PHYSICAL CHEMISTRY

Academician of the Academy of Sciences of the Ukrainian SSR Yu. K. Delimarskii, V. F. Grishchenko, and A. V. Gorodyskii

1962

SovietRxiv

Fig. 1. Scheme for measuring the capacitance of the double layer: 0 —audio-frequency generator, 1 —cell, 2 —active resistance

Figure 1: Fig. 1. Scheme for measuring the capacitance of the double layer: 0 —audio-frequency generator, 1 —cell, 2 —active resistance

Abstract

Full Text

PHYSICAL CHEMISTRY

Academician of the Academy of Sciences of the Ukrainian SSR Yu. K. Delimarskii, V. F. Grishchenko, and A. V. Gorodyskii

CAPACITANCE OF THE DOUBLE LAYER IN THE BINARY MELT $PbCl_2$—KCl

The capacitance of the double electric layer in melts has been studied by few authors ([1–6]). These investigations were carried out in order to determine points of zero charge, the contact potential difference, and to elucidate the kinetics of certain electrode processes. Measurements of capacitance in melts of different composition were episodic in character: the capacitance was measured when one ion was completely replaced by another ([1,5]). For investigating the dependence between the capacitance of the double layer and the composition of the electrolyte, the study of binary melts is of interest. These data may prove useful both for characterizing the double electric layer and for physicochemical analysis of melts and for judging the chemical interaction between the components of a salt melt. In this respect, the capacitance of the double layer has not been investigated at all. We chose for study the system $PbCl_2$—KCl, for which the phase diagram is well known ([7]).

Fig. 1. Scheme for measuring the capacitance of the double layer: 0 —audio-frequency generator, 1 —cell, 2 —active resistance

Measurements of the double-layer capacitance were carried out by means of experimental methods developed by us ([6]). The schematic diagram of the apparatus is shown in Fig. 1. The voltage from an audio-frequency generator 0 with a frequency of 500 Hz was applied to the series-connected cell 1 and active resistance 2. The voltages U_0, U_1, U_2 were measured with an oscillograph. The active component of the vector U_1 is equal to

$$U_{1,a} = \frac{U_0^2 - U_1^2 - U_2^2}{2U_2}, \tag{1}$$

its reactive component is equal to

$$U_{1,c} = \sqrt{U_1^2 - U_{1,a}^2}, \tag{2}$$

and the reactive resistance of the cell is equal to

$$X = \frac{R \cdot U_{1,c}}{U_2}. \tag{3}$$

Another method used for determining the value X consisted in using a phase-sensitive voltmeter, which directly gave the value $U_1 \cdot \sin(U_1, U_2)$, if the vector U_2 was used as the reference voltage.

For the binary melt $PbCl_2$—KCl, it would have been most interesting to study the capacitance of a lead electrode. However, the capacitive resistance of the cell Pb (l) |$PbCl_2$, KCl| Pb (l) was equal to zero. This is naturally explained by the absence of electrochemical polarization and charging of the lead electrode in this circuit. Therefore platinum electrodes were chosen for the capacitance measurements. The measurements were carried out on two electrodes prepared from platinum wire sealed into glass, with a diameter of 384

0.5 mm. The length of the free end was 2 mm. The cell was a porcelain crucible filled with the molten salt. Before the measurement the electrodes were boiled in concentrated hydrochloric acid.

The data we obtained, together with the phase diagram of the system, are presented in Fig. 2. Curve 2 represents the isotherm of capacitive resistance, taken at 540°. Curve 3 represents the capacitive resistance measured at temperatures 50° above the corresponding points on the liquidus curve of the phase diagram. The extrema of both curves correspond to the extrema on the phase diagram.

Thus, capacitive resistance can be used as a property for physicochemical analysis of molten salt systems. Curve 2 can be interpreted as follows. When lead chloride is diluted with potassium chloride from 100 to 77% $PbCl_2$, the composition of the melt and the capacitance of the double layer change correspondingly, which apparently indicates a similar change in the composition of the melt and the composition of the double layer. In the range from 77 to 52% $PbCl_2$, the capacitance of the double layer and, evidently, its composition remain practically constant. This may possibly be explained by specific adsorption of the product of electrolytic dissociation of the compound $2PbCl_2 \cdot KCl$ and by the discrepancy between the composition of the double layer and the overall composition of the electrolyte. At 52% $PbCl_2$, a rearrangement of the double layer occurs, which corresponds to the next plateau on the composition—capacitive-resistance isotherm.

Fig. 2. Composition—property diagram of the $PbCl_2$—KCl melt: 1 —phase diagram, 2 —isotherm of capacitive resistance at 540°, 3 —capacitive resistance at temperatures 50° above the liquidus curve.

Fig. 2. Composition-property diagram of the $PbCl_2$—KCl melt: 1 —phase diagram, 2 —isotherm of capacitive resistance at 540°, 3 —capacitive resistance at temperatures 50° above the liquidus curve

Figure 2: Fig. 2. Composition-property diagram of the $PbCl_2$—KCl melt: 1 —phase diagram, 2 —isotherm of capacitive resistance at 540°, 3 —capacitive resistance at temperatures 50° above the liquidus curve

As a result of the work carried out, a method is proposed for investigating composition—double-layer-capacitance curves in order to judge the structure of the electrical double layer in molten salts, and the capacitance of the double layer on platinum electrodes in the binary melt $PbCl_2$—KCl has been studied. The assumption is put forward that complex ions from the melt are specifically adsorbed, causing a difference between the composition of the double layer and the overall composition of the melt.

Institute of General and Inorganic Chemistry
Academy of Sciences of the Ukrainian SSR

Received
5 II 1962

REFERENCES CITED

1. S. V. Karpachev, A. G. Stromberg, *ZhFKh*, **7**, 754 (1936); **10**, 739 (1937); **13**, 1831 (1939); **18**, 47 (1944); *Zs. phys. Chem.*, **176**, 182 (1936). *Acta physicochim. URSS*, **12**, 523 (1940).

2. Yu. P. Nikitin, O. A. Esin, *DAN*, **83**, 341 (1952); **107**, 847 (1956); **111**, 133 (1956).

3. H. A. Laitinen, R. Osteryoung, *J. Electrochem. Soc.*, **107**, 847 (1955); H. A. Laitinen, D. K. Roe, *Collection*, **25**, 3065 (1960).

4. R. B. Stein, *C. R.*, **246**, 2611 (1958).

5. E. A. Ukše, N. P. Bukin, D. I. Leikis, *DAN*, **135**, 1183 (1960).

6. A. V. Gorodyskii, E. V. Panov, *Dokl. AN USSR*, **61**, No. 2 (1962).

7. N. K. Voskresenskaya, N. N. Evseeva, S. I. Berul, I. P. Vereshchitina, *Handbook on the Fusibility of Systems of Anhydrous Inorganic Compounds*, 1, Publishing House of the Academy of Sciences of the USSR, 1961, p. 363.

Note: Figure translations are in progress. See original paper for figures.

original.