

THIS REPORT HAS BEEN DELIMITED  
AND CLEARED FOR PUBLIC RELEASE  
UNDER DOD DIRECTIVE 5200.20 AND  
NO RESTRICTIONS ARE IMPOSED UPON  
ITS USE AND DISCLOSURE,

**DISTRIBUTION STATEMENT A**

APPROVED FOR PUBLIC RELEASE;  
DISTRIBUTION UNLIMITED.

**UNCLASSIFIED**  
**AD**

**161787**

FOR  
MICRO-CARD  
CONTROL ONLY

**1** **OF** **1**  
Reproduced by

**Armed Services Technical Information Agency**

**ARLINGTON HALL STATION; ARLINGTON 12 VIRGINIA**

**UNCLASSIFIED**

**"NOTICE:** When Government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the U.S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto

AD NO. 161787  
ASTIA FILE COPY

161787

Technical Report  
to the  
Office of Naval Research  
on  
CAPACITY OF THE ELECTRICAL  
DOUBLE LAYER AND ADSORPTION  
AT POLARIZED PLATINUM ELECTRODES

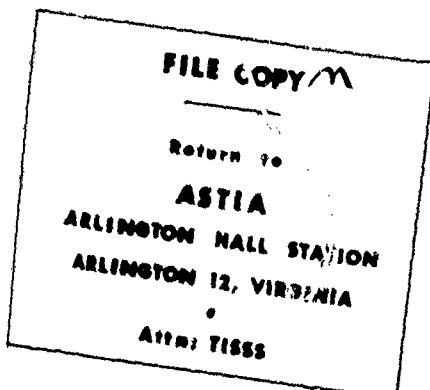
by  
Norman Hackerman and Pranjivan V. Popat

March 15, 1958

Contract Nonr-375(02)

Department of Chemistry  
The University of Texas

Austin 12, Texas



FC

CAPACITY OF THE ELECTRICAL DOUBLE LAYER AND  
ADSORPTION AT POLARIZED PLATINUM ELECTRODES

By

Norman Hackerman and Pranjivan V. Popat  
Department of Chemistry  
University of Texas  
Austin, Texas

ABSTRACT

The differential capacity of the electrical double layer at polarized platinum electrodes has been investigated as a function of the type and concentration of anions. The method of charging curves, utilizing a square-wave signal was employed. The "hump" in the potential-capacity curve is characteristic of the anion involved and is explained in terms of adsorption or desorption of the anion. The tenacity of adsorption is found to increase with the covalent character of the adsorbed anion:  $I^- > Br^- > Cl^- > SO_4^{--} > NO_3^-$  and  $F^-$ . Evidence is presented to indicate that the adsorbed iodide, bromide and chloride ions are dehydrated before their anodic discharge. Fluoride and nitrate ions do not appear to be dehydrated even on the anodic side of the zero point of charge. A similarity is established between polarized platinum and mercury electrodes and the location of the zero point of charge for platinum is indicated. An interpretation is given for the observed effect of chemisorbed anions on the hydrogen overvoltage on platinum.

INTRODUCTION

A knowledge of the structure of the electrical double layer (edl) at a metal-solution interface is of importance in understanding the mechanism of electrode processes. Determination of the differential capacity of polarized metal electrodes as a function of polarizing potential provides an important tool for investigating the structure of the edl. Extensive investigations of this type at polarized mercury electrodes have been reported and there are good reviews of both experimental and theoretical work (1-5).

On the other hand, the progress with solid metal electrodes is relatively slow. The main difficulty lies in obtaining a clean and reproducible metal surface. This is essential for getting reproducible and reliable capacity data, because, unlike mercury for which such data can be verified by electrocapillary measurements, there is no independent method of verifying the same for solid metals. Moreover, there is no theoretical

treatment available for the edl at solid metal electrodes, since very little is known about it.

Among solid metal electrodes platinum, because of its noble character, has been the subject of considerable interest and investigation. Ershler (6), and Dolin and Ershler (7) studied the capacity of smooth platinum electrodes in acidic and alkaline media, as a function of the frequency of alternating current. They were primarily interested in determining the slow stage in the discharge of hydrogen ions. Schuldiner (8) used capacity measurements to estimate the true surface area of a polarized platinum electrode. Robertson (9) was concerned mainly with the effect of a.c. frequency and electrolyte concentration on the impedance of polarized platinum electrodes in HCl solutions. Kheifets and Krasikov (10) used capacity measurements to investigate the effect of surface active substances on the overvoltage of hydrogen evolution on platinum. Sarmousakis and Prager (11) recently determined the impedance of polarized platinum electrodes in KBr and KI solutions.

There are so many variables and experimental difficulties involved in this type of work that Grahame (2) did not observe much similarity between the results of various investigators published before 1955, and found it impossible to tell which, if any, of the results are reliable.

Apart from reproducibility and reliability, other problems of immediate interest concerning polarized platinum electrodes include (i) determination of the zero point of charge (zpc) and (ii) whether or not there exists a similarity between polarized platinum and mercury electrodes. No similarity between the two is observed in the work of Robertson (9) or of Sarmousakis and Prager (11).

Breyer (12) has recently reviewed the main problems concerning the edl in general. One of these is whether the ions at the metal-solution interface are solvated. Studies concerning the effect of anions at the air-solution interface (13) and at mercury-solution interface (1,14) have generally led to the belief that anions at the metal-solution interface are much less hydrated than cations and that, with the possible exception of the fluoride ion (14) they are largely bonded to the electrode surface by covalent bonds. However, the problem is still far from settled (12). Moreover, the degree of covalent character of the adsorbed anion must be a function of the polarizability of the anion involved, but no such attempt to correlate the two has been made even for mercury electrodes. For platinum electrodes no systematic investigation of the capacity as a function of the type and concentration of anion over a sufficiently wide range of potential is available.

Whether or not the cations at the interface are hydrated is even less clear. Grahame (15) believes that the arguments against cation hydration are stronger than those for it. The chief argument for cation hydration is the observation that the cathodic branch of the electrocapillary curve is almost independent of the nature of the cation. Grahame maintains that this experimental finding can be explained by assuming that the nature of the solvent rather than the specific properties of the attracted cations

is the determining factor in the capacity measurements. However there appears hardly any conclusive evidence to prove or disprove either position. Breyer (12) has suggested that the state of the cation, exactly as that of the anion, must be a function of the applied potential and that the cations also must undergo dehydration (if only partially) either before or during electrodeposition. In this connection, it is of interest to study the behavior of different cations at polarized platinum electrodes.

One of the reasons for the slow progress in the field of the edl in general lies in the fact that the capacity measurements by the impedance bridge method are tedious and time-consuming (12). Moreover, the method is limited to low capacities, i.e. to microelectrodes which, with solid metals, are difficult to prepare.

Recently, Brodd and Hackerman (16) reported a variation of the charging curve method of capacity measurement which is suitable for projected surface areas of about  $1-3 \text{ cm}^2$ , and which is relatively fast. They utilized a square-wave signal to obtain time-potential traces on a cathode-ray-oscilloscope. This method has been modified by McMullen and Hackerman (17), who obtained reproducible results with mercury and other metal electrodes. The results with mercury electrodes were in good agreement with those obtained by the more accurate impedance bridge method. They assumed an electric analog circuit for polarized metal electrode. The analog consisted of a condenser of capacity,  $c$ , in parallel with a resistance of  $R_p$  ohms, both of these being in series with a resistance of  $R_e$  ohms.  $R_p$  represents the resistance of the dielectric of the medium and  $R_e$  represents the resistance of the electrolyte solution. The square-wave signal passed through a standard resistance of  $R_s$  ohms before entering the solution. McMullen and Hackerman showed that, provided the charging times are sufficiently small ( $t \ll R_s C$ ), the slope of the time-potential trace for any value of  $R_p$  and  $R_e$  can be obtained as a linear function and is given by:

$$\frac{dE_c}{dt} = \frac{E_i}{R_s C}$$

where  $E_i$  is the magnitude of the input square-wave signal. If therefore, the frequency of the square-wave signal is high enough to give a linear function on the oscilloscope, the capacity can be calculated using this relationship.

