "electrochemical" surface; (c) the co-ion distribution can

TABLE I
Surface Area Determination of AgI Suspensions

No.	Method	Temp.	AgI sample		Surface area (m. ² /g.)
			Condition	Age	
1	Double layer capacity	Room	Wet	100 days	5.76
2	BET with N ₂ -vapor	-196°C.	Dried	Freshly prepared	12
3	BET with CCl ₄ -vapor	Room	Dried	Very old	0.85
4	BET with benzene vapor	Room	Dried	100 days	4-6
5	Ads. of methylene blue	Room	Wet	100 days	3.8; 7.4
6	Negative adsorption of sulfate ions	Room; 5°C.	Wet	100 days	5-6

be exactly calculated by the Gouy-Chapman theory. However, the experimental precision so far obtained has been low owing principally to the small values of $\Delta c/\sqrt{c}$ so that the agreement between areas obtained in this way with those obtained from double layer capacitance must be fortuitously good.

III. RESULTS AND DISCUSSION

a). Double Layer Capacities in Solutions of Monovalent Symmetrical Electrolytes

The adsorption of potential-determining ions on AgI expressed as σ as a function of ψ is given in Fig. 1 for three concentrations of KF. (It is known from the work on mercury (1) that the fluoride ion shows no tendency to specific adsorption; the same is expected to be true for AgI.)

The isotherms of Fig. 1 are independent of the direction in which σ and ψ are changed. In the study of a given electrolyte, the curves were established as follows. The suspension was made positive by addition of some AgNO_3 , the salt concentration adjusted, and then titrated, with a KI solution to the extremity of the measurable range at the negative side. The electrolyte concentration was then increased to $10^{-1} M$ and titrated backward as far as possible. The point of intersection with the abscissa of the 10^{-1} curves, found in this way appeared to be displaced slightly (generally less than 10 mv.) from that of the 10^{-3} curves. This can be attributed either to a shift of the z.p.c. with the electrolyte concentration or to (an accumulation of) experimental errors. To make isotherms comparable the 10^{-1} curve was shifted parallel to the abscissa; this means that the z.p.c. in 10^{-1} solutions was taken equal to that of 10^{-3} solutions. The ones last mentioned were, in turn, taken to correspond to the value of Van Laar (see Section II, *a*).

The manipulation has only a minor influence on the capacity (slope of the curve).

On the silver side of the z.p.c. a correction had to be made for silver ion consumed by precipitation of AgCl , the chloride being delivered by the salt bridge. For justification of this correction see Section III, *c*.

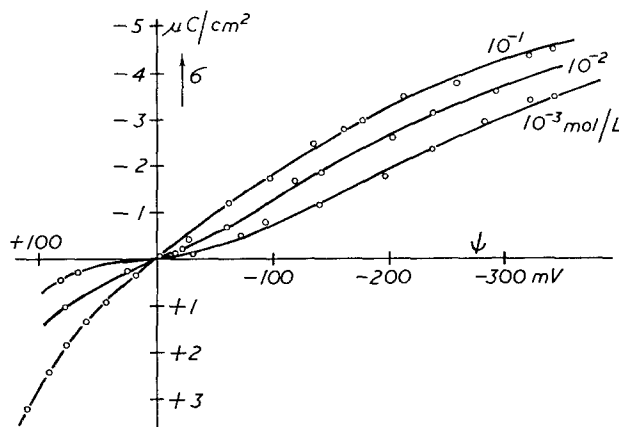


FIG. 1. Adsorption of I^- and Ag^+ ions on AgI in solutions of KF.

The adsorption isotherms show a close resemblance to similar isotherms obtained previously in NaClO_4 (Mackor (7c)) and $\text{KNO}_3 + \text{NaNO}_3$ mixtures (Van Laar (6)). There is also some analogy with isotherms on mercury (Grahame (1)) or on silver sulfide (Iwasaki and de Bruyn (12)).

