RELATION BETWEEN THE CAPACITY OF THE DOUBLE LAYER AND THE TEMPERATURE IN MOLTEN SALTS

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Translated from Zhurnal Prikladnoi Khimii, Vol. 36, No.9, pp. 1965-1969, September, 1963
Original article submitted May 8, 1962

The study of the electrical double layer in molten salts is of importance both for the theory of electrode processes at high temperatures, and for the solution of purely practical problems concerning the effect of different types of compounds on the electrodeposition processes in relation to their adsorbability at the electrode-molten electrolyte boundary.

Investigations carried out earlier [1-4] have shown that, for all the metals studied, the relationship between the capacity of the double layer and the potential takes the form of a curve possessing a minimum. The value of the potential at the minimum in such cases corresponded with the potential maximum for the electrocapillary curves of the corresponding metals. By creating the necessary conditions, with the exception of dispersion (a large surface area for the electrode under investigation and alternating current of relatively high frequency [5]), we have been able to measure the specific capacity of the double layer with an accuracy lying within the limits 3-5%. Thus, the capacity of a lead electrode in an equimolecular melt of potassium and sodium chlorides at 700°, near to the zero charge potential, amounted to 34-36 microfarads/cm^2.

The present communication is devoted to the results of an investigation of the double layer in melts consisting of alkali metal halides at various temperatures.

METHODS AND RESULTS

A detailed description of the method of measuring the capacity of the double layer in molten salts has been given in previous papers [1-3]. The only modification consisted in some change in the construction of the quartz capillary for liquid metals. The height of the capillary was 2 cm, while its diameter was such to ensure that the meniscus of the metal had an area of around 0.05-0.08 cm^2. This permitted of practical elimination of dispersion capacity even at a frequency of 20 kilohertz. Measurement was conducted in an atmosphere of argon. The comparison electrode consisted of the half-element

$$Pb \mid 2.5 \text{ mol. \% } PbCl_2 + \text{investigated electrolyte}.$$

Figure 1 gives the results of measuring the capacity of a lead electrode in an equimolecular mixture of potassium and lithium chlorides, while Fig. 2 gives the same for an equimolecular mixture of potassium and sodium chlorides, using various temperatures. The figures reveal that increase in temperature results in a shift of the capacity-potential curves in the direction of higher capacity and more positive potentials. At the same time the character of the curves changes, since they become more sharp, that is, the change of capacity with potential occurs more rapidly.

Similar results were obtained using a lead electrode in melts of sodium chloride, cesium chloride and potassium iodide.

Measurements carried out on solid* and liquid aluminum electrodes at temperatures of 450, 600, and 700° in an equimolecular melt of potassium and lithium chlorides, show qualitatively the same relationship between capacity of the double layer and temperature as that obtained for the lead electrode (Fig. 3).

* Since the true value of the solid surface exceeds the apparent value, in calculating the specific capacity on solid electrodes it has been assumed that the value of C_{min} for these would coincide with the value of C_{min} for a liquid lead electrode under the same conditions. The coefficient for recalculation obtained in this way amounted to 3.4-3.5.

For a liquid indium electrode, and also for solid and liquid silver electrodes, increase in temperature was accompanied by increase in capacity of the double layer and displacement of the minimum in the capacity-potential curve in the direction of more negative potentials (Figs. 4 and 5).

The table gives values of the displacement of C_{min} when the electrolyte temperature is changed by 100°.

The displacement of the capacity curves with change in temperature in one direction or the other along the potential axis is only relative, since change in temperature also causes change in the potential of the comparison electrode. Thus, each capacity curve in Figs. 1-5 is actually measured on its own scale of potentials, and direct comparison of them is impossible.