The method is being utilized in this laboratory for a series of investigations concerning the structure of the edl at platinum and other metal electrodes.

## II. EXPERIMENTAL

The circuit diagram used was that described by McMullen and Hackerman (17). The frequency of the input square-wave signal was 500 c.p.s. and the standard resistance,  $R_s$ , was 15,000 ohms in all cases. The change in the electrode potential due to the square-wave signal was of the order of 10 millivolts.

The all-glass, pyrex cell used in all experiments was similar to that described by Brodd and Hackerman (16). A large area platinized platinum cylindrical gauze was used as a non-polarizable auxiliary electrode. One potentiometer was used as a source of applied polarizing potentials and another for measuring electrode potentials against saturated calomel electrode (SCE) as the reference. All potential measurements reported in this study are against SCE as the reference.

All water used for preparing solutions was triple distilled, conductivity water (specific conductance of about  $1 \times 10^{-7}$  mho/cm.). All salts, of analytical reagent grade, were further purified by at least one recrystallization from conductivity water. All solutions (except those containing bromide or iodide) were still further purified by pre-electrolysis at  $3 \text{ ma/cm}^2$  for about 20 hours in helium atmosphere. Bureau of Mines grade A helium reported as 99.997 per cent pure (with less than  $10^{-6}$  per cent of either oxygen or water vapor) was bubbled through the pre-electrolysis cell during pre-electrolysis and through the experimental cell throughout the capacity measurements. The rate of helium bubbling during capacity measurements was maintained uniformly low. Incoming helium passed through a pre-saturator containing conductivity water, and outgoing helium passed through a trap containing conductivity water which prevented any back diffusion of air into the system. Contamination by grease or other organic materials was carefully avoided.

Platinum wire (0.016" dia) of reagent grade, supplied by Baker Co., New Jersey, was used throughout. Test pieces of the wire, about 9 cm. long, were sealed in 6 mm. pyrex tubes. The length of the test electrode actually exposed to the solution was 7.5 cm., which gave an apparent area of  $1 \text{ cm}^2$ . The tube holding the test electrode was sealed to a pyrex glass holder which fitted the cell. Contact between the test electrode and the rest of the circuit was made by a column of mercury. Each electrode was used only once.

Of the several methods of treating the electrode that were tried, the following, which gave reproducible and consistent results, was used throughout. The electrode was thoroughly washed with conductivity water and then slowly heated to bright red color for several minutes. Before introducing it into the cell, it was allowed to cool to room temperature in a clean, pyrex tube holder. All experiments were carried out at room temperature ( $25^\circ$  to  $30^\circ \text{ C.}$ ) unless otherwise stated.



The same procedure of treating the electrode, of its polarization and of capacity measurement was consistently followed throughout this investigation.

### III. EXPERIMENTAL RESULTS

#### Variation Of Capacity With Time

Preliminary experiments indicated that the capacity of polarized platinum electrodes at a given electrode potential varies with time. The curves of Figure 1 are representative of this behavior. Sarmousakis and Prager (11), using an impedance bridge also found that the capacity of platinum electrodes in 1.0 N KBr and KI solutions decreased with time, first rapidly and then more slowly. Curves (d) and (e), of Figure 1 show that time-variation of capacity was observed also when the solution contained a surface active substance. The behavior illustrated by curve (a), Figure 1, was most common when the change in capacity with a change of polarizing potential was very small, whereas the behavior illustrated by curves (b) and (c) was common when there was considerable change in capacity with a change in polarizing potential. Behavior illustrated by (e) was observed when the solution contained a surface active substance. In absence of a surface active substance, the maximum capacity was attained fairly rapidly. It will be noticed that the time required for the capacity to attain a constant value varies from 30 to 60 minutes. Delahay and Trachtenberg (18) showed that adsorption of a surface-active substance (n-hexanol) on a mercury electrode is diffusion controlled, and that it takes from 30 to 60 minutes to reach equilibrium. The variation of capacity with time in absence of a surface active substance, however, cannot be explained on the basis of diffusion alone because the concentration of ions in these solutions is so large (1.0 M) that their diffusion is not likely to be of major importance. It is more likely that ionic adsorption or desorption itself, whenever it occurs, is a slow process as discussed later.

Before taking the final capacity data, enough time was allowed for the steady state to be attained. While taking the final data it was ascertained that no noticeable change in the capacity value occurred within a period of about ten minutes at a given potential.

#### The Effect Of Anions

This was investigated in neutral 1.0 M solutions of NaF, KCl, KBr, KI,  $\text{KNO}_3$ , and  $\text{K}_2\text{SO}_4$  respectively. These solutions were selected so that a comparison could be made with similar work on mercury, and whenever possible, with platinum. Substitution of a sodium salt in place of potassium salt was not expected to interfere with the effect of the fluoride ion

Fig. 1 Variation of Capacity with Time

- $\Delta$  (a) 0.1 M  $\text{Na}_2\text{SO}_4$  (0.4 volts)
- $\square$  (b) 0.1 M  $\text{Na}_2\text{SO}_4$  (0.1 volts)
- $\circ$  (c) 0.1 M  $\text{K}_2\text{Cr}_2\text{O}_7$  (0.75 volts)
- $\blacktriangledown$  (d) 0.1 M  $\text{Na}_2\text{SO}_4 + 7 \times 10^{-3}$  M/l n-caproic acid  
(1.0 volt)
- $\bullet$  (e) 0.1 M  $\text{Na}_2\text{SO}_4 + 7 \times 10^{-3}$  M/l n-caproic acid  
(0.9 volt)