By graphical differentiation of the isotherms of Fig. 1 the corresponding differential capacities are obtained. They are presented in Fig. 2. By way of comparison the theoretical diffuse double layer capacity Cd as calculated from the Gouy-Chapman theory is given in Fig. 2 (dotted line) for 10^{-3} and $10^{-2} M$ solutions of a monovalent binary electrolyte.

The observed capacity C closely resembles the theoretical Cd in solutions of low concentration near the z.p.c.

This is exactly what must be expected from the Gouy-Stern theory. According to this theory the double layer consists of a diffuse and a non-diffuse part. Their capacities Cd and Cm , respectively, are in series, and provided there is no specific adsorption:

$$\frac{1}{C} = \frac{1}{Cd} + \frac{1}{Cm}. \quad [5]$$

The value of Cd can be calculated to be

$$Cd = \sqrt{\frac{\epsilon n e^2}{2\pi k T}} \cosh\left(\frac{y}{2}\right), \quad [6]$$

in which ϵ is the dielectric constant, n the number of ions of either sign per milliliter in the bulk, e the elementary charge, k the Boltzmann con-

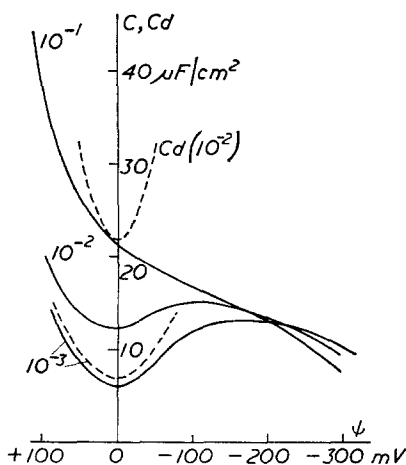


FIG. 2. Differential capacity C of the double layer on AgI in 10^{-3} , 10^{-2} , and $10^{-1} M$ KF-solutions as a function of the potential. Dotted lines: capacity Cd according to the diffuse double layer theory.

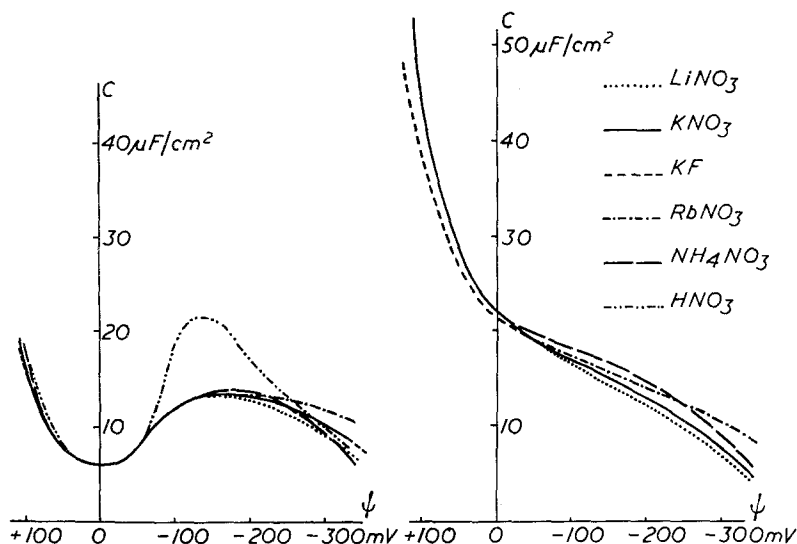


FIG. 3. Differential capacity of the double layer on AgI in solutions of some monovalent nitrates and KF. *a.* 10^{-3} mole/l. *b.* 10^{-1} mole/l.

stant, T the absolute temperature, and $y = e\psi_s/kT$. The potential ψ_s on the boundary between the diffuse double layer and the molecular condenser can be calculated from

$$\sigma = \sqrt{\frac{2en^0kT}{\pi}} \sinh \frac{y}{2}. \quad [7]$$

As follows from Fig. 2 the total capacity is smaller than the diffuse one. This is in agreement with Eq. [5]. Especially at very high potentials $Cd^{-1} \sim 0$ (see Eq. [6]), and the capacity is governed predominantly by its nondiffuse part, which appears to be independent of the electrolyte concentration, as was also found to be the case for mercury (1).

