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INVESTIGATION OF THE ELECTRIC DOUBLE LAYER IN SALT MELTS*

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Abstract—Capacitance measurements have been carried out on a number of liquid metals: lead, cadmium, tin, aluminium, antimony, silver, thallium, bismuth, indium, gallium and tellurium, as well as on solid aluminium, magnesium and silver, in salt melts of alkali-metal halides. By means of the comparison with electrocapillary curves, it has been shown that the capacitance/potential curves have a minimum at the potential of zero charge of the metal. Quantitative correspondence between the capacitance curves and the electrocapillary curves has been established. The behaviour of lithium and sodium halides differs markedly from that of potassium and caesium halides.

The possible structure of the double layer in salt melts is discussed.

Résumé—La capacité de la couche double à la surface de métaux liquides—plomb, cadmium, étain, aluminium, antimoine, argent, thallium, bismuth, indium, gallium, tellure—ainsi que de métaux solides—aluminium, magnésium, argent—a été determinée en milieu d'halogénures de métaux alcalins fondus.

On a pu montrer, que le minimum des courbes de capacité se trouve au potentiel du maximum des courbes électrocapillaires, qui correspond à une charge nulle.

Il existe une correspondance quantitative entre les courbes de capacité et les courbes électrocapillaires.

Une différence marquée a été établie entre le comportement des sels de lithium et de sodium d'une part et de potassium et de césium d'autre part.

On discute quelques hypothèses concernant la structure de la couche double en milieu de sels fondus.

Zusammenfassung—Es wurde die Kapazität der Doppelschicht verschiedener flüssiger Metalle—Blei, Kadmium, Zinn, Aluminium, Antimon, Silber, Thallium, Bismuth, Indium, Gallium und Tellur-sowohl als auch fester Metalle—Aluminium, Magnesium und Silber—in Schmelzen von Alkalihalogeniden gemessen. Ein Vergleich mit Elektrokapillarkurven zeigt, dass das Minimum der Kapazitätskurven beim Nullpunktspotential des betreffenden Metalles liegt. Die Kapazitäts- und Elektrokapillarkurven stehen in quantitativen Einklange. Das Verhalten von Lithium- und Natriumsalzen ist von dem der Kalium- und Cesiumsalzen wesentlich verschieden. Es wurden Hypothesen über die Struktur der Doppelschicht in Salzschmelzen formuliert.

HEVESY AND LORENZ[1] were the first to make an attempt to study the properties of the metal/salt-melt interface. They determined the electrocapillary curves of lead in molten alkali-metal halides. But the experimental technique of that time was such that it was possible to obtain only a very rough picture of the change in the interfacial tension with the potential. Karpachev and Stromberg[2] and Kusnezov[3–5] essentially improved the technique of electrocapillary measurements in melts. These authors obtained extensive experimental data and established the basic features of electrocapillary phenomena in molten salts; in particular, they determined the potentials of zero charge of numerous metals in a KCl–LiCl eutectic mixture.

Randles and White[6] were the first to measure the double layer capacitance for the $Hg/LiNO_3 + KNO_3$, $Hg/LiCLO_4 + NaClO_4$ and $Hg/NaHSO_4 + KHSO_4$ systems at relatively low temperatures (125–215°C).

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We have investigated the dependence of the double layer capacitance in salts on the nature of metal and salt and on temperature.[7–12] The results of these measurements are given in the present paper.

EXPERIMENTAL TECHNIQUE

An impedance bridge described earlier[13] was used. The measurements were made at sinusoidal current frequencies from 20,000 to 200,000 c/s, the voltage amplitude across the cell being 5–10 mV.