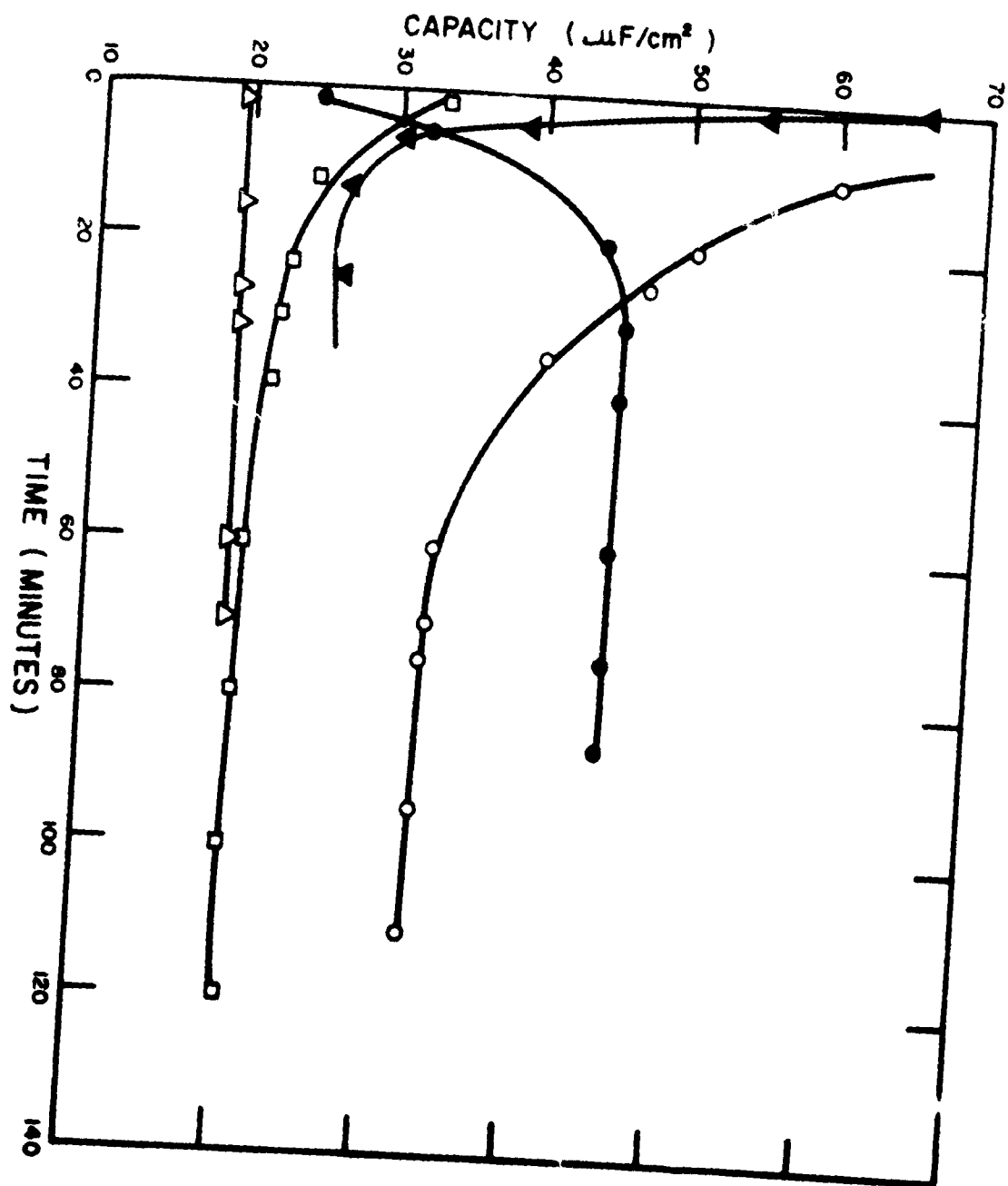


Fig. 2 The Effect of Halide Ions On The Capacity of Polarized  
Platinum Electrodes

- $\Delta$  (a) 1.0 N NaF
- $\circ$  (b) 1.0 N KCl
- $\blacksquare$  (c) 1.0 N KBr
- $\bullet$  (d) 1.0 N KI

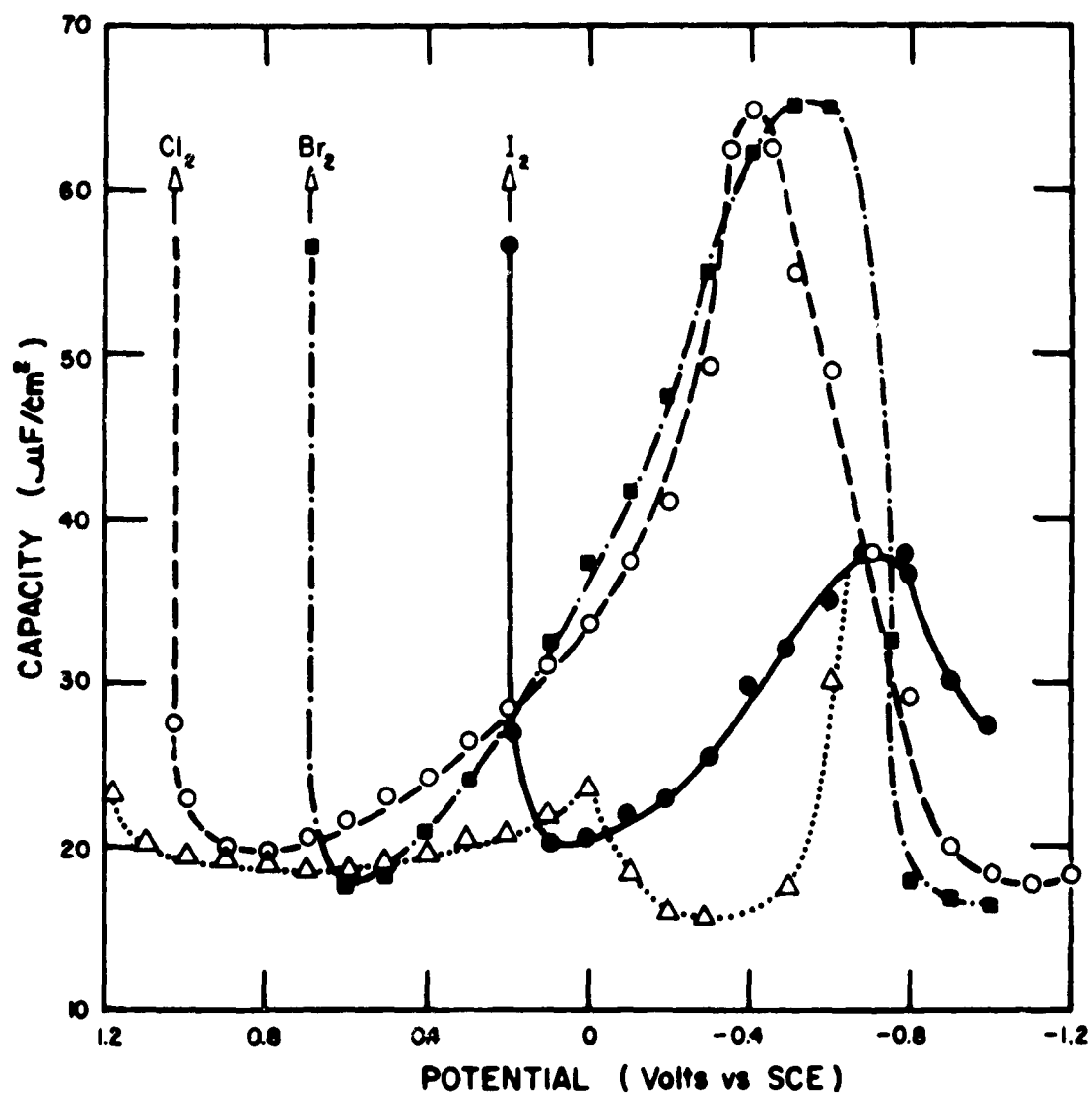
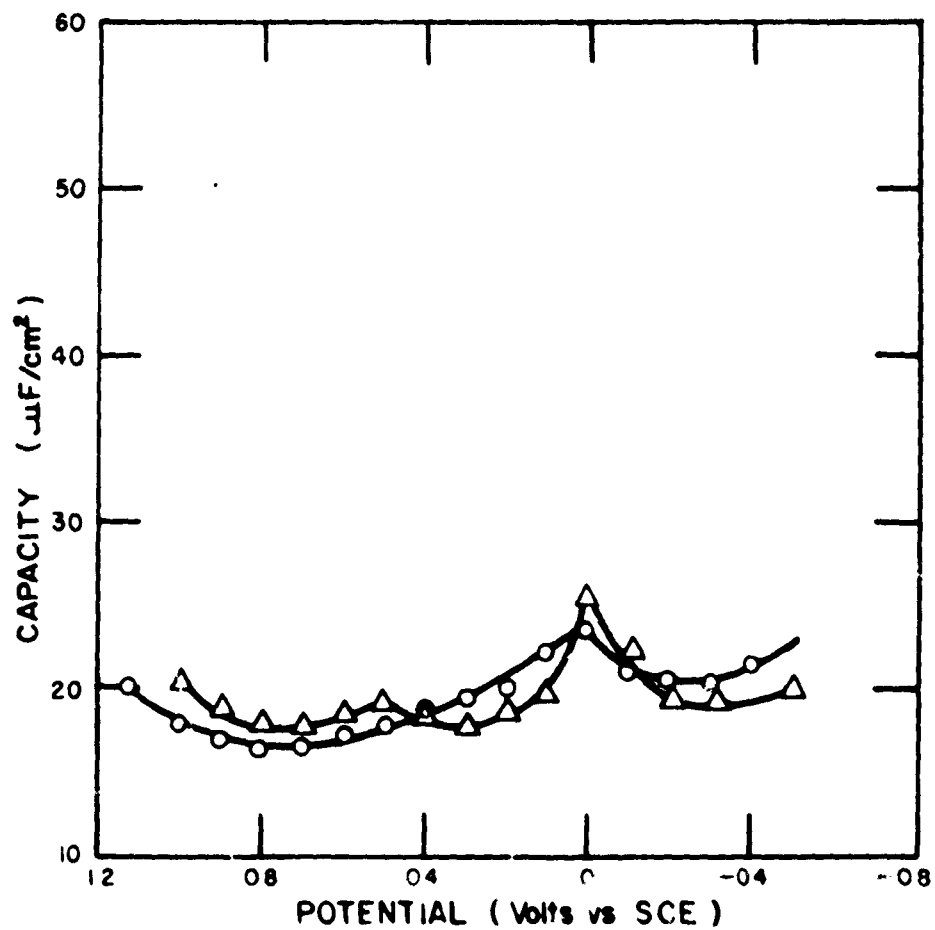