The capacity rises sharply as the AgI is made increasingly positive. For mercury such a behavior is due to specific adsorption of anions. The behavior of AgI may have the same explanation. At any rate we shall limit our considerations mainly to negative surfaces.

All capacity curves show some tendency to decrease at very high negative potentials. This can possibly be attributed to the fact that the adsorption of I^- ions on AgI proceeds only on active centers which will be saturated long before the total surface area is occupied. A further discussion of this possibility is published elsewhere by one of us (13).

The influence of the nature of the counter- and co-ion is illustrated in Fig. 3, from which the following may be read:

a. As expected all capacities merge in the region where the diffuse part of the double layer prevails.

b). The influence of the co-ion is negligible within the experimental error: compare, for example, KF and KNO_3 on negative AgI or KNO_3 and RbNO_3 on positive AgI.

c). The influence of the cations at the negative side follows the lyotropic order:



This sequence was also found for mercury by Grahame (14) and is reflected in the flocculation values of the negatively charged AgI-sol (15).

d). The capacity on the positive side decreases in the order



In Fig. 3 the NaClO_4 -curve is not given for the sake of clarity.

e). The shapes of the HNO_3 and NH_4NO_3 -curves are somewhat deviating. The proton, owing to the small dimensions of the H_3O^+ ion, seems to be able to follow the diffuse pattern up to a higher surface potential. The character of the NH_4NO_3 -curve might be connected with a possible specific relation between the AgI and the NH_4^+ -ion (complex formation).

The phenomena described in this section can be illustrated by Fig. 4, giving Stern capacities for some monovalent electrolytes, calculated from

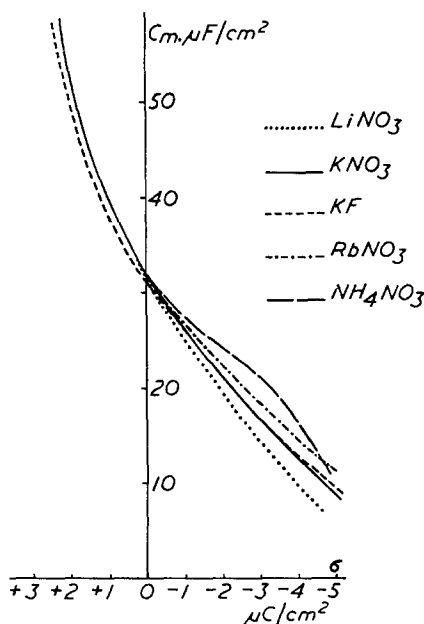


FIG. 4. Differential capacity of the molecular condenser of the double layer on AgI in solutions of some monovalent electrolytes.

the experimental 10^{-1} capacity curves with the aid of Eqs. [5], [6], and [7].

The curves are qualitatively similar to those for mercury, the capacities are of the same order of magnitude, and the specific influence of ions is in the same order (1, 14). There are, however, a few striking quantitative differences. The Stern capacity changes more strongly with surface charge for AgI than for mercury and the lyotropic effects are also more pronounced for AgI. Both these effects might be connected with the somewhat more discrete character of the double layer for AgI (13).

b). *Double Layer Capacities in Solutions of Asymmetrical Electrolytes*

Sets of representative capacity curves are given in Figs. 5, 6, 7, 8, and 9. In these curves the solid lines represent the experimental capacities, whereas the dotted lines represent the diffuse capacities now to be calculated from

$$C_d = \sqrt{\frac{en^2}{8\pi kT}} \cdot z_- z_+ \frac{|e^{-z_- \psi} - e^{-z_+ \psi}|}{\sqrt{-z_- e^{-z_+ \psi} + z_+ e^{-z_- \psi} + z_- - z_+}}. \quad [8]$$

In [8] z_- and z_+ are the valencies of the negative and the positive ion (sign included), and n is the electrolyte concentration in neutral molecules/cm.³; for $z_+ = 1$ and $z_- = -1$ [8] changes into [6].