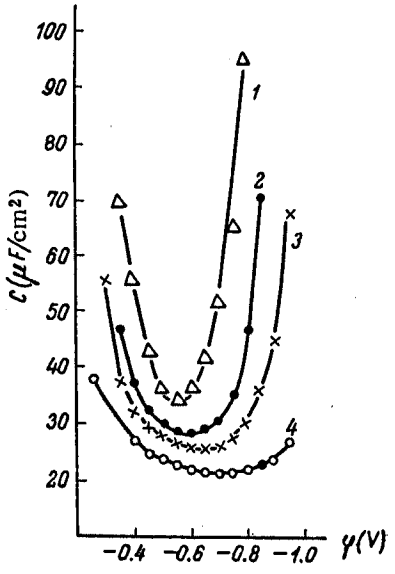

Fig. 1. Capacity (C, microfarads/cm²) of a lead electrode in an equimolecular melt of potassium and lithium chlorides. Temperature (°C): 1) 800; 2) 700; 3) 600; 4) 450.

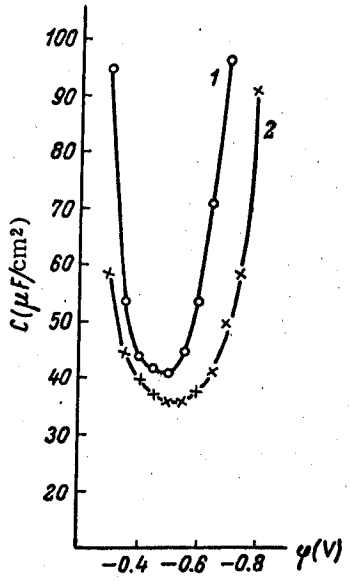

Fig. 2. Capacity of a lead electrode in an equimolecular melt of potassium and sodium chlorides. Temperature (°C): 1) 800; 2) 700.

It may nevertheless be observed that the shift of potential at the minimum for lead and aluminum, on the one hand, is in the opposite direction from that for silver and indium, on the other. This leads to the conclusion that the relative position of the potentials of zero charge for the various metals must also change with change in temperature.

DISCUSSION OF RESULTS

The data on the effect of temperature on the relationship between the capacity of the electrical double layer and the potential provide evidence against the hypothesis of a diffuse structure for the double layer in molten salts [6], since increase of temperature would in such a case inevitably lead to a reduction in the capacity, and not to the increase which is in fact observed.

Increase in capacity with increase in temperature must be explained on basis of the same ideas on the structure of the double layer in molten salts as have already been indicated [5]. It was there suggested that the value of the capacity is determined by the thickness of the double layer, which may be altered by deformation of the ions themselves, and the structural-geometrical deformation of the preelectrode layer of the electrolyte. Increase in temperature increases the quantity and dimensions of internal holes and cavities in the molten salt [7], which facilitates penetration of cations into the surface of the metal, followed by their adsorption. The result is a contraction of the double electrical layer. It would be expected that this effect would reveal itself more strongly for electrolytes with small cathodes, a suggestion confirmed by the data in the table.

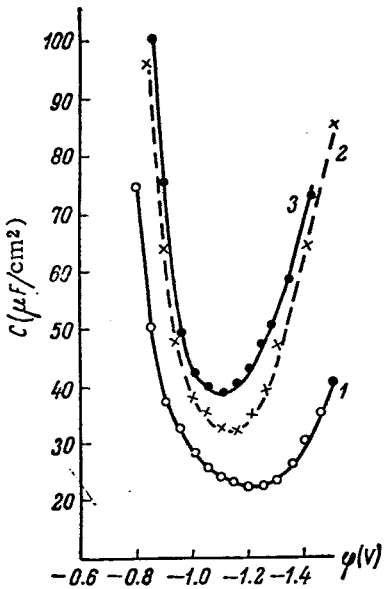

Fig. 3. Capacity of an aluminum electrode in an equimolecular melt of potassium and lithium chlorides. Temperature (°C): 1) 450; 2) 600; 3) 700.

