TWO-FREQUENCY MEASUREMENTS OF THE ZERO-CHARGE POTENTIAL

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UDC 541.3

We report here a study of the possible use of nonlinear ac methods to study electrochemical systems having a "nonlinear" capacitance. As Barker has shown [1], a potential dependence of the differential capacitance leads to a shift of the charge on the electrode surface under the influence of an alternating current passing through the cell (for a constant average electrode potential):

$$\Delta q = \frac{V^2}{4} C'_\varphi, \tag{1}$$

where V is the amplitude of the ac voltage across the double layer, and C_φ' is the derivative of the differential capacitance of the double layer with respect to the potential for a given average electrode potential.

We used a two-frequency method, monitoring the potential [2], to study systems having a "nonlinear" capacitance on well-polarizable electrodes for the case in which electrode reactions may be neglected. According to this method, two sinusoidal currents of the same amplitude and different but close frequencies, ν_1 and ν_2, are passed through the electrochemical cell [3]. A potentiostat imposes a constant potential φ, or one changing by a specified law, on the test electrode. Then the potential dependence of the amplitude $V_{\Delta\nu}$ of the harmonic component of the potential, at the difference frequency $\Delta\nu = \nu_1 - \nu_2$, is detected. The high-frequency currents are regulated by virtue of the small capacitance of ballast capacitors (C_b = 25-50 pF) connected between the cell and the voltage generators.

The amplitude $V_{\Delta\nu}$ of the difference-frequency voltage measured across the cell terminals is

$$V_{\Delta\nu} = \frac{V_g^2 C_b^2}{2} \left| \frac{C'_\varphi}{C^3} \right|, \tag{2}$$

where V_g is the amplitude of the voltages measured across the output of each high-frequency voltage generator when the two voltages are equal, C_b is the capacitance of the ballast capacitors, and C and C_φ' are the differential capacitance of the electrode and its derivative with respect to the potential.

If the equivalent circuit of the double layer is assumed to consist of two nonlinear capacitive elements in series, the expression for the amplitude of the difference-frequency voltage becomes

$$V_{\Delta\nu} = \frac{V_g^2 C_b^2}{2} \left| \frac{C'_1}{C_1^3} + \frac{C'_2}{C_2^3} \right|. \tag{3}$$

For a simple model of the double layer consisting of two series-connected capacitors, one may interpret C_1, C_2, C_1', and C_2' as the differential capacitances of the diffuse and dense parts of the double layer and their derivatives with respect to the potential.

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. (Presented by Academician A. N. Frumkin, January 20, 1971.) Translated from Doklady Akademii Nauk SSSR, Vol. 199, No. 3, pp. 638-639, July, 1971. Original article submitted January 20, 1971.

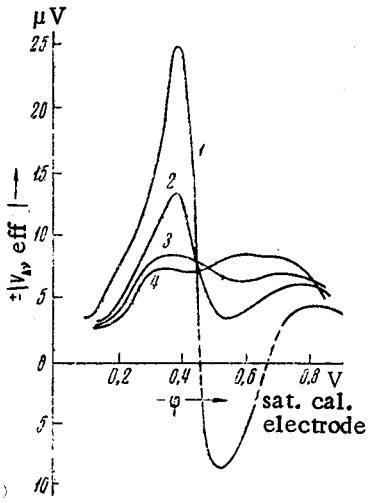

Fig. 1. Potential dependences of the effective difference-frequency voltage at various Na_2SO_4 concentrations at 500 kHz. 1) 0.03 N; 2) 0.1 N; 3) 0.3 N; 4) 1 N.

Using Grahame's assumptions [4] that the capacitance of the dense layer depends only on the charge on the electrode surface, and not on the electrode concentration, and that the potential at which the derivative of the diffuse-layer capacitance with respect to the potential vanishes does not depend on the electrolyte concentration, we see from Eq. (3) that the $V_{\Delta\nu}-(\varphi)$ curves should intersect at a single point at different electrolyte concentrations.

In an experimental check of this conclusion, we measured the difference-frequency voltage ($\Delta\nu$ = 1 kHz) at a mercury electrode in 1 N, 0.3 N, 0.1 N, and 0.03 N Na_2SO_4 at frequencies of 50, 100, 200, and 500 kHz and 1 and 2 MHz.

Figure 1 shows illustrative potential dependences of the effective difference-frequency voltage for various electrolyte concentrations at 500 kHz.

The shape of these curves agrees with Eq. (3). The curves corresponding to concentrations of 0.03 N, 0.1 N, and 0.3 N Na_2SO_4 intersect the curve corresponding to the 1 N solution at potentials of −0.440, −0.450, and −0.470, respectively (with respect to a saturated calomel reference electrode). We believe the displacement of the intersection is due to asymmetry of the valence type of the electrolyte [5].

It should be emphasized that impedance measurements of the zero-charge potential of an electrode through a determination of the minimum on the $C(\varphi)$ curve is possible only in extremely dilute electrolytic solutions and at comparatively low frequencies (of the order of hundreds of Hz), while measurement of the zero-charge potential through a determination of the intersection of the $V_{\Delta\nu}(\varphi)$ curves is possible at comparatively high concentrations (> 0.1 N) and at higher frequencies (> 50 kHz).

The authors thank Academician A. N. Frumkin, B. M. Grafov, V. S. Krylov, and B. B. Damaskin for useful discussions of these results; and L. G. Lozhkina, E. A. Šolomatin, S.S. Topilin, V. F. Mogilenko, and A. F. Vikulova for much assistance in this study.

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