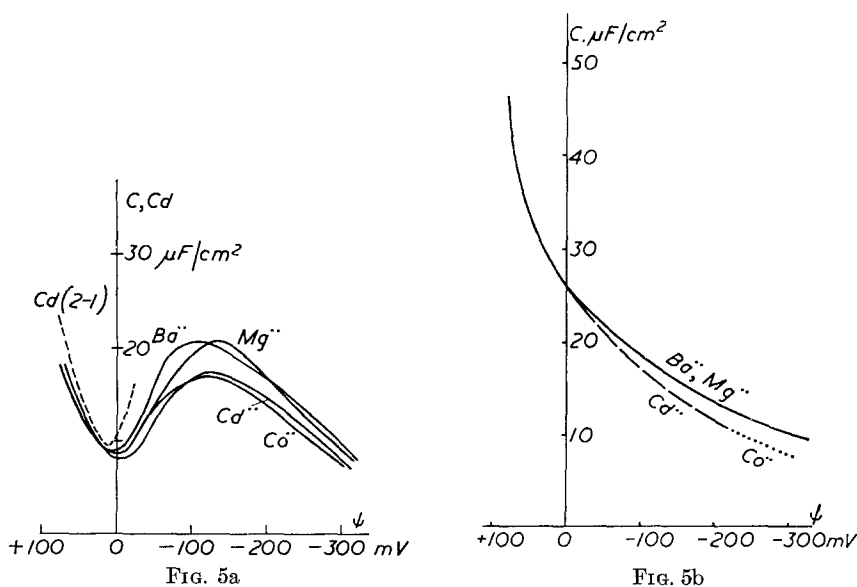


FIG. 5. Differential capacity of the double layer on silver iodide in solutions of some bivalent nitrates. a. 10^{-3} mole/l. Dotted line: C_d . b. 10^{-1} mole/l.

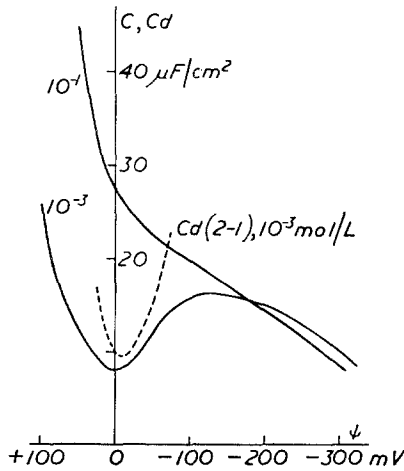


FIG. 6. Differential capacity of the double layer on AgI in 10^{-3} and 10^{-1} M K_2SO_4 . Dotted: Cd in 10^{-3} M solution.

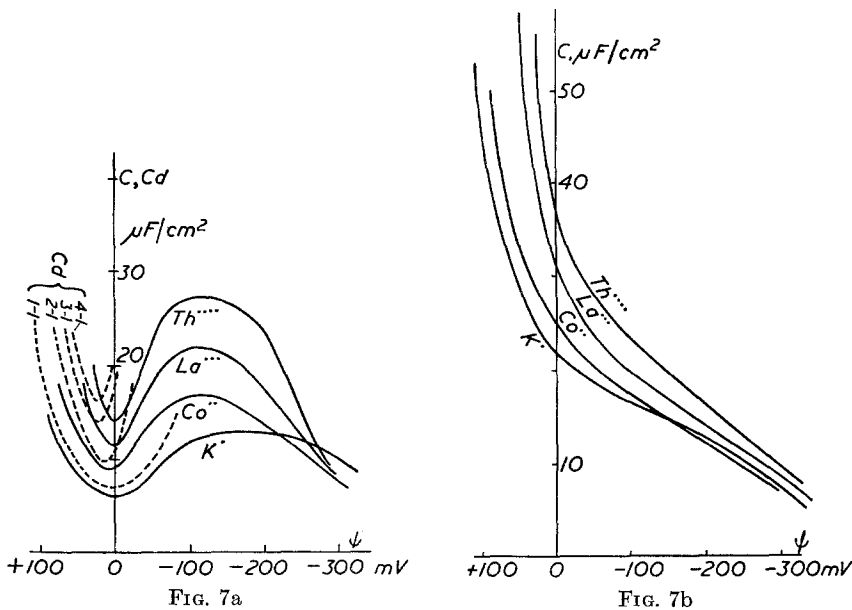
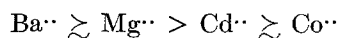


