

CAPACITY OF THE RENEWABLE GOLD ELECTRODE IN MIXED SODIUM
FLUORIDE/SODIUM CHLORIDE SOLUTIONS OF CONSTANT IONIC
STRENGTH

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The capacity of the renewable gold electrode was measured in $(0.2 - x)M$ NaF + xM NaCl solutions over the range of x from 10^{-3} to 0.2 and at potentials between -0.6 and 0.9 V. Frequency-independent equilibrium values of electrode capacity were determined and the potentials of zero charge of the gold electrode in said solutions were calculated. The results are compared with literature data.

In a preceding paper [1] the electric double-layer capacity of the renewable gold electrode was studied in sodium fluoride solutions. It was shown that over a sufficiently wide range of potentials and NaF concentrations, the experimental data can be described satisfactorily by Gouy-Chapman-Stern-Grahame theory for electrolytes not exhibiting specific adsorption. It was of interest with the same method of surface preparation to study the capacity of the gold electrode in a system containing chloride ions, which have a tendency toward chemisorptive interaction with the metal surface [2-7]. On one hand this would allow results obtained by capacity measurements of the renewable electrode in specifically adsorbing electrolytes to be compared with similar data obtained on a remelted metal surface [2-4], and thus to elucidate the special effects of different methods of electrode surface preparation on these data. On the other hand, measurements over a wider adsorbate concentration range than used in [2-4], and an examination of the frequency dependences of adsorption impedance, could be used to obtain detailed information concerning the thermodynamics and kinetics of chlorine adsorption on the gold electrode which is lacking in the literature. Thermodynamics and kinetic aspects of chloride ion adsorption on gold will be discussed in subsequent papers. In the present paper, the experimental data for the capacity of the renewable gold electrode obtained in chloride-ion-containing solutions will be subjected to an initial analysis, and the results of this analysis will be compared with literature data.

The studies were conducted in solutions having the composition: $(0.2 - x)M$ NaF + xM NaCl over a range of x from 0.0 to 0.2. The solutions were prepared with twice distilled water from twice recrystallized sodium chloride and from sodium fluoride calcined at $600^{\circ}C$, which were of "specially pure" grade. For oxygen removal, the solutions were purged under atmospheric pressure with hydrogen obtained electrolytically. The values of solution pH were maintained between 4 and 5, so as to eliminate the complications associated with hydroxyl ion adsorption [8].

The capacitive (X) and resistive (R') components of impedance were measured in a series equivalent network with a fast-response impedance meter; its functional circuit and its use in electrochemical investigations have been described in [9]. The data presented in this work were obtained by averaging at least three values of X and R' , each measured under the conditions of fixed potential within 5 sec of renewal of the gold electrode surface. The reproducibility of the X and R' values in the experiments was $\pm 5\%$.

The studies were conducted at a temperature of $25^{\circ}C$. The potentials are reported on the normal hydrogen scale.

Measurements of the current flowing at the renewable gold electrode in $0.2 M$ NaF solutions had shown that this is small over the range of potentials extending from the start of