Fig. 3 The Effect Of Nitrate And Sulfate Ions On the  
Capacity of Polarized Platinum Electrodes

- O (a) 1.0 N  $\text{KNO}_3$
- $\Delta$  (b) 1.0 N  $\text{K}_2\text{SO}_4$



### The Effect Of Electrolyte Concentration

Representative curves showing the effect of electrolyte concentration on the capacity of platinum electrode as a function of polarizing potential are given in Figures 4 and 5, where each curve represents an average of at least three independent experiments which were reproduced within experimental error. It must be mentioned here that the precision of measurements in 0.01 M solution was slightly lower because of considerable IR drop due to increased resistance of the electrolyte solution. Also the method in its present form is more precise between about 60 and 10  $\mu\text{F}/\text{cm}^2$ . Beyond 60  $\mu\text{F}/\text{cm}^2$  the slope of the time potential trace is too small to measure accurately and below 10  $\mu\text{F}/\text{cm}^2$ , the time potential pattern extends beyond the range of the oscilloscope.

Figure 4 shows that dilution of the chloride solution has considerable effect on the capacity of platinum electrodes in the intermediate range of potentials. The potentials at which the capacity maximum appears in each case are -0.4, -0.3 and -0.25 volts for 1.0, 0.10 and 0.01 N solutions of KCl respectively. The relative positions and magnitudes of the minimum capacity in the anodic region of potential differ only slightly for the three concentrations. Similar effect of dilution was observed with KBr solutions (1.0 M and 0.1 M) for which the curves are not shown. The capacity maximum appeared at -0.55 volts with 1 M KBr and at -0.50 volts with 0.1 M KBr. The effect of dilution of KI and NaF solutions was not studied.

Figure 5 shows that dilution of nitrate solution has practically no effect on the capacity of platinum electrodes. The results with 1.0 N and 0.1 N  $\text{KNO}_3$  were practically identical (though the points are shown slightly separate for clarity). Dilution of sulfate solution had very slight effect on capacity. It is of interest to mention here that Rice and Hackerman (19) in their studies on zeta potentials of platinum, gold and silver with streaming current technique found no effect of dilution of nitrate solution, and very slight effect of dilution of sulfate solution on the zeta potentials of these metals.

### The Effect Of Temperature

Figure 6 gives the results of some preliminary experiments on the effect of temperature on the potential-capacity curve for platinum electrodes. Curve (b) for 50° C. with 0.1 M KCl is the average of three runs which agreed with one another most closely. For some reason the reproducibility at higher temperature was not as good as at room temperature. Curve (a) for room temperature (25±3° C.) is reproduced for comparison. Note that the position of the capacity maximum is considerably displaced to more anodic values and that the potential range within which the hump occurs is also reduced.



Fig. 4 The Effect of Chloride Ion Concentration On  
The Capacity of Polarized Platinum Electrodes

- (a) 1.0 N KCl  
□ (b) 0.1 N KCl  
○ (c) 0.01 N KCl

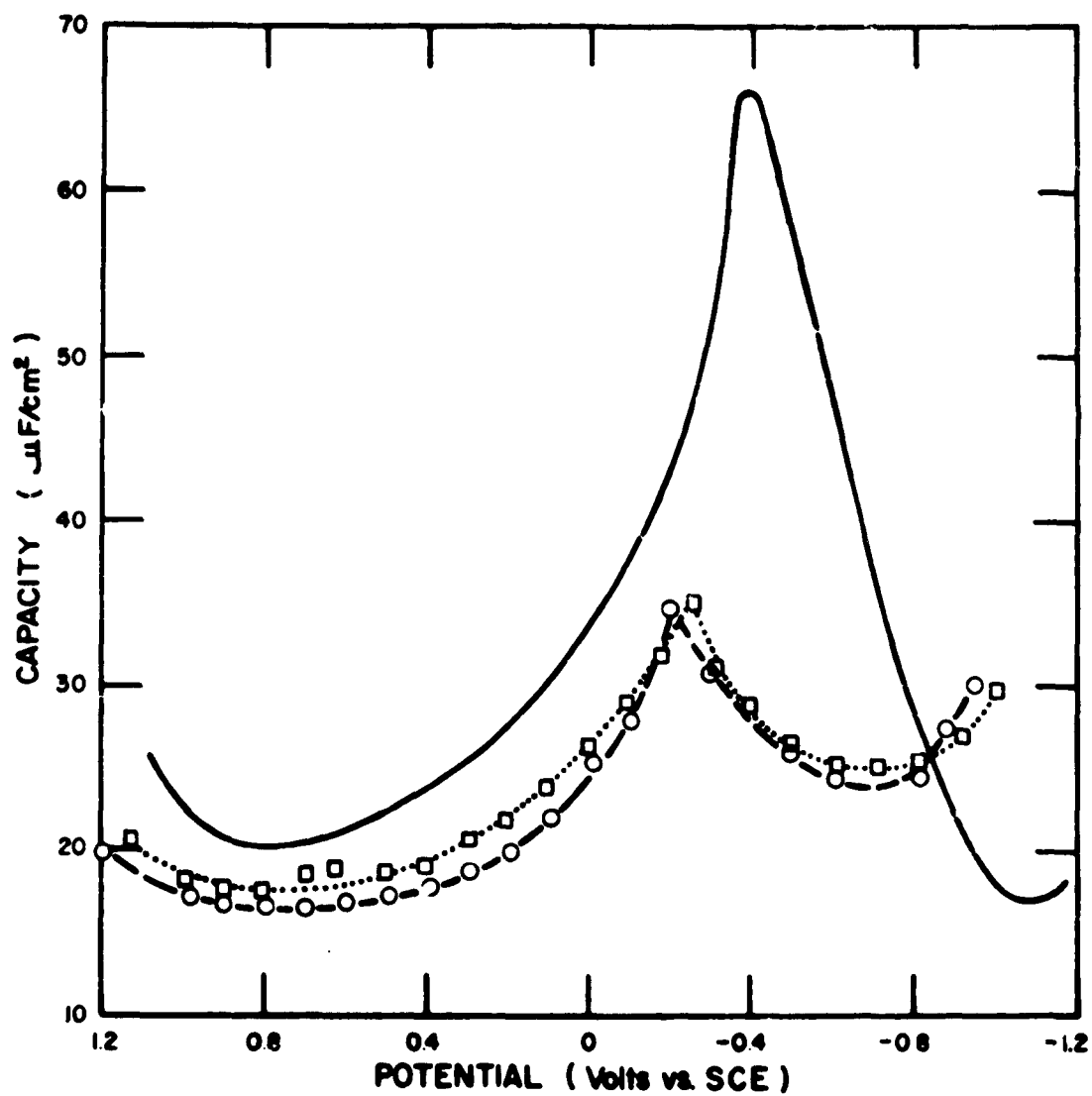


Fig. 5 The Effect of Nitrate and Sulfate Ion Concentration  
on The Capacity of Polarized Platinum Electrodes

- $\triangle$  (a) 1.0 N  $\text{KNO}_3$
- $\square$  (b) 0.1 N  $\text{KNO}_3$
- $\blacktriangledown$  (c) 0.01 N  $\text{KNO}_3$
- $\circ$  (d) 0.2 N  $\text{Na}_2\text{SO}_4$
- $\bullet$  (e) 0.02 N  $\text{Na}_2\text{SO}_4$