The measurements were made in a cylindrical quartz cell in which were inserted

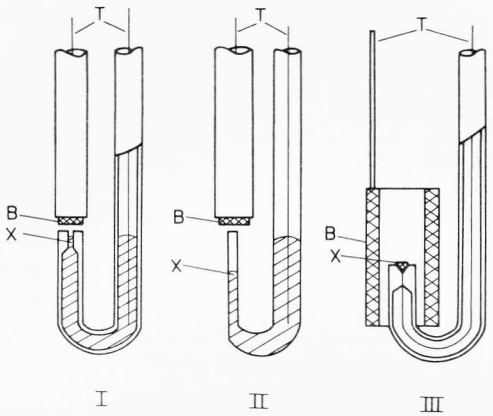

FIG. 1. Design of electrodes. X, electrode investigated; B, auxiliary graphite electrode; T, molybdenum contact wire.

the electrode to be investigated, two auxiliary graphite electrodes for dc and ac polarization, a reference electrode (Pb/10 wt-per cent $PbCl_2$ + electrolyte) contained in a quartz test tube with a capillary opening, a tube for supply and removal of inert gas and a thermocouple. A dry argon atmosphere was maintained during the measurements.

The quartz cell was put into a thick-walled steel container placed in a crucible resistance furnace. The electrolyte temperature was kept constant within $\pm 1°C$.

The most complicated problem was the design of the electrode, which was to meet the following requirements:

(a) the surface of the liquid electrode should be readily replaceable and its properties well reproducible;

(b) the surface area of the electrode should be readily determinable; it should not change in the course of one experiment.

The electrode shown in Fig. 1 (I) meets these requirements fairly well. It is a quartz hook-like tube ending in a rather short capillary (0·04–0·06 cm in diameter). The tube and the capillary were filled with liquid metal, the surface of which in the capillary served as the operating surface of the electrode.

By means of this electrode fairly reproducible results could be obtained, but it had some essential defects: its capacitance and resistance depended greatly on the ac frequency. This dispersion of the capacitance became small enough only at frequencies of 180–200 Kc/s. As shown by calculations,[8] this capacitance dispersion can be

accounted for by the penetration of the electrolyte between the capillary walls and the metal. On account of high electric conductivity of salt melts the dispersion caused by this penetration of the liquid is observed in their case at higher frequencies than in aqueous solutions.

It was possible to decrease the dispersion caused by the penetration of the liquid by increasing the operating surface of the electrode.* Therefore, the design of the electrode was altered (Fig. 1 (II)). The electrode was made from a cylindrical quartz tube with a diameter of 0·15–0·20 cm. The height of the tube was 2–2·5 cm. The surface of the metal in this tube approached that of a hemisphere and was 0·035–0·080 cm^2. By using electrodes of this kind it was possible to measure the double layer capacitance at frequencies of 15–20 Kc/s.

In Table 1 are listed the capacitance values for lead in a NaCl melt with varying electrode surface areas at the frequency of 20 Kc/s. The value of specific capacitance scarcely depends on the electrode surface. Therefore, the influence of the penetration of the electrolyte may be neglected.

TABLE 1. SPECIFIC CAPACITANCE OF Pb IN NaCl AT 820° FOR ELECTRODES WITH DIFFERENT SURFACE AREAS ($\mu F/cm^2$)

S,cm^2 \ $-\varphi$,V	0·30	0·35	0·40	0·45	0·50	0·55	0·60	0·65	0·70
0·043	100·5	68·0	48·0	45·0	47·0	54·5	69·0	91·7	112·5
0·057	—	67·0	51·0	45·5	46·5	54·0	73·0	94·0	—
0·076	101·5	70·0	49·0	44·5	46·0	54·0	74·0	89·5	113·5
C	101·0	68·3	49·3	45·0	46·5	54·2	72·0	91·7	113·0
$\Delta C\%$	0·5	2·5	2·6	1·1	1·1	0·4	2·8	2·4	0·4

At frequencies below 12–15 Kc/s however, the dispersion of capacitance was observed in the case of electrodes of the second type as well. A third type of the electrode is shown in Fig. 1 (III). The metal drop sat in a small funnel with a molybdenum contact sealed in its bottom. This electrode was not suitable for routine measurements because its surface was not reproducible, but it could be used in single experiments. These experiments showed that at frequencies below 12–15 Kc/s the dispersion of capacitance in the case of the electrode of the third type differed but little from that with the electrodes of the second type. Hence the principal reason of the dispersion of capacitance at lower frequencies was not the penetration of the electrolyte, but the existence of electrochemical reactions, especially if the high values of exchange currents and diffusion rates in salt melts are taken into account.[14]

Only by comparing results of the capacitance and the electrocapillary measurements made under identical conditions can it be conclusively proved that the capacitance measured is the true capacitance of the electric double layer. It is most expedient to compare the results of electrocapillary measurements with those obtained by the

* The surface area of the electrode could not be made very large, however, since that would result in an increase in the capacitance measured, which might reduce the accuracy of the measurements.

double graphical integration of the capacitance curves[16] in accordance with the equation

$$\Delta\sigma = \sigma_{max} - \sigma = 10 \int d\varphi \int C \, d\varphi,$$

where σ_{max} is the interfacial tension at the maximum of the electrocapillary curve.