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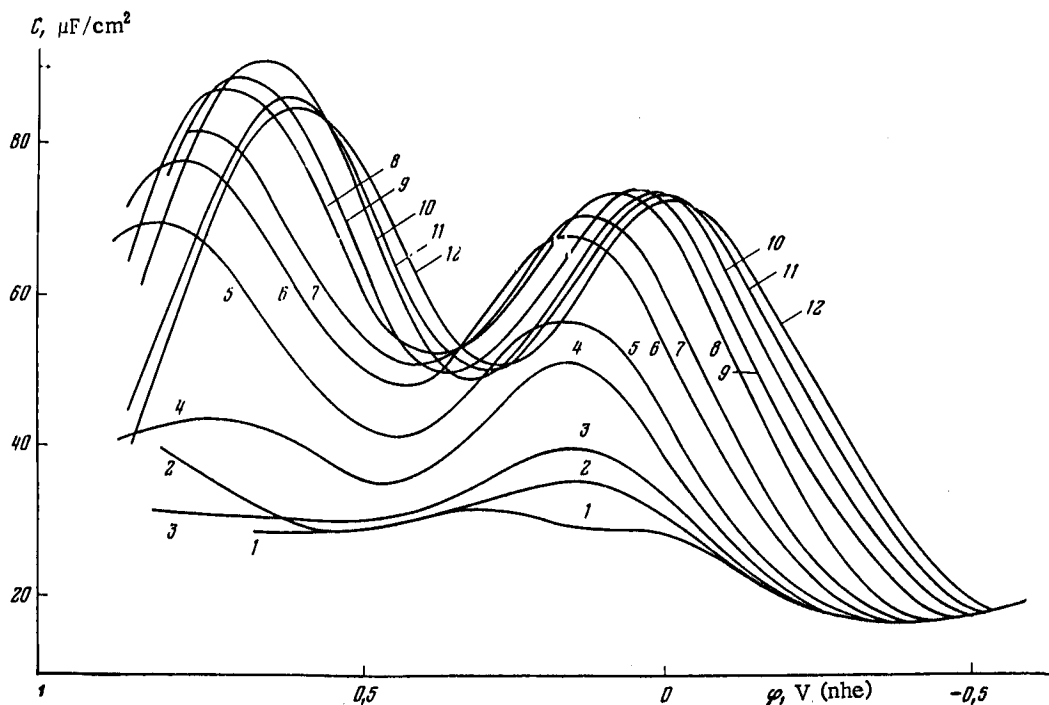


Fig. 1. The capacity of a renewable gold electrode measured at 21 Hz as a function of electrode potential in $(0.2 - x)$ M NaF + x M NaCl solutions, with x -values of: 1) 0; 2) $1 \cdot 10^{-5}$; 3) $5 \cdot 10^{-5}$; 4) $1 \cdot 10^{-4}$; 5) $2 \cdot 10^{-4}$; 6) $5 \cdot 10^{-4}$; 7) $1 \cdot 10^{-3}$; 8) $5 \cdot 10^{-3}$; 9) $1 \cdot 10^{-2}$; 10) $2 \cdot 10^{-2}$; 11) 0.1; and 12) 0.2.

metal surface oxidation to the start of vigorous hydrogen evolution. To a first approximation the current in the system did not change when the amounts of sodium chloride mentioned above were added to the solution.

The behavior of the measured capacity, $C = 1/\omega X$, in solutions containing chloride ions is markedly different from that in NaF solutions over the same potential range (Fig. 1). Thus, the values of capacity measured at low frequencies become significantly higher than those found in sodium fluoride solutions, and the plots of C against potential, ϕ , acquire a characteristic shape of curves with two "humps" similar to those obtained in [2] in measurements at a remelted gold electrode in potassium chloride solutions. In the range of ϕ one observes a marked dependence of capacity on the applied ac frequency. Taken in conjunction with the lack of marked faradaic processes in this range of ϕ , the above behavior of measured capacity can be explained in terms of adsorption processes on the gold electrode which are related to the presence of chloride ions in the solution.

With the aim of determining frequency-independent equilibrium values of capacity, the measured values of the components of electrode impedance were converted to the parallel equivalents via the relation, $C_p = X/\omega(X^2 + R^2)$. Values found for this quantity are shown in Fig. 2 as functions of frequency plotted as C_p against $\omega^{1/2}$. Quantity $R = R' - R_e$ was determined from the measured values of R' and the value of electrolyte resistance, R_e , found by extrapolation of a plot of R' against $\omega^{-1/2}$ to infinite frequency. One can see from Fig. 2 that for the most negative potentials reported, the C_p values thus calculated are independent of the applied ac frequency, just as in sodium fluoride solutions [1]. One can assume, therefore, that the faradaic process of hydrogen evolution which is possible at these potentials does not introduce any substantial error into the C_p values being determined. But the frequency dependence of C_p is significant at more positive potentials (Fig. 2a), and increases with increasing sodium chloride concentration (Fig. 2b). The latter is an indication for its connection with the adsorption-desorption processes of chloride ions on gold. The data presented in Fig. 2 also show that over some range of potentials which is characteristic for each adsorbate concentration, the plots of C_p against $\omega^{1/2}$ can be approximated satisfactorily by a straight line, and hence can be extrapolated sufficiently accurately to zero frequency [10]. Outside this interval the plots of C_p against $\omega^{1/2}$ are essentially nonlinear at low frequencies, which in the absence of information concerning the kinetic features of

