V. M. BORISOV, Yu. Ya. GOLGER

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V. M. BORISOV, Yu. Ya. GOLGER

MEASUREMENT OF THE THERMODYNAMIC AND ADSORPTION POTENTIALS OF A DIELECTRIC MINERAL FOR THE PURPOSE OF STUDYING THE FLOTATION PROCESS

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In recent years, in the study of flotation, methods for measuring electrochemical quantities have often been used. As is known, the magnitude of the ζ-potential ($^{1-3}$) characterizes the state of the electrical double layer. Therefore, its investigation makes it possible to analyze the mechanism of action of individual reagents in flotation and other adsorption-flotation phenomena.

Of still greater interest from this point of view are measurements of the total potential jump at the solid–liquid phase boundary, measurements of the thermodynamic or φ-potential ($^{7-9}$). The works of A. N. Frumkin and his school have established the relation between the φ-potential and surface tension, and between the φ-potential and the contact angle of wetting (^{4,5}).

The dependence of the contact angle of wetting on the φ-potential is expressed by a curve similar to a parabola, the maximum of the contact-angle curve lying near that value of the thermodynamic potential at which the charge of the double layer $\varepsilon = 0$. It has also been established that the presence of specifically adsorbing organic substances shifts somewhat the position of the maximum of the curve (^{6}). Analytically, the dependence of the change in surface tension on the change in φ-potential is expressed by the well-known Lippmann equation:

$$\frac{d\sigma}{d\varphi} = -\varepsilon.$$

In a number of cases, interesting results were obtained by means of measurements of the φ-potential ($^{10-12}$). However, in all the above-mentioned works, both physicochemical and applied, the thermodynamic potential of conducting electrodes was measured: metals or semiconductors with comparatively low specific resistance. The present work shows that in studying flotation phenomena one may use the method of measuring the thermodynamic potential not only of conductors but also of dielectrics. Calcite was chosen as such a nonconducting dielectric mineral.

The electrode for measuring the φ-potential of calcite was constructed on the principle of the glass electrode. The potential of the nonconducting mineral was successfully measured because the resistance of the specimen was lowered

Fig. 1. Effect of soda and calcium chloride on the thermodynamic potential of calcite

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by reducing its thickness. A calcite plate 0.03–0.05 mm thick, prepared on a microscope slide as an ordinary uncovered thin section, was washed with acetone and distilled water and, with the aid of an adhesive substance (for example, molten rosin or glue No. 88), was fastened to the end of a glass tube. The cylindrical vessel thus obtained was filled with a saturated solution of calcium chloride and a platinum electrode was inserted. In the sealed state, such a calcite electrode was ready for measurements. A saturated calomel electrode was used as the reference electrode. The potential difference between the calcite-

with silver and calomel electrodes at a temperature of 20° was measured with a tube potentiometer of the LP-5 type.

The distilled water used in the experiments had an electrical conductivity of the order of $(2 \div 3) \cdot 10^{-5}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$. This indicates that impurities were present in the water in considerable amounts. However, in these experiments there was no intention of carrying out measurements under especially pure conditions. The aim of the work was only to establish the fundamental possibility of measuring the thermodynamic potential of calcite as a function of the composition of the liquid phase and of using these measurements in the study of the interaction of the mineral surface with flotation reagents. Proceeding from the same considerations, it was not the equilibrium value of the φ-potential that was measured, but rather its value attained after a 5-minute contact of the electrode with the solution. Such a contact time corresponds approximately to the contact time of minerals with reagents in a flotation pulp.

Fig. 1. Effect of soda and calcium chloride on the thermodynamic potential of calcite (on the abscissa is plotted the decimal logarithm of the concentration of the substance, expressed in g-equiv/l)

In Figs. 1 and 2 the results of experiments with a calcite electrode are presented. The potential-determining ions for calcite, as is known, are the ions Ca^{2+} and CO_3^{2-}. Therefore, when the concentration of $CaCl_2$ in the solution is increased, the potential of the calcite electrode should shift in the positive direction, whereas an increase in the concentration of CO_3^{2-} ions in the solution should produce the opposite effect. As can be seen from Fig. 1, the experimental results mainly confirmed these assumptions. The addition of sodium oleate to the liquid phase also shifts the potential of the calcite electrode in the negative direction. Figs. 1 and 2 show results obtained on one and the same calcite electrode. The numbers at the points denote the numbers of successive measurements.

Fig. 2. Effect of sodium oleate on the thermodynamic potential of calcite

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Figure 2: Fig. 2. Effect of sodium oleate on the thermodynamic potential of calcite

As is known, the dependence of the thermodynamic potential on the concentration of potential-determining ions is expressed by the Nernst equation:

$$\varphi = \varphi_0 + \frac{RT}{zF} \ln C,$$

where F is the Faraday number, z is the number of electrons participating in the exchange between the electrode and one ion, and C is the concentration of the potential-determining ions.

As can be seen from Fig. 1, within the concentration ranges for soda $5 \cdot 10^{-4} \div 2 \cdot 10^{-1}$ g-equiv/l, and for calcium chloride $1 \cdot 10^{-3} \div 2 \cdot 10^{-1}$ g-equiv/l, a rectilinear dependence of the φ-potential on the logarithm of the concentration of the potential-determining ions was obtained.

It follows from the Nernst equation that when the concentration changes by one order of magnitude, the φ-potential should change by RT/zF, which at 20° is 29 mV. In our measurements this quantity was 11–12 mV. The deviation observed in the experiments from the thermodynamic dependence may be explained by three reasons: 1) the presence in the system of surface-active substances and other impurities, 2) the nonequilibrium character of adsorption phenomena,

and 3) the fact that the electrode was made from a real crystal, in which there may be various kinds of defects and microinclusions.

Experiments showed that the value of the calcite potential in distilled water depends on which of the solutions the electrode had previously been in. This phenomenon can evidently be explained in the same way as the cause of the acid and alkaline hysteresis of the glass electrode is explained ([13]). Apparently, it is associated with the long duration of desorption of potential-determining ions from the deeper layers of calcite.

Thus, the potential of the calcite electrode depends to a considerable extent on its "prehistory." Experiments showed that in some cases different electrodes have different potential values under identical conditions. Preliminary soaking of the electrode in distilled water or drying in air can also change the absolute value of its potential.

At the same time, it should be especially emphasized that, despite a certain instability of the absolute values of the ϕ-potential of the calcite electrode, in all cases regularities similar to those shown in Figs. 1 and 2 were observed.

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