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Abstract

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CAPACITANCE OF THE ELECTRIC DOUBLE LAYER IN MOLTEN SALTS

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The structure of the electric double layer in molten salts has, up to the present time, practically not been investigated, although this question is of substantial importance both for theory and for practice. Some data on the capacitance of the double layer at a mercury electrode in nitrate melts and on platinum in chlorides have been published by Randles and White (1) and by Laitinen et al. (2). However, these works do not make it possible to judge the special features of the structure of the double layer in melts.

Recently we have undertaken a systematic investigation of the capacitance of the electric double layer in molten salts. The present article is a preliminary report on the results obtained. The experiments were carried out in an argon atmosphere at 700–800° C. The measuring cell was a quartz beaker closed with a molybdenum-glass lid on a ground joint. The electrodes were mounted in the lid. As the holder for the electrode under investigation, a quartz tube was used, the end of which was bent upward and drawn out into a capillary. The tube was filled with the liquid metal being studied, the working surface of which was a hemisphere bounded by the walls of the capillary. Rods of spectrally pure graphite, the lateral surface of which was protected by quartz tubes, served as electrodes for polarization by direct and alternating current. The reference electrode was a lead electrode

$$\mathrm{Pb/KCl,\ NbCl\,(1:1),\ 2.5\ mol.\%\ PbCl_2},$$

which was placed in a quartz tube with a capillary opening. The potential of such an electrode on the chlorine potential scale was 1.39 V. In all experiments the electrolyte was an equimolar molten mixture of sodium and potassium chlorides. Measurements of the capacitance and resistance of the cell at a given potential were carried out with an impedance bridge at frequencies from 20 to 200 kHz.

Fig. 1. Dependence of the capacitance of the double layer on the potential for liquid metal electrodes in a KCl—NaCl melt at 700° and $f = 200$ kHz.
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Figure 2: Dispersion of capacitance and resistance for liquid electrodes in KCl—NaCl melt.

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Figure 1 presents curves of the dependence of capacitance on potential for lead and cadmium electrodes at a frequency of 200 kHz. In all cases the dependence of capacitance on potential had a sharply pronounced minimum; moreover, the potential corresponding to the minimum capacitance was determined by the nature of the metal and did not depend on the frequency of the alternating current or (within 100°) on temperature. The capacitance and resistance of the cell depended on frequency,

and the dispersion, with increasing frequency, gradually vanished (see Fig. 2). We assumed that the dispersion of capacitance with frequency near the minimum is associated with the penetration of electrolyte between the walls of the capillary and the liquid metal. As the frequency of the alternating current is increased, the part of the metal surface shielded by the capillary walls gradually drops out of the measurements and the capacitance decreases. An analogous cause of dispersion was established by Grahame ([3]) in measurements of the capacitance of the double layer in aqueous solutions. It should only be noted that, because molten electrolytes have conductivities hundreds of times higher than those of their solutions, the dispersion effect in our experiments was much more pronounced and persisted to higher frequencies than is the case in solutions.

Fig. 2. Dispersion of capacitance and resistance for liquid electrodes in KCl—NaCl melt. *1a*, *1b* —C and R for the Pb electrode ($S = 4.9 \cdot 10^{-3}$ cm^2); *2a*, *2b* —C and R for the Cd electrode ($S = 6.2 \cdot 10^{-3}$ cm^2); *3a*, *3b* —the same for the Cd electrode ($S = 14.1 \cdot 10^{-3}$ cm^2).

Taking into account the character of the dependence of capacitance on frequency, we took as the true value of the capacitance of the double electric layer of the electrode under study the value measured at 200 kHz. At this frequency the working surface of the electrode was taken to be the surface of a hemisphere with a diameter equal to the diameter of the capillary. To verify the correctness of this determination of the specific capacitance, we measured the capacitance of cadmium electrodes having different surface areas. From the data presented in Fig. 2 the following ratios follow: $C'_{\mathrm{Cd}} : C''_{\mathrm{Cd}} = 1 : 2.36$; $S'_{\mathrm{Cd}} : S''_{\mathrm{Cd}} = 1 : 2.28$.

Thus, it may be considered that at a frequency of 200 kHz the effect of shielding of the electrode surface by the walls of the holder can be neglected. In this case the specific capacitance of cadmium at the potential $\varphi = -0.8$ V is 36 μF/cm^2. For lead at the potential $\varphi = -0.55$ V, a close value is obtained: $C = 38$ μF/cm^2.