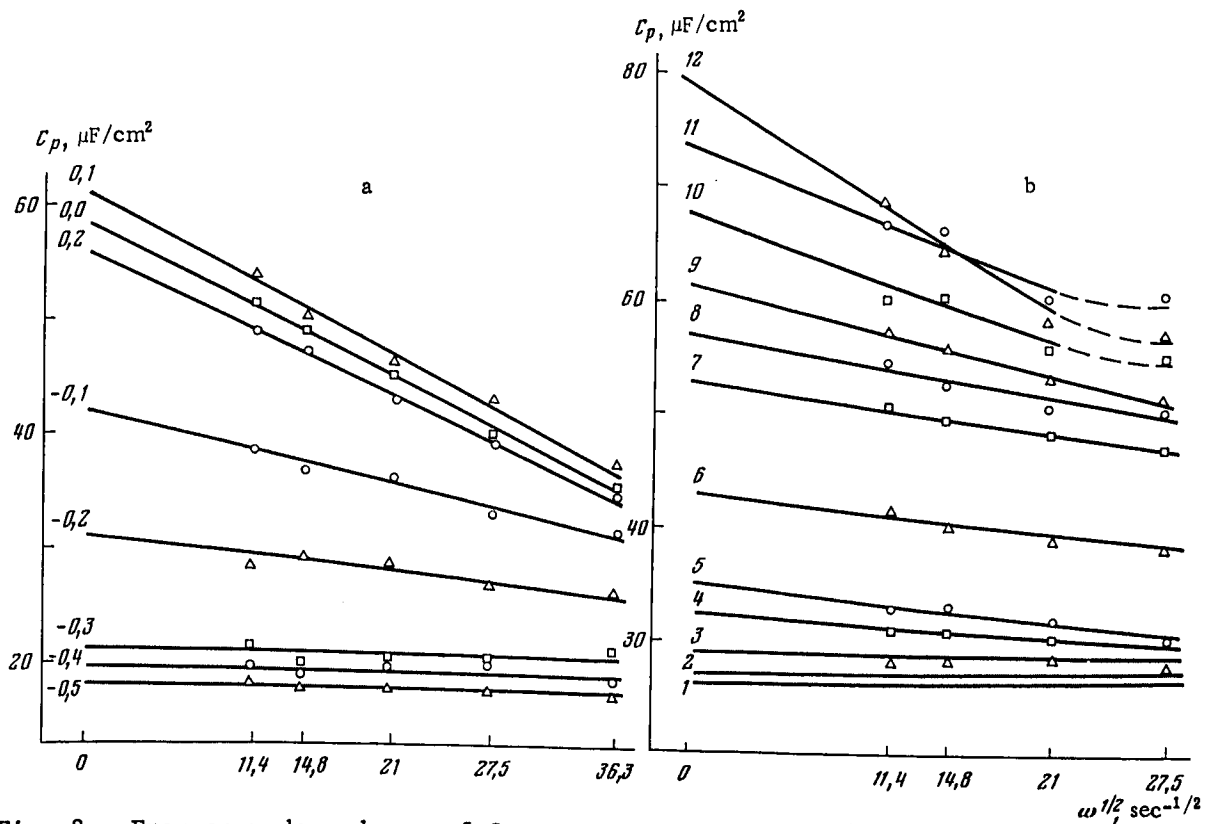


Fig. 2. Frequency dependence of C_p at constant $x = 2 \cdot 10^{-4}$ (a) and at constant $\phi = -0.1$ (b); the numbers at the curves in part (a): values of potential; the numbers at the curves in (b): concentrations as in Fig. 1.

chlorine adsorption in this region is an obstacle in the way of exact determination of equilibrium electrode capacity.