FIG. 7. Differential capacity of the double layer on AgI. Influence of the charge of the cation. a. 10^{-3} mole/l. Dotted lines: Cd. b. 10^{-1} mole/l.

From these figures the following can be read:

a). It is seen that the qualitative appearances of these curves are of the same character as those of the (1-1) curves (Figs. 3 and 4).

b). The lyotropic order for bivalent cations on negative AgI is



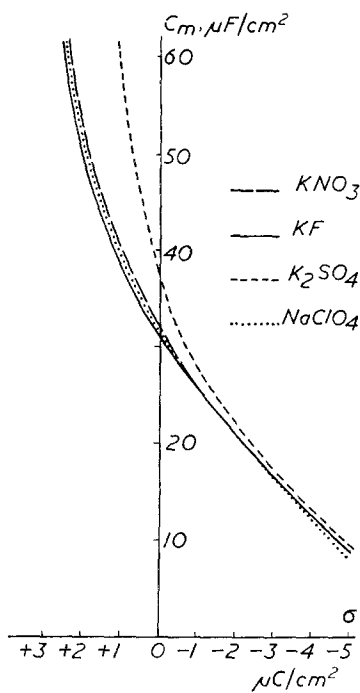


FIG. 8. Differential capacity of the molecular condenser of the double layer on AgI. Influence of the anion.

The mutual differences are somewhat less pronounced than those between the monovalent cations. This is also the case with their flocculation values (15).

c). The capacity maximum at the negative side of the z.p.c. in 10^{-3} *M* solutions is reached at a lower (less negative) potential than in 10^{-3} (1-1) solutions. Furthermore the capacities at the maximum are higher. This can be seen as a consequence of the stronger compression of the diffuse part of the double layer by the multivalent counter ion. As a further consequence of the great increase in *Cd*, *Cm* (which is less dependent on ψ) can prevail at lower surface potentials.

d). On increasing cationic charge the capacity of the diffuse part shows an increasing minimum value and a stronger curvature. This is reflected in the experimental 10^{-3} *M* curves in the region near the zero point of charge.

e). Theoretically a shift in the minima of *Cd* to the side of positive surface charge is expected. This is not clearly reflected in the experimental curves (Fig. 7*a*). However, the experimental determination of the minimum of *C* involves the establishment of the point of inflection in curves of the type of Fig. 1 (10^{-3} curve) in a region of low slope. This process cannot be performed without some arbitrariness. The uncertainty in the establish-

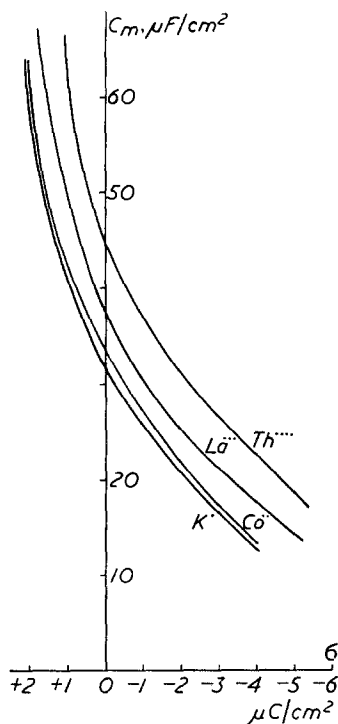


FIG. 9. Differential capacity of the molecular condenser of the double layer on AgI. Influence of the charge of the cation.

ment of the experimental minimum is accompanied by some uncertainty as to the exact location of the z.p.c. in millimolar solutions of asymmetrical electrolytes. It deviated from its value in 10^{-3} KNO_3 by a small amount, as was found by van Laar (6) and by us. The deviations, however, were poorly reproducible and not very systematic. For that reason we preferred to make use of the well-established z.p.c. in 10^{-3} KNO_3 . Consequently this problem must be considered to be not yet solved.

