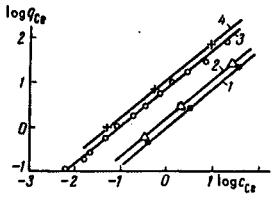

Fig. 5. Adsorption isotherm for cerium(III): 1) pH = 2.80; 2) pH = 3.20; 3) pH = 3.58; 4) pH = 4.00.

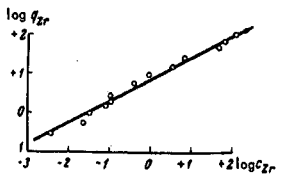

Fig. 6. Adsorption isotherm for zirconium at pH 3.60.

The adsorption is, within the limits of reproducibility of adsorption measurements, practically independent of the previous history of the solution and is equilibrium adsorption. The value of the pre-exponential coefficient A in the adsorption isotherm and its dependence on pH were determined from graphical analysis of the isotherms, taking into account the relative change in the specific surface of the precipitate, i.e.

$$A = A_0(\mathrm{pH})\frac{\epsilon}{\epsilon_0}. \qquad (2)$$

The dependence of A_0 on pH for cerium and zirconium is shown in Fig. 7; for strontium it is independent of pH within the range 2.0–4.5. The relationship is a linear one, which agrees well with theoretical conclusions[14,13] based on localisation of secondary exchange adsorption in a monolayer. Finally, the expression for adsorption in an electrical double layer with heterogeneous energy contour is

$$q = \frac{\epsilon}{\epsilon_0} A_0(\mathrm{pH})c^{1/n} \qquad (3)$$

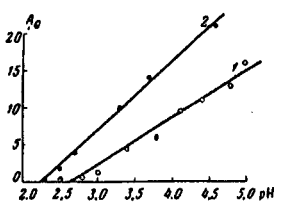

Fig. 7. Dependence of adsorption coefficient A_0 on pH: 1) for cerium; 2) for zirconium.

SUMMARY

1. The adsorption isotherm for cations on basic iron(III) acetate is expressed over a wide concentration range by Eqn. (1). The value of the coefficient n is independent of the pH of solution and is a function of the charge on the cation. The value of coefficient A, on the other hand, does depend on the pH. This affects the value of the specific surface of the precipitate and the electrical double layer at the solid–solution boundary in accordance with Eqn. (2).

2. The cation adsorption isotherm for secondary adsorption in an electrical double layer on precipitates of hydroxide type can be expressed explicitly by Eqn. (3).

1. I. Kurbatov and M. Kurbatov, J. Amer. Chem. Soc., 60, 1923 (1945); 69, 437 (1947); J. Phys. Colloid Chem., 55, 1070 (1951).
2. V. Pushkarev, Zhur. Neorg. Khim., 1, 170 (1956).
3. A. G. Morachevskii and A. Novikov (in print).
4. A. Braun, J. Chem. Soc., 121, 1736 (1922).
5. H. Freundlich and G. Schucht, Z. phys. Chem., 85, 641 (1914).
6. A. Lottermoser and A. Rose, ibid., 62, 359 (1908).
7. L. Levy, Compt. rend., 186, 1619 (1928).
8. E. Rudenko and V. Nikolaev, Izv. Akad. Nauk SSSR, Ser. Khim., 1045 (1936).
9. I. Ginzburg and A. Ponomarev, Izv. Akad. Nauk SSSR, Ser. Geol., 85 (1939).
10. R. Weinland and E. Gusseman, Ber., 42, 3001, 3381 (1909); Z. anorg. Chem., 66, 157 (1910).
11. A. Krause, Z. anorg. Chem., 169, 273 (1928).
12. W. Hertz, ibid., 20, 16 (1899).
13. E. N. Gapon, Zhur. Fiz. Khim., 11, 782 (1938); 15, 655, 659 (1941).
14. A. N. Frumkin, Dokl. Akad. Nauk SSSR, 69, 821 (1949).

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DETECTION OF CONCENTRATION POLARISATION BY MEASUREMENT OF ELECTRODE IMPEDANCE

D. I. Leikis and L. L. Knots

The first question which arises in investigating the kinetics of electrode processes is whether the rate of the process is limited by the diffusion of reactant species to the electrode–electrolyte boundary or by the diffusion of reaction products away from this boundary — in other words, whether concentration polarisation occurs at the electrode. In several papers measurement of the components of the impedance of the electrode in alternating current of variable frequency has been employed to settle this question. Its use is based on the fact that concentration polarisation at an electrode is equivalent to a capacitance and a resistance connected either in parallel or in series, the phase shift of the whole unit being 45°, and the components of the impedance varying linearly with $\omega^{-\frac{1}{2}}$, where ω is the a.c. frequency[1-3].

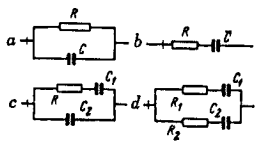

Fig. 1.

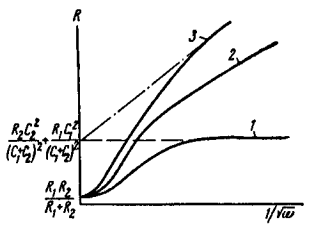

Fig. 2.