The equilibrium capacity values, $C_p(0)$, found by extrapolation of the above plots to zero frequency are presented in Fig. 3 as functions of potential of the renewable gold electrode and of adsorbate concentration in the solution. Curve 1 in the same figure shows the potential dependence of capacity of the renewable gold electrode in 0.2 M NaF solution without chloride ions. One can see when comparing this curve with curves 2 to 12 that the capacity changes due to chloride ion adsorption on gold extend over practically the entire range of potentials studied, except for potentials more negative than -0.5 V where the capacity values in solutions with and without adsorbate are approximately the same. The lack of frequency dispersion of the C_p at the same potentials (Fig. 2) is additional evidence that the chloride ions are desorbed from the gold electrode surface at potentials more negative than $\phi = -0.5$ V, and electric double-layer structure in solutions with and without adsorbate is the same.

Remembering this, we calculated the value of total electrode charge (q) in solutions with adsorbate at -0.5 V by integration of curve 1 of Fig. 3 starting from 0.16 V, where q is zero, according to the data of [1, 2]. Using this value of electrode charge we then calculated the q as functions of potential by back integration for different adsorbate concentrations in the solution (Fig. 4). According to the data of this figure, there is a systematic shift of the potential of zero charge ($\phi_{z.c.}$) of the renewable gold electrode toward more negative values as the NaCl concentration in the solution is increased in the system being studied. In Fig. 5, the calculated zero-charge potentials are presented as functions of the logarithm of sodium chloride activity. Similar data obtained in [2, 3, 5-7] when studying the potentials of zero charge of gold in binary alkali metal chloride solutions are reported for comparison in the same figure.

One can see from a comparison of the data reported in Fig. 5 that at high chloride concentrations, where the ionic strength of the electrolytes being compared is approximately the same, the $\phi_{z.c.}$ values calculated from the results of measurements of the present work are in

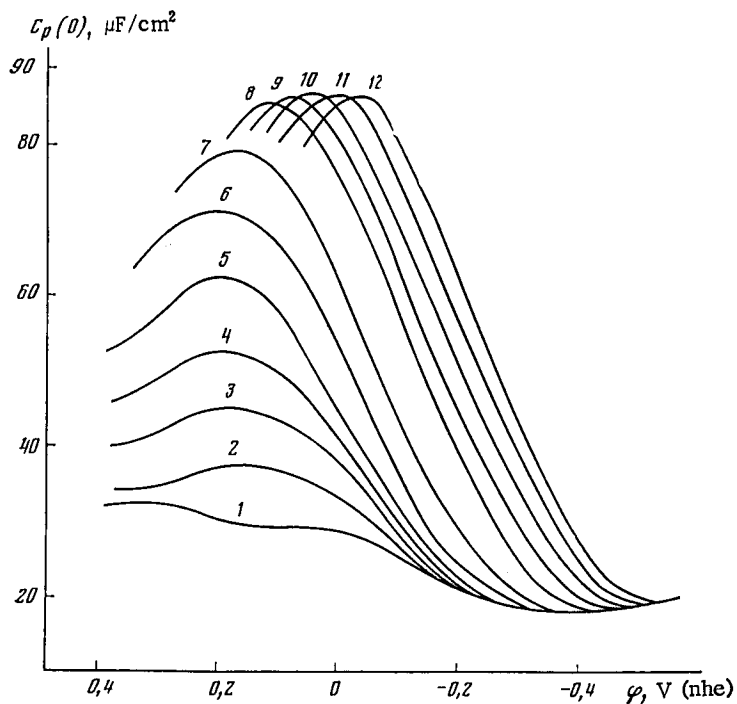


Fig. 3. Potential dependence of $C_p(0)$. The concentrations are indicated in Fig. 1.