In this connection it should be noted that no real significance has to be attributed to the fact that at positive AgI $C > Cd$ for La^{3+} and Th^{3+} , which would mean that C_m should be negative.

c). Cases of Pseudocapacity

The electrolytes treated above showed no specific relation to Ag^+ or I^- ions. When this condition is not fulfilled, the adsorption process can be accompanied by a supplementary Ag^+ or I^- ions consuming process, leading to a nonreal capacity ("pseudocapacity").

Chloride ions interfered by precipitation of $AgCl$. Experiments in which a known amount of chloride ions was added showed that precipitation of

AgCl (consumption of Ag^+ without change in e.m.f.) occurred at the value calculated from the solubility product of AgCl. The conclusion that this precipitation is not influenced by the presence of suspended AgI could be employed in the correction for KCl, delivered by the salt bridge, as described in Section II, b.

Lead can interfere by precipitation of PbI_2 but the solubility product is so high that it is not reached. Capacity curves were of the same type as those presented in Fig. 5: (Curves are not given for sake of clarity.)

Thallium forms a sparingly soluble iodide with a solubility product of 3.6×10^{-8} . This is reached easily in not too dilute solutions of TlNO_3 . Before the solubility product was reached the capacity was markedly higher than those of the other monovalent electrolytes. The solubility product could be established experimentally from the (known) Tl-concentration and the p_I , at which the consumption of iodide ions increases sharply under formation of a precipitate of TlI (the bright yellow color of which could be distinguished easily from the pale yellow of the AgI). We found 1.9×10^{-9} , independent of the amount of AgI and Tl-concentration. It is possible that an epitaxis of TlI on AgI is responsible for this deviation from the literature value. A similar effect was found by Bergna and de Bruyn (16), who found Ag_2O to precipitate on positive AgI before its solubility product was reached. In connection with the anomalous behavior of Tl its low flocculation value can be mentioned ($\frac{1}{5}$ of that of other monovalent electrolytes).

Cadmium. In the greater part of the potential range $\text{Cd}\cdot\cdot$ behaved about as $\text{Co}\cdot\cdot$ (Fig. 5). At high iodide concentration in $10^{-1} M$ $\text{Cd}(\text{NO}_3)_2$ -solution a too high consumption of I^- -ions was observed before the solubility product was reached. We presume that the complex formation



is responsible. From the estimated deviation of the "normal" behavior, the concentration of $\text{CdI}\cdot$ can be found. As further the equilibrium concentrations of $\text{Cd}\cdot\cdot$ and I^- are known, the equilibrium constant can be evaluated. We found

$$p_K = -\log \frac{[\text{CdI}\cdot]}{[\text{Cd}\cdot\cdot][I^-]} = 1.89$$

in reasonable agreement with $p_K = 1.76$ as found by Quintin and Pelletier (17).

In the region of complex formation the capacity curve is omitted in Fig. 5b.

SUMMARY

A method is described for obtaining differential double layer capacities on silver iodide. Especially the influence of the nature and concentration

of indifferent electrolytes was investigated, viz., the nitrates of Li⁺, K⁺, Rb⁺, NH₄⁺, H⁺, Tl⁺, Mg²⁺, Ba²⁺, Co²⁺, Cd²⁺, Pb²⁺, La³⁺, Th⁴⁺, the fluoride, chloride, and sulfate of K⁺, NaClO₄ in 10⁻³ and 10⁻¹ M solutions. Capacities showed definite analogy with those on mercury. The influence of the counter ion was in the lyotropic order. The capacity of the molecular condenser, calculated with the assumption of absence of specific adsorption, was independent of the electrolyte content.

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