The results of the comparison of the calculated curves for lead in molten sodium and potassium chlorides with the experimental ones are presented in Fig. 2.[15] There is

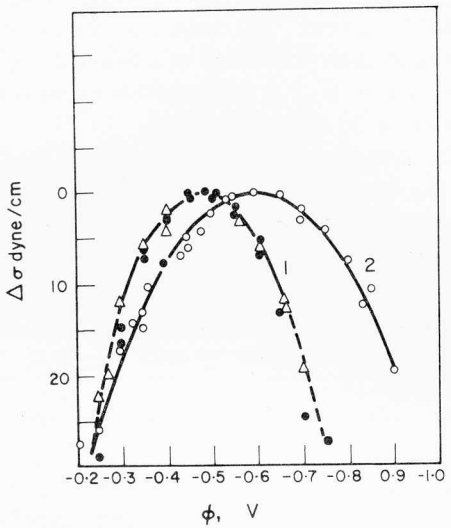

FIG. 2. Electrocapillary curves of lead in NaCl and KCl melts at 820°C. The points are experimental data; the curves have been obtained by the integration of the capacitance curves.

a quite satisfactory agreement between the capacitance and the electrocapillary measurements.

RESULTS OF MEASUREMENTS AND THEIR DISCUSSION

We have obtained capacitance curves for a number of liquid metals: lead, cadmium, tin, aluminium, antimony, silver, thallium, bismuth, indium, gallium and tellurium as well as for solid aluminium, magnesium and silver. In most measurements a molten equimolecular KCl–NaCl mixture was used. In the case of solid aluminium and magnesium and liquid tellurium an equimolecular KCl–LiCl melt was used.

In most cases, the capacitance curves were close to parabolic, with a pronounced minimum and practically symmetrical branches. For silver, thallium and tin, however, there was a step on the right hand (cathodic) branch of the curve, the nature of which is not yet clear.

The results obtained have been discussed in detail.[7,8] Table 2 gives the potentials of the minimum on the capacitance curves. For comparison there are given also the values of the potentials of the maxima on the electrocapillary curves according to Karpachev and Stromberg[2] and Kusnezov.[3–5] These electrocapillary curves were obtained for a KCl–LiCl melt mostly at 450°C (except for the data for Ag, Sb and Te, which were obtained at 1050, 750 and 550°C respectively). A pool of liquid lead served as a reference electrode in earlier work,[2–5] being by *ca.* 200 mV more negative than our reference electrode. Therefore, all the data of Karpachev, Stromberg and

TABLE 2. POTENTIALS OF THE MINIMUM OF THE C/φ CURVES FOR METALS IN KCl–NaCl AND KCl–LiCl MELTS

Metal	°C	φ_{min} V	φ_{max} V	Metal	°C	φ_{min} V	φ_{max} V
Mg	500	−1·76	—	Ag	700	−0·49	—
Al	700	−1·12	−0·5	Ag	1000	−0·62	−0·50
Al	500	−1·04	—	Pb	700	−0·55	−0·58
Tl	700	−0·87	−0·85	Bi	700	−0·32	−0·48
In	700	−0·82	−0·72	Sn	700	−0·32	−0·35
Cd	700	−0·80	−0·82	Sb	700	−0·17	−0·20
Ga	450	−0·63	−0·60	Te	550	+0·40	+0·40
Ga	700	−0·60	−0·60				

Kusnezov[2–5] have been recalculated in the table according to our scale. In all cases, the potential of the minimum of the C/φ curve can be seen to be close to that of the maximum of the electrocapillary curve, *ie* to the potential of the zero charge of the relevant metal. The only exception is aluminium, for which the electrocapillary measurements