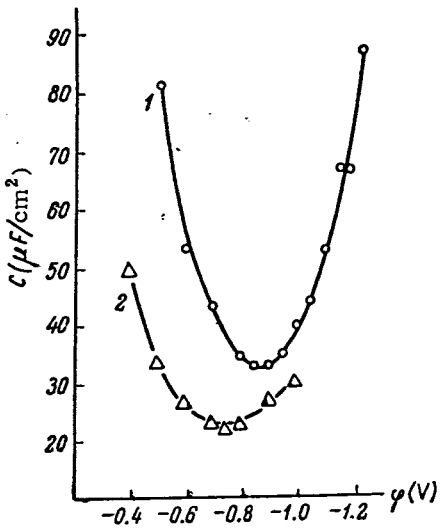

Fig. 4. Capacity of an indium electrode in an equimolecular melt of potassium and lithium chlorides. Temperature (°C): 1) 700; 2) 480.

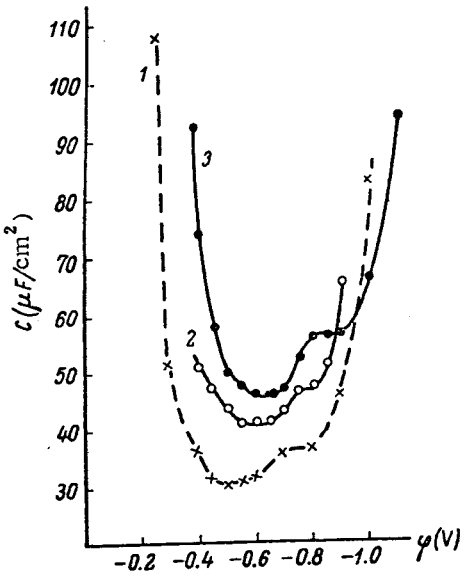

Fig. 5. Capacity of an indium electrode in an equimolecular melt of potassium and sodium chlorides. 1) Temperature of solid silver = 700°; 2) temperature of solid silver = 900°; 3) temperature of liquid silver = 1000°.

Displacement of Minimum Capacity on Changing the Temperature by 100°

Metal	Electrolyte	ΔC_{min} (μF per cm^2 · 100°)	Temperature range (°C)
Lead	CsCl	3.3	700—800
	KCl—LiCl (1 : 1)	3.9	450—800
	KCl—NaCl (1 : 1)	5.0	700—800
	KI	3.3	730—800
	NaCl	11.0	820—860
	LiCl	11.0	700—800
Aluminum	KCl—LiCl (1 : 1)	5.1	450—700
Indium	KCl—LiCl (1 : 1)	4.5	480—700
Silver	KCl—NaCl (1 : 1)	5.0	700—1000

In moving from a solid metal to the liquid form, we find no appreciable change in the form or position of the capacity curve. This fact is in good agreement with the data of Leikis and Sevast'yanov [8] on the capacity of the double layer of solid and liquid gallium close to the melting point. In particular, attention is directed to the fact that the horizontal surface at the cathodic branch characteristic of the capacity-potential curve of the silver electrode is also found for solid and liquid metals, and has thus nothing to do with the state of aggregation of the metal.

SUMMARY

Investigations of the effect of temperature on the capacity of the double layer at lead, silver, indium and aluminum electrodes in molten alkali metal halides have been performed. It has been shown that increase of temperature of the electrolyte is in all cases accompanied by increase in the capacity of the double layer, while change in the state of aggregation of the metal has no appreciable effect on the nature and position of the capacity curves.

It has been shown that the results obtained are in agreement with the hypothesis indicated earlier on the part played by structural-geometrical deformation of the fused salt, in determining the capacity of the double layer, and show the inapplicability of the assumption of a diffuse structure of the double layer in fused substances.

The authors wish to express their great appreciation to A. N. Frumkin, B. N. Kabanov, and D. I. Leikis for their interest in the work and their part in discussing the results.

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