In studies of the kinetics of electrode processes, a linear relation between the components of the impedance of the electrode and $\omega^{-\frac{1}{2}}$ was usually the criterion for concentration polarisation[2]. Such a relationship can be observed over a comparatively wide frequency range, however, only if the capacitive reactance of the double layer within this range is considerably greater than the resistance in the concentration term, and can be neglected in comparison with the latter, since they are connected in parallel. If it is impossible to neglect the capacitive reactance of the double layer, e.g. if its capacitance is extremely high, or if the concentration polarisation is high (diffusion in solid phase restricted), the dependence of the components of the impedance on $\omega^{-\frac{1}{2}}$ is more complicated, and the criterion of linearity cannot be used to detect concentration polarisation.

On analysing the dependence of the components of the electrode impedance on $\omega^{-\frac{1}{2}}$, taking into account the capacitance of the double layer, however, we discovered a property of the active component of the impedance as a function of $\omega^{-\frac{1}{2}}$ which can be readily used to decide whether concentration polarisation is present at the electrode. We assumed that in the absence of concentration polarisation any electrode can be simulated to a first approximation by one of the four circuits depicted in Fig. 1 *. The impedance of this electrode is $\dot{Z}_0 = R_0 - jX_0$, where R_0 and X_0 are the active and reactive components. Let us write down the impedance for each of the circuits in Figs. 1*a*–1*d*:

$$\dot{Z}_{0(1)} = \frac{R}{1+(\omega RC)^2} - j\,\frac{\omega R^2 C}{1+(\omega RC)^2} = R_{0(1)} - jX_{0(1)}; \quad (1)$$

$$\dot{Z}_{0(2)} = R - j\,\frac{1}{\omega C} = R_{0(2)} - jX_{0(2)}; \quad (2)$$

$$\dot{Z}_{0(3)} = \frac{RC_1^2}{\omega^2R^2C_1^2C_2^2+(C_1+C_2)^2} - j\,\frac{\omega^2R^2C_1^2C_2^2+\omega^{-1}(C_1+C_2)}{\omega^2R^2C_1^2C_2^2+(C_1+C_2)^2} = R_{0(3)} - jX_{0(3)}; \quad (3)$$

$$\dot{Z}_{0(4)} = \frac{\omega^2C_1^2C_2^2R_1R_2(R_1+R_2)+R_1C_1^2+R_2C_2^2}{\omega^2(R_1+R_2)^2C_1^2C_2^2+(C_1+C_2)^2} - j\,\frac{\omega C_1C_2(R_1^2C_1+R_2^2C_2)+\omega^{-1}(C_1+C_2)}{\omega^2(R_1+R_2)^2C_1^2C_2^2+(C_1+C_2)^2} = R_{0(4)} - jX_{0(4)}; \quad (4)$$

$$\lim_{\omega\to 0} R_{0(1)} = R; \quad (5)$$

$$\lim_{\omega\to 0} R_{0(2)} = R; \quad (6)$$

$$\lim_{\omega\to 0} R_{0(3)} = \frac{RC_1^2}{(C_1+C_2)^2} < R; \quad (7)$$

$$\lim_{\omega\to 0} R_{0(4)} = \frac{R_1C_1^2}{(C_1+C_2)^2} + \frac{R_2C_2^2}{(C_1+C_2)^2} < R_1+R_2. \quad (8)$$

It is evident from the above that in all the circuits R_0 is a function tending to an upper limit, which cannot exceed the resistances of the electrochemical stage of the electrode process or the sum of such stages, if they occur in parallel [Eqns. (5)–(8)]. Inclusion in the electrode-simulating circuit of a resistance equivalent to concentration polarisation makes this function unbounded, since the latter is an unbounded function of $\omega^{-\frac{1}{2}}$. This is illustrated by Fig. 2, in which curve *1* shows the general variation of the active component R_0 as a function of $\omega^{-\frac{1}{2}}$ for circuit *d* in Fig. 1; curve *3* shows the corresponding curve obtained when a concentration-dependent resistance is connected in series with the whole circuit *d* in Fig. 1. Curve *2* (Fig. 2) shows the variation in R_0 when the concentration-dependent resistance is included in series with C_1 or C_2 (circuit *d* in Fig. 1). It is evident from Fig. 2 that inclusion of a concentration-dependent resistance transforms R_0 from a bounded to an unbounded function.

It is thus possible by measuring the variation of the active component of the impedance with $\omega^{-\frac{1}{2}}$ to judge whether concentration polarisation is present at an electrode. A limit to the active component of the impedance as $\omega \to 0$ is a criterion of the absence of concentration polarisation. Unlimited increase in the active component of the electrode as $\omega \to 0$ indicates the occurrence of concentration polarisation. A linear relation between R_0 and $\omega^{-\frac{1}{2}}$ occurs in the presence of concentration polarisation in general only at frequencies which are sufficiently low for the effect of the resistance of the reaction and the capacitance of the double layer to be neglected but not so low that the normal course of non-stationary diffusion is disturbed by convection.

In conclusion, we wish to thank Professor B. N. Kabanov for valuable advice.

* We assume that the capacitive elements of the circuits, corresponding to the capacitance of the double layer or the adsorption capacitance, as well as the resistance elements, corresponding to the resistances of the separate reaction stages, remain unchanged while their frequency dependence is being measured.

1. B. Ershler, Zhur. Fiz. Khim., 22, 683 (1948).
2. B. Ershler and K. Rozental', "Trudy Soveshchaniya po Elektrokhimii" (Transactions of the Conference on Electrochemistry), Izd. Akad. Nauk SSSR, 1950, Moscow, 1953, p. 446.
3. H. Gerischer, Z. phys. Chem. (Leipzig), 198, 287 (1951).

Institute of Electrochemistry,
Academy of Sciences of the USSR

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