IMPORTANCE OF POLARIZATION PROCESSES NEAR THE ELECTRODES IN MEASUREMENTS OF THE DIELECTRIC CONSTANT OF CONDUCTING MEDIA

V. S. Gangnus, A. N. Sus, and V. V. Berezin

We attempt in the present work to analyze from a unified viewpoint the complicated laws which are observed in experiments when the dielectric constant of media with rather high positive conductivity is measured. The proposed method allows the calculation of the basic parameters of a measuring cell and of the dielectric constant of media.

In measuring $\varepsilon$ of conductive media, considerable difficulties associated with the dispersion of the capacitance are encountered. Basically, the capacitance of the measuring cell increases with decreasing frequency of the variable current. The increase in the capacitance goes with increasing conductivity of the medium and with decreasing frequency. The experimentally observed laws governing the phenomena are very complicated. At the present time there is no unity of opinion on the mechanism of the phenomena.

We consider in the present article a method which allows us to analyze from a unified viewpoint the laws observed in measurements of $\varepsilon$ of conductive media. The measuring cell is shown as equivalent circuit (Fig. 1), where $C_1$ and $R_1$ denote the polarization-induced capacitance of the electrode and the resistance of the layer near the electrode, respectively; $C_2$ and $R_2$ denote the capacitance and the resistance of the solution to be examined, respectively; and $C_e$ and $R_e$ denote the experimentally measured capacitance and resistance, respectively. $C_e$ and $R_e$ are associated with the parameters of the cell by the following relations

$$C_e = \frac{\omega^2 R_1 R_2 C_1 C_2 (C_1 + C_2) + R_1 C_1 + R_2 C_2}{\omega^2 R_1 (C_1 + C_2)^2 + (R_1 + R_2)^2},$$

(1)

$$R_e = \frac{\omega^2 R_1 R_2 (C_1 + C_2) + (R_1 + R_2)^2}{\omega^2 R_1 R_2 (R_1 C_1 + R_2 C_2) + (R_1 + R_2)}.$$

(2)

Equations (1) and (2) describe the frequency dependence of both the capacitance and resistance of the cell.

The form of the dispersion curve $(C_e/C_2) = \psi(\omega)$ is given by the form of Eq. (1) and the frequency dependence of the cell parameters $C_1$, $C_2$, $R_1$, and $R_2$. In the case of pure solutions, the quantities $C_2$ and $R_2$ are practically independent of the frequency. According to our measurements, the parameter $R_1$ is also independent of the frequency.

According to our concepts of electrochemistry, the polarization-induced capacitance $C_1$ of the electrode is a sum of capacitances: the capacitance $C_d$ of the double layer and the capacitance $C_p$ of a pseudocapacity [1]

$$C_1 = C_d + C_p = C_d + \frac{A}{\lambda_{\max}}.$$

(3)

The capacitance of the double layer is independent of the frequency and is given by the metal—solution contact. The polarization-induced capacitance increases at low frequencies due to the presence of the pseudo-
capacitance. For solutions with \( \sigma = 10^{-3} \ \Omega^{-1} \cdot \text{cm}^{-1} \), the increase is experimentally observed even at frequencies of several hundred kilohertz.

Let us analyze Eq. (1) under the assumption that the parameters of the cell are frequency-independent. In our ensuing discussion, a cell of this type is called a cell with fixed parameters:

a) at high frequencies

\[
\omega^2 R_1^* R_2^* C_1 C_2 (C_1 + C_2) > (R_1^* C_1 + R_2^* C_2), \\
\omega^2 R_1^* R_2^* (C_1 + C_2)^2 > (R_1^* + R_2^*)^2
\]

(4)

the influence of the polarization-induced capacitance is missing and the true capacitance (dielectric constant) is measured:

\[
\omega \to \infty; \quad C_e \to \frac{C_1 C_2}{C_1 + C_2} = C_2 \quad \text{for} \quad C_1 \gg C_2.
\]

(5)

b) At frequencies at which the quantities in Eq. (4) are of the same order of magnitude, \( C_e \) increases. This frequency interval is the interval of dispersion.

c) At low frequencies at which the inequalities (4) change their sign, the capacitance of the cell is independent of the frequency

\[
\omega \to 0; \quad C_e \to \frac{R_1^* C_1 + R_2^* C_2}{(R_1^* + R_2^*)^2} = C_1 \left( \frac{R_1}{R_1^* + R_2} \right)^2 \quad \text{for} \quad R_1^* C_1 > R_2^* C_2.
\]

(6)

The dispersion curve \( C_e/C_2 = \psi(\omega) \) for a cell with fixed parameters is shown in Fig. 2 (curve 1). The dispersion curve corresponds to solutions with a conductivity \( \sigma = 10^{-3} \ \Omega^{-1} \cdot \text{cm}^{-1} \). The dispersion curve for a real cell (in which the frequency dependence of the capacitance \( C_1 \)) appears) is shown as curve 2 on Fig. 2.

A comparison of the dispersion curves reveals that the dispersion of a cell with fixed parameters is equal to the dispersion of a real cell. The dispersion of the polarization-induced capacitance \( C_1 \) slightly reduces the dispersion of the capacitance of the cell. Substantial differences in the form of the dispersion are observed only at very low frequencies \( f < 10^4 \ \text{Hz} \). A smooth increase in \( C_e \) occurs in place of the plateau of the case of a fixed-parameter cell.

The following conclusions can be drawn from our above considerations.

The experimentally observed dispersion of the cell capacitance results from the features of the equivalent circuit of the cell proper. The dispersion of the polarization-induced capacitance \( C_1 \) is of secondary importance and manifests itself only at very low frequencies.

Thus, the frequently found opinion that the dispersion of the cell capacitance can be explained by the dispersion of the polarization-induced capacitance [2] is wrong. Curve 3 of Fig. 2 gives an idea of the dispersion of the polarization-induced capacitance, \( C_1/C_2 = \phi(\omega) \). It follows from the figure that for \( \sigma = 10^{-3} \ \Omega^{-1} \cdot \text{cm}^{-1} \) the dispersion starts from frequencies \( \sim 10^6 \ \text{Hz} \). In the case of solutions of high conductivity, the dispersion curves are more strongly bent and are shifted toward increased frequencies. Let us consider some applications of Eqs. (1) and (2).

**Calculation of the Parameters of the Measuring Cell**

Equations (1) and (2) can be used to calculate the cell parameters \( C_2, R_3, C_1, \) and \( R_1 \). When Eq. (1) is used with three similar frequencies \( \omega_1, \omega_2, \) and \( \omega_3 \), and when the cell parameters are assumed to change only insignificantly in this frequency interval, the joint solution of the three equations leads to an expression for \( C_2 \) which is obtained with the measured values of \( C_e \) and \( \omega \):