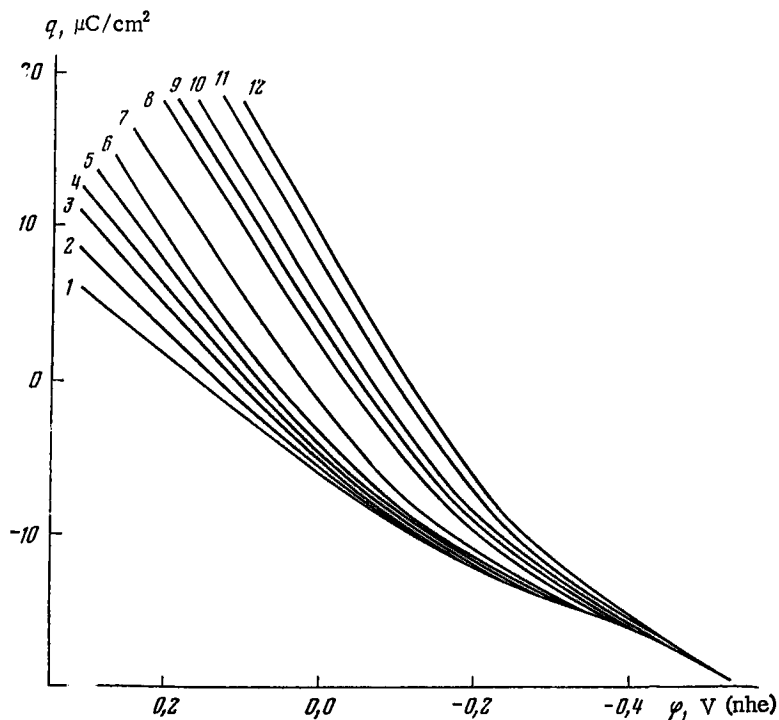


Fig. 4. Total electrode charge as function of electrode potential. The concentrations are indicated as in Fig. 1.

satisfactory agreement with the data of [2, 3, 5, 6]. For lower adsorbate concentrations the differences in the $\varphi_{z.c.}$ values are appreciable. Thus, the zero-charge potential of gold in 0.01 M chloride solutions is -0.018 V according to the data of [2], -0.08 V according to the data of [5], and -0.18 V according to the data of [7], while in the present work it is found to be -0.05 V. This difference in the $\varphi_{z.c.}$ values can be attributed both to experimental errors and to the fact that in their determination in [2, 3], nonequilibrium values of electrode capacity were used. It is also possible, however, that the difference arises from a

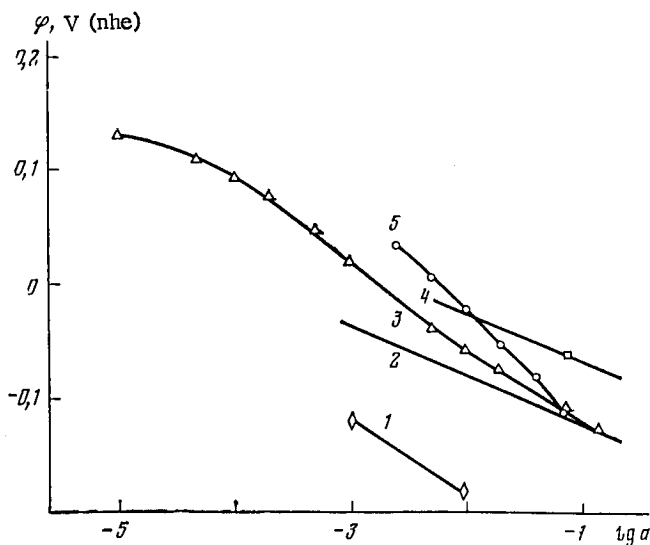


Fig. 5. Zero-charge potentials of the gold electrode as functions of the activity of chloride ions in aqueous alkali metal chloride solutions according to data of [7] (1), [5] (2), the present work (3), [6] (4), and [2, 3] (5).

neglect of the potential drop in the diffuse part of the double layer, which in the dilute binary electrolytes used in [2-7] is larger than in the mixed electrolytes of rather high total ion concentration which were used in the present work. It occurs to us, therefore, that available information does not offer sufficiently convincing arguments so far to claim that significant differences exist in the conditions of specific chloride ion adsorption on gold electrodes with remelted surfaces and with surfaces deformed during their renewal.

In conclusion we wanted to call attention to the fact that substantial errors can arise when nonequilibrium values of electrode capacity are used in this sort of calculation, even when they have been measured at rather low frequencies (10 to 15 Hz) (compare Figs. 1 and 3). Extrapolation of the measured capacity to zero frequency without prior knowledge of the kinetic model of the adsorption process is insufficiently reliable. Hence in studying specific adsorption processes on metals it would be useful to work at frequencies much less than 10 Hz, as was done in [11] in studies of double-layer structure in electrolytes not exhibiting specific adsorption. We plan to perform such studies on the gold electrode in solutions containing chloride ions.

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