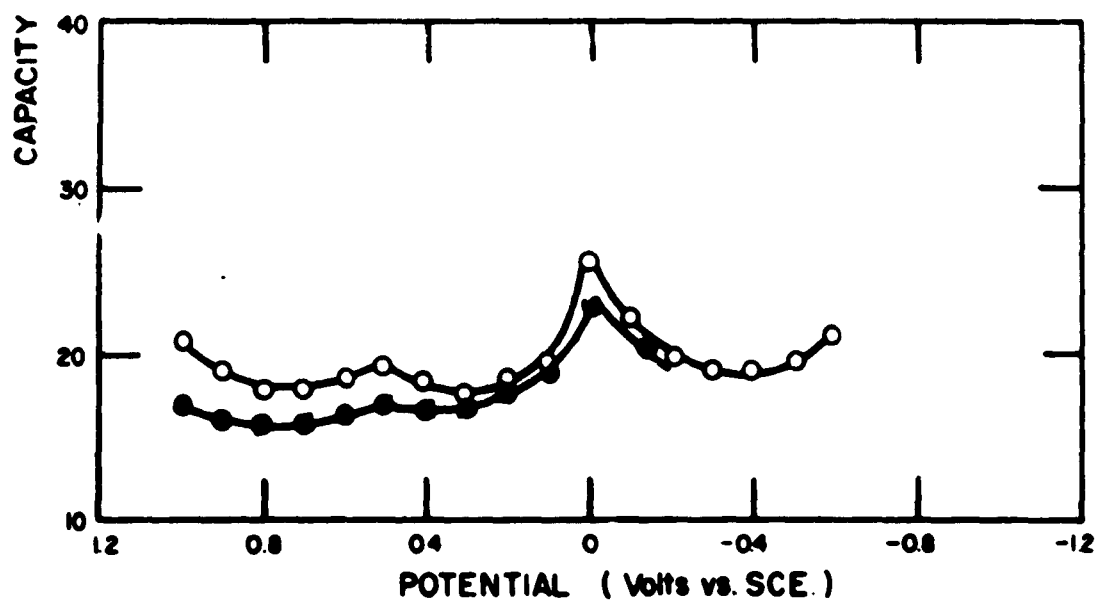
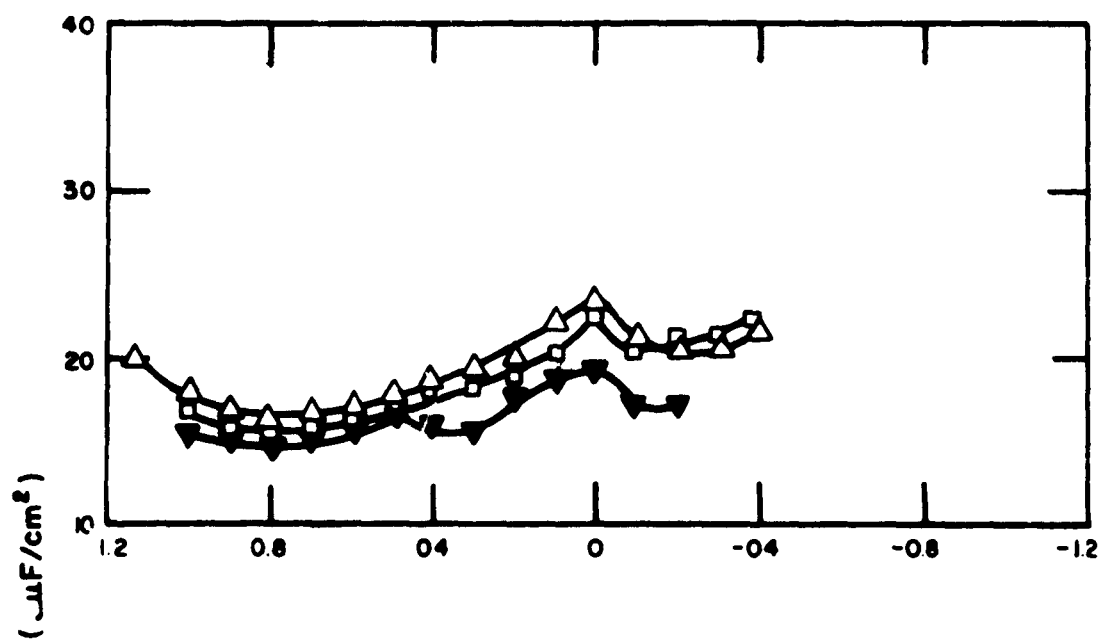
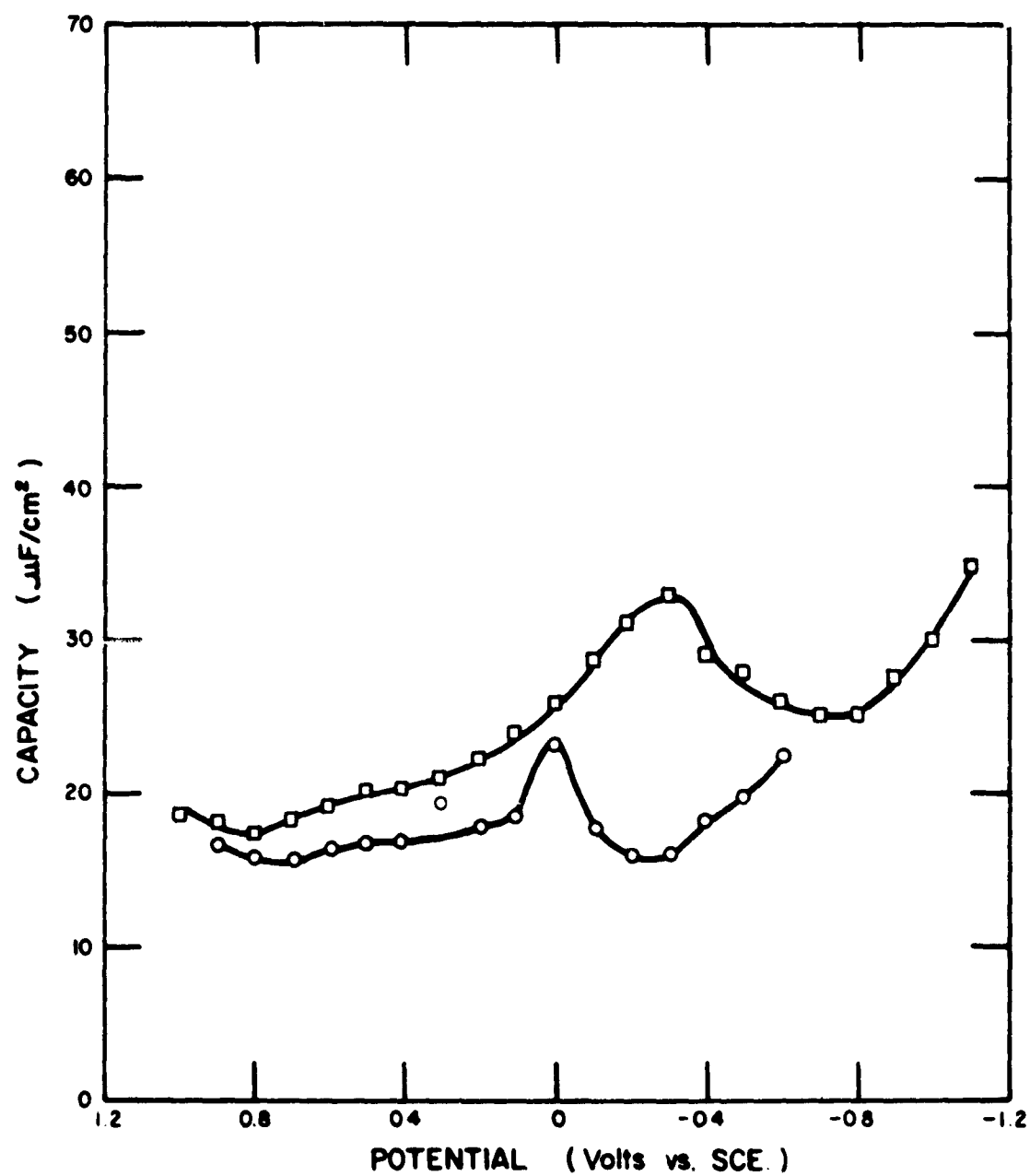


Fig. 6 The Effect of Temperature On The Capacity of  
Polarized Platinum Electrodes

- (a) 0.1 N KCl at 50° C.
- (b) 0.1 N KCl at about 25° C.