Table 1

Metal	Electrolyte	Temp., °C	φ at the maximum of the electrocapillary curve, V	Metal	Electrolyte	Temp., °C	φ at the minimum of the capacitance curve, V
Lead	KCl–LiCl	450	-0.58 ± 0.02	Lead	KCl–NaCl	700	-0.55
Cadmium	KCl–LiCl	450	-0.82 ± 0.02	Cadmium	KCl–NaCl	700	-0.80
Thallium	KCl–LiCl	420	-0.85 ± 0.02	Thallium	KCl–NaCl	700	-0.87
Antimony	KCl–LiCl	1050	-0.10 ± 0.02	Antimony	KCl–LiCl	500	-0.92
Antimony	KCl–LiCl	750	0.00 ± 0.02	Antimony	KCl–NaCl	700	-0.17
Tin	KCl–LiCl	420	-0.43 ± 0.02	Tin	KCl–NaCl	700	-0.32
Bismuth	KCl–LiCl	420	-0.48 ± 0.02	Bismuth	KCl–NaCl	700	-0.32

Table 1 compares the values of the potentials of the maxima of electrocapillary curves and the minima of capacitance curves for a number of metals. As is seen from the data in Table 1, the potential corresponding to the minimum capacitance is close to the potential of the maximum of the electrocapillary curve of the corresponding metal ([4,5]).

When comparing our data with those of S. V. Karpachev and A. G. Stromberg ([4,5]), it should be borne in mind that these authors used as the reference electrode a stationary lead electrode, whose potential at 700° was 200 ± 20 mV more negative than the potential of the reference electrode used by us. In Table 1 the data of S. V. Karpachev and A. G. Stromberg are given after conversion to our potential scale.

The coincidence of the potentials corresponding to the minimum capacitance with the potentials of the maxima of the electrocapillary curves makes it possible to use the method of measuring capacitance in melts to determine the zero points of metals. Moreover, it should be expected that, if the capacitance

Fig. 3. Electrocapillary curves of Pb (1) and Cd (2), obtained by integration of the C–φ curves of Fig. 1. Points are experimental data taken from work ⁽⁵⁾

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measured by us is the capacitance of the double electric layer, then double integration of the C–φ curves should yield electrocapillary curves coinciding with the experimental ones. Such coincidence would be impossible if a significant fraction of the measured capacitance were pseudocapacitance, or if the specific capacitance per unit surface had been determined by us incorrectly.

Fig. 3. Electrocapillary curves of Pb (1) and Cd (2), obtained by integration of the C–φ curves of Fig. 1. Points are experimental data taken from work ⁽⁵⁾.

In Fig. 3 are shown the electrocapillary curves obtained by graphical integration of the capacitance curves (Fig. 1) under the following boundary conditions ⁽⁵⁾:

$$\text{for Pb at } \varphi = -0.55\ \text{V}, \quad \sigma = 444\ \text{dyn/cm};$$

$$\text{for Cd at } \varphi = -0.80\ \text{V}, \quad \sigma = 568\ \text{dyn/cm}.$$

The experimental points taken from work ⁽⁵⁾ are also plotted there. Taking into account some difference in the experimental conditions, the agreement between the calculated and experimental data should be regarded as satisfactory.

Thus, on the basis of the results obtained, the following conclusions may be drawn. The capacitance of the double electric layer in molten electrolytes is minimal at the potential of zero charge of the metal. The minimum of the C–φ curve in melts corresponds to a capacitance of 36–38 μF/cm^2. The existence of a capacitance minimum on the C–φ curves in melts requires a special explanation. This minimum can hardly be explained by analogy with dilute aqueous solutions by diffuseness of the double layer, since, first, the presence of diffuseness in such concentrated ionic systems as molten salts appears unlikely, and, second, the minimum capacitance in the present case is so large that the thickness of the double electric layer cannot substantially exceed one ionic diameter.

The increase in the capacitance of the double layer with increasing charge of the metal surface may be associated with deformation of the electron shells of the ions, as well as with densification of the structure of the molten salt (displacement of holes from the near-electrode layer). With a strong shift of the potential in the positive or negative direction, pseudocapacitance apparently appears, caused by the occurrence of the process of self-dissolution of the electrode or discharge of alkali-metal cations. The possibility of reduction of Na$^+$ or K$^+$ ions at potentials more positive than the standard pothe potentials of the corresponding metals is probably associated with depolarization due to the energy of alloy formation ([6]).

In conclusion, we take this opportunity to express our deep gratitude to Academician A. N. Frumkin and Professor B. N. Kabanov for their valuable advice in carrying out and discussing the present work.

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