### The Effect Of Cations

It was observed during this investigation that the curves for 0.1 M  $K_2SO_4$  and 0.1 M  $Na_2SO_4$  did not coincide in the extreme cathodic region of potential. The results are shown in Figure 7. Such differences in the behavior of cations have not been observed with mercury electrode. More extensive investigation with different cations is in progress.

## DISCUSSION OF RESULTS

### A. Adsorption of Anions

The most interesting portion of the potential-capacity curves of Figures 2-7 is the "hump" that appears in the intermediate range of potentials in each case. An examination of the relative position and shape of each hump (Fig. 2) indicates that it is a function of the anion involved.

Similar humps in the potential-capacity curves have been reported for mercury electrodes in various electrolytes (1,14) and Grahame (20) has proposed an "ice-layer" theory to explain the observed effects of electrolyte concentration and temperature on the capacity humps with mercury electrodes in NaF and  $KNO_3$  solutions. According to this theory, the surface of the electrode may be covered with a "pseudo-crystalline ice-like layer" of solvent through which anions pass only with difficulty, but without activation energy. This "semi-rigid" layer is supposed to melt only gradually since the hump disappears gradually with rise in temperature.

A different and perhaps more satisfactory interpretation of similar humps found with platinum electrodes is proposed here. Before doing so, it is probably better to discuss briefly the significance of other parts of curves of Figure 2.

The steep rise at the extreme left of each curve (except for NaF) represents the pseudo capacity due to the discharge of the halide ion under consideration. The potential at which this occurs is found to be a characteristic function of the anion involved.

The steep rise at the right of each curve (see Fig. 2, curve a) represents the pseudo capacity due to the discharge of hydrogen ions in each case. The potential at which this occurs also appears to be a function of the anion involved.

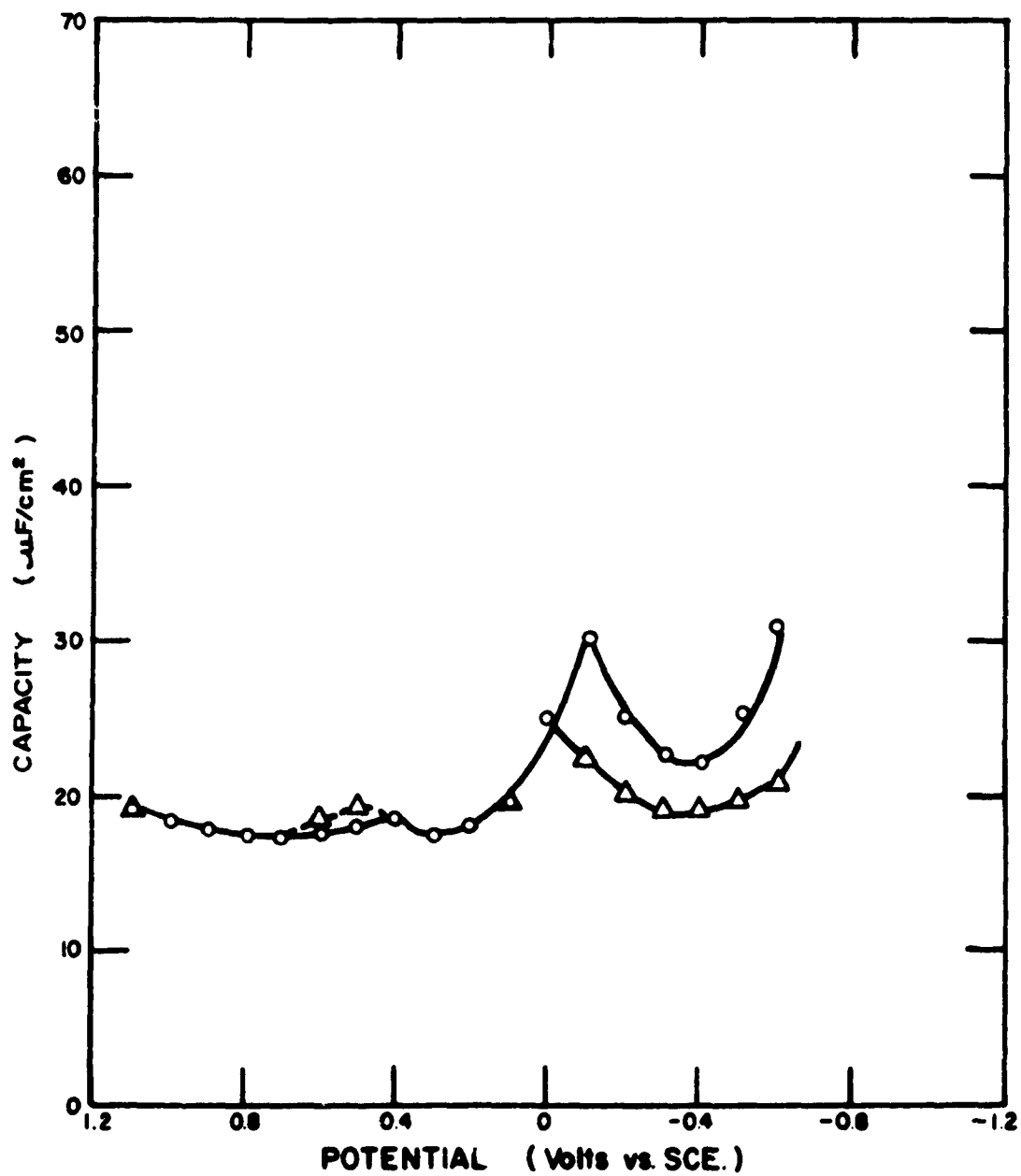
Between these two limits, the electrode behaves more or less as an ideal polarized electrode.

At the minimum to the left of the hump, the anions populate the inner region of the edl, whereas at the minimum to the right of the hump the

Fig. 7 The Effect of Cations on the Capacity of  
Polarized Platinum Electrodes

- $\Delta$  (a) 0.1 M  $\text{Na}_2\text{SO}_4$
- $\circ$  (b) 0.1 M  $\text{K}_2\text{SO}_4$





cations populate the inner region of the edl.

According to the interpretation proposed here, each hump in the capacity-potential curve for platinum electrodes in various anions represents a rearrangement of the edl. The main process during this rearrangement is the desorption of anions in going from left to right. The reverse process, i.e. adsorption of anions occurs if the potential is altered in the reverse direction. Similar humps (or peaks) due to desorption of surface active substances have been known (1). Particularly, Kheifets and Krasikov (10) reported the presence of a single peak due to desorption of a surface active anion such as caprylate ion. (Desorption of a surface active neutral molecule normally produces two peaks, one on either side of the zpc.)

In the present case, each hump is characteristic of the anion involved. The most important feature of the hump in this connection is the potential at which the capacity maximum occurs in each case. These values\* are -0.80, -0.55, -0.40 and 0.00 volts for  $I^-$ ,  $Br^-$ ,  $Cl^-$  and  $F^-$  ions respectively. Another important feature of each hump is the potential range within which each hump occurs. This decreases in the following order:  $I^- > Br^- > Cl^- > F^-$ .

On the basis of these observations it can be concluded that the appearance of the humps with various anions under investigation must be due to their desorption as the potential is made more cathodic. The rise in capacity during desorption must apparently be due to the flow of "anion-current" and in that sense the humps probably represent pseudo-capacity. It must be made clear that both branches of each hump represent desorption exactly as in the case of organic surface active anions. The cations are also involved in this dynamic process, but their contribution to the hump appears negligible as shown later.

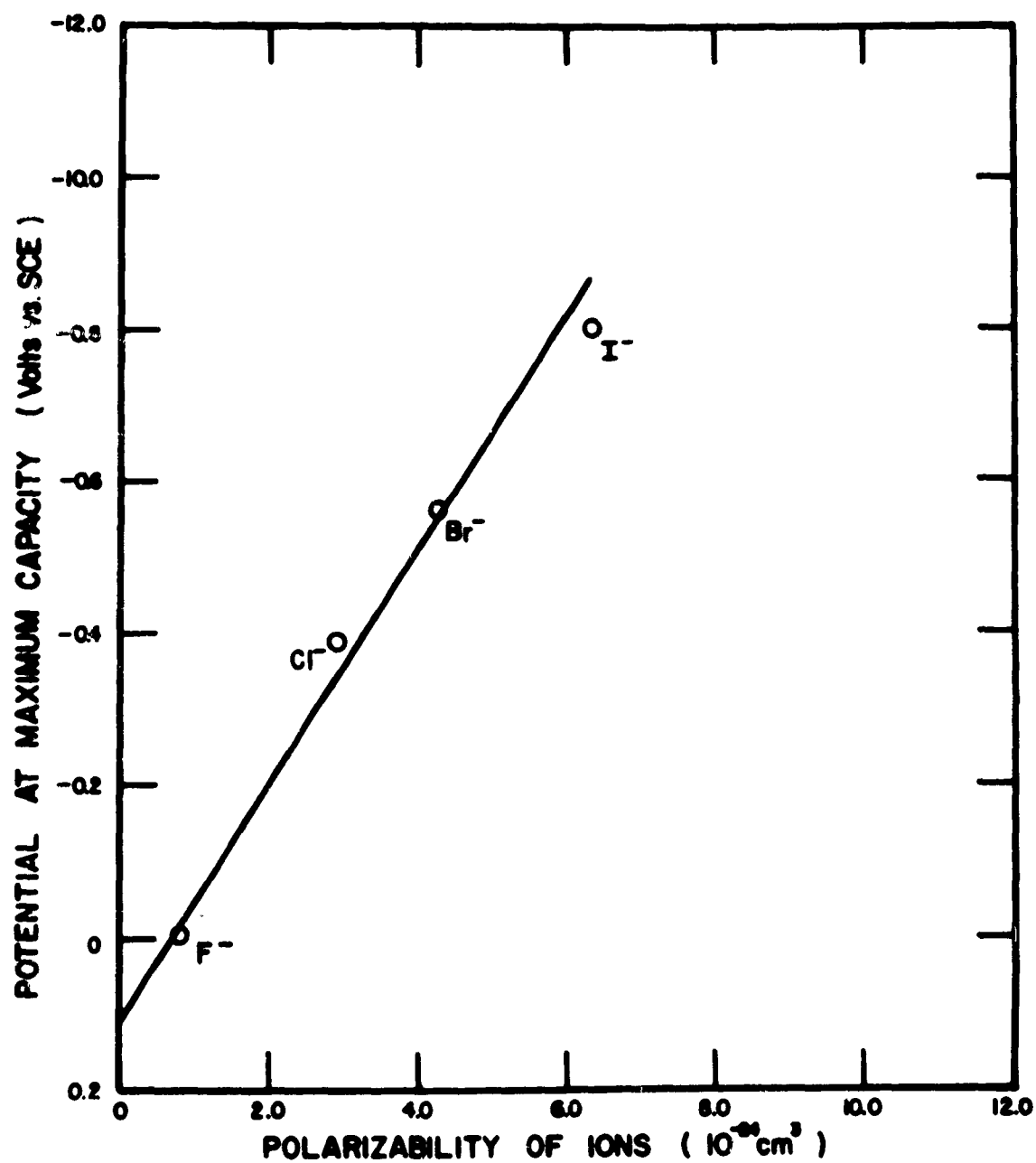
It follows that the halide ions are adsorbed on the platinum surface in the following order:  $I^- > Br^- > Cl^- > F^-$ . Note that the numerical values of the polarizability (in the units of  $10^{-24} \text{ cm}^3$ ) of these ions are (21): 0.81, 2.98, 4.24 and 6.45 for  $F^-$ ,  $Cl^-$ ,  $Br^-$  and  $I^-$  ions respectively. A plot of the polarizability of each halide ion against the potential of the capacity maximum for each hump suggests a linear relationship (Fig. 8). Thus, the iodide ion (most strongly adsorbed) must have the largest degree of covalent character while the fluoride ion (least adsorbed) the smallest.

On the basis of the foregoing interpretation of the hump and from the relative size and the degree of covalent character of the adsorbed halide ions, we can assume that the anions, during adsorption, must be dehydrated in the following order:  $I^- > Br^- > Cl^- > F^-$ , and that the process of dehydration (going from right to left) must be occurring within the potential range of each hump. Additional support for this assumption

---

\* These values have not been corrected for junction potentials.

Fig. 8 Relation Between The Polarizability of Halide  
Ions and The Potential At Which The Maximum  
Capacity Occurs In The Hump For Each Halide Ion.



is found in the fact that only a slight increase of potential beyond the minimum on the left of the hump produces a steep rise in capacity (Fig. 2) due to the discharge of the halide ions (except for  $F^-$ ) under consideration. Evidently, these anions must be dehydrated before their discharge.

Whether the fluoride ions are dehydrated on the anodic side of the hump is less clear. That they show the highest degree of ionic character would indicate that they are not appreciably dehydrated. In this connection, the following observations are of interest. (i) The curve for fluoride ions shows a shallow minimum in the anodic region. (ii) the polarizability of  $OH^-$  ions is 1.89 (21) and that of water dipoles is 1.44 (22) compared to 0.81 for fluoride ions. (iii) The anodic process at the extreme left is oxygen evolution and not fluorine evolution. These observations support the assumption that fluoride ions are probably not dehydrated on the anodic side and further indicate that the inner region of the edl is largely populated by  $OH^-$  ions and oriented water dipoles. In this case, the hump could be attributed to the desorption of  $OH^-$  ions and reorientation of water dipoles.

Curve (a), Figure 3 for the nitrate ions is very similar to that for the fluoride ions and can be interpreted similarly. Note that the position and magnitude of the hump in the two cases are about the same. (The anodic process in presence of nitrate ions is also oxygen evolution.) This similarity further supports the assumption that  $OH^-$  ions and water dipoles are preferentially adsorbed in these cases.

Curve b, Figure 3 for the sulfate ions also shows a marked similarity with the fluoride and nitrate ions though they appear slightly more adsorbed than the latter. Moreover, the behavior of sulfate ions appears slightly anomalous as it gives rise to a slight "dip" at about 0.4 volts. Similar "dips" are well known with mercury electrodes in very dilute solutions near the zpc of the electrode, and are believed to be due to the decrease in the capacity of the diffuse part of the edl at or near the zpc (23). Whether the present slight "dip" is associated with the divalent character of the anions or with the capacity of the diffuse part of the double layer is difficult to decide (14).

The foregoing interpretation of the humps is further supported by the observations regarding the effect of electrolyte concentration and temperature (Figs. 4 to 6) on the potential-capacity curves. With chloride and bromide ions which are strongly adsorbed, dilution reduces the hump and shifts the capacity maximum to the left indicating that specific adsorption is a function of the anion concentration as one would expect.

With nitrate and fluoride ions which show least specific adsorption, dilution should have no effect on capacity as demonstrated by the curves for nitrate ions (Fig. 5). Behavior of sulfate ions is also similar.

The effect of higher temperature with the chloride system (Fig. 6) is as expected on the basis of the above discussion; that is, specific

adsorption should decrease with increase in temperature. In this respect, the effect of temperature is more pronounced than that of dilution.

#### B. Adsorption of Cations

Preliminary results given in Figure 7 indicate that potassium ions in the edl are probably less hydrated than sodium ions. Considering the relative sizes of the two ions, this is not unexpected. If confirmed, this experimental finding would mean that cations are also dehydrated before their cathodic discharge.

The contribution of cations to the hump is relatively small (Fig. 2, curve (a) and Fig. 7). This would indicate that  $K^+$  or  $Na^+$  ions are held at or near the platinum electrode mainly by the electrostatic forces. More extensive work, with more sensitive method is required before final conclusions can be drawn.

#### C. Similarity Between Platinum And Mercury Electrodes

A qualitative comparison of the various curves reported in the present work with those for mercury electrodes (1,14) reveals a basic, qualitative similarity between the two electrodes within the corresponding range of potentials where no electrochemical reaction occurs. Robertson (9) did not observe such similarity probably because he used acid solutions and therefore missed the point of comparison, i.e. the hump.

On the basis of this similarity we can assume that the foregoing interpretation of the humps with platinum electrodes may also apply, qualitatively to those with mercury electrodes. If so, this would provide a perhaps more satisfactory explanation of the humps than that given by Grahame's "ice-layer" theory.

#### D. Capacity Minimum And The Zero Point Of Charge (zpc)

The determination of the zpc of a metal electrode has been a matter of considerable practical and theoretical interest. The zpc is usually taken as the potential at which a well defined minimum occurs in the potential-capacity curves in dilute ( $< 0.01 N$ ) solutions. With more concentrated solutions, however zpc is not well defined even for mercury electrodes. Significantly, the zpc for mercury lies within the potential range of the hump observed with more concentrated solutions as expected from the present interpretation of the humps.

Findings of the present investigation suggest that it may be worthwhile to determine zpc for platinum in very dilute solutions of fluoride or nitrate ions, using, preferably an impedance bridge. In absence of such information, attempts have been made to estimate this value from the data with concentrated solutions. Thus Robertson (9) has reported a value of about 0.79 volts for platinum in 1 N HCl whereas McMullen and Hackerman (17) reported a value of  $0.5 \pm 0.2$  volts for platinum in 1 N  $Na_2SO_4$ .

If the present interpretation of the potential-capacity curves is correct, then Robertson's value of 0.79 volts (which agrees with the present data) cannot represent the zpc for platinum because, at this potential the chloride ions are firmly adsorbed at the metal surface as shown before. This conclusion is further supported by the fact that the potential of the capacity minimum in the anodic region is a function of the anion involved (Fig. 2). Closer analysis reveals that this minimum is related to the two processes occurring on either side of the minimum, namely, the discharge of the halide ion on the left and their desorption on the right. From the similarity with mercury, one would expect at the zpc for platinum, another and sharper minimum which should lie within the potential range of the humps obtained in presence of the anions that are specifically adsorbed.

It is difficult to understand Robertson's value (9) of 1.85 volts as the potential difference between platinum and mercury electrodes at the corresponding capacity minima, because, using his value of 0.75 volts (vs. normal calomel electrode) at the minimum capacity for platinum and -0.5 volts (vs. normal calomel electrode) as the zpc for mercury, this difference should be about 1.25 volts. Moreover, the value of the work function for platinum (6.3 e.v.) used by him appears doubtful in the light of more recent data (24). The value of 5.3 e.v. (16) appears more accurate. On this basis the constant potential difference between platinum and mercury should be about 0.8 volts (using 4.5 e.v. as the work function of mercury), and the estimated value of the zpc for platinum should be about 0.4 volts (vs SCE).

The slight dip in the curves for sulfate solutions (Figs. 3, 5 and 7) at about 0.4 volts may be re-examined in this light. It is more likely that this is the zpc for platinum. This is supported by the observation that in the presence of surface active neutral substances (25) minimum capacity is obtained at about 0.4 volts, with desorption peaks on either side of this potential. From this it would follow that the slight humps with fluoride, nitrate and sulfate ions (which occur on the right of the zpc) probably involve a reorientation of water dipoles.

The significance of the more or less shallow portion of the curves with these anions is not fully understood. From a practical standpoint, this is the region that is most suitable for determining surface areas by capacity measurements (16).

#### Hydrogen Overvoltage On Platinum

It has been mentioned before that the steep rise of capacity at the extreme right in each curve (Fig. 2) represents a pseudo capacity due to hydrogen evolution. In presence of fluoride ions (Fig. 2, curve a) this occurs at about -0.65 volts which is roughly the potential of reversible discharge of hydrogen ions in a solution of pH 7.0. This indicates that fluoride ion (least adsorbed) has practically no effect on the hydrogen overvoltage on platinum. Nitrate and sulfate ions behave similarly.

With other anions, however, hydrogen overvoltage appears to be dependent on, among other things, the degree of covalent character (or polarizability) of the adsorbed anions. The hydrogen overvoltage thus increases in this order:  $I^- > Br^- > Cl^- > F^-$ . The effect of anions on the hydrogen overvoltage (Fig. 2) appears much greater than one would expect. (The potential region of hydrogen evolution was not studied in any detail because, when this work was in progress, the significance of the various portions of these curves was not well understood.) No previous work on hydrogen overvoltage on platinum in neutral solutions of the anions studied here is available for comparison.

It must be pointed out here that the interpretation given by Sarmousakis and Prager (11) for the steep rise of capacity in the cathodic region of their curves for the bromide and iodide solutions (as due to the discharge of hydrogen ions, etc.) seems incorrect on the following grounds:

- (i) If this rise in capacity represented hydrogen evolution, then the capacity should continuously rise with more cathodic potentials. This is contrary to what is experimentally observed in their work and more clearly in the present work. Evidently, they did not cover sufficient potential range and therefore missed the hump as well as the potential of hydrogen evolution.
- (ii) If the rise in capacity under question represented hydrogen evolution, then the electrode potential should become insensitive to further changes (in more cathodic direction) of the applied potential. This was not observed in the present work. Also, the time-potential trace on the oscilloscope did not register any curvature indicating the absence of any electrochemical reaction in this region.
- (iii) Sarmousakis and Prager followed Dolin and Ershler (7) in their interpretation. However, the latter workers used acid solutions whereas the former used neutral solutions of KBr and KI. The potential of hydrogen evolution must be different in the two classes.

It is interesting to note that Figure 2 suggests a convenient method of estimating the magnitudes of hydrogen overvoltages with different anions in neutral solutions.



# REFERENCES

1. D. C. Grahame, Chem. Revs., 41, 441 (1947).
2. D. C. Grahame, Ann. Rev. Phys. Chem., 6, 337 (1955).
3. R. Parsons, Modern Aspects of Electrochemistry, Chap. 3, Ed. J. O'M. Bockris, Academic Press, Inc., New York, 1954.
4. P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, 1954.
5. P. Delahay, Ann. Rev. Phys. Chem., 8, 229, (1957).
6. B. Ershler, Acta Physicochim. (U.R.S.S.), 7, 327 (1937).
7. P. Dollin and B. Ershler, ibid., 13, 747 (1940).
8. S. Schuldiner, J. Electrochem. Soc., 99, 488 (1952).
9. W. D. Robertson, ibid., 100, 194 (1953).
10. V. L. Kheifets and B. S. Krasikov, Doklady Akad. Nauk. S.S.S.R., 94, 101 (1954).
11. J. N. Sarmousakis and M. J. Prager, J. Electrochem. Soc., 104, 454 (1957).
12. B. Breyer, Revs. Pure and App. Chem., 6, 249 (1956).
13. For references see N. K. Adam, The Physics and Chemistry of Surfaces, 3rd Ed., Oxford University Press, 1941, pp. 133-134.
14. D. C. Grahame and B. A. Soderberg, J. Chem. Phys., 22, 449 (1954).
15. D. C. Grahame, J. Electrochem. Soc., 98, 343 (1951).
16. R. J. Brodd and N. Hackerman, ibid., 104, 704 (1957).
17. J. J. McMullen and N. Hackerman, (to be published). 202447
18. P. Delahay and I. Trachtenberg, J. Am. Chem. Soc., 79, 2355 (1957).
19. L. Rice and N. Hackerman, (Unpublished results).
20. D. C. Grahame, J. Am. Chem. Soc., 79, 2093 (1957).
21. J. A. A. Ketelaar, Chemical Constitution, Elsevier Publishing Co., New York, 1953, p. 90.
22. B. E. Conway, "Electrochemical Data," Elsevier Publishing Co., New York, 1952, p. 26.
23. M. A. V. Devanathan, Trans. Faraday Soc., 50, 373 (1954).
24. C. J. Smithells, Metals Reference Book, Vol. 2, Interscience Publisher Inc., New York, 1955, p. 668. Also, see Ref. (22) p. 31.
25. N. Hackerman, (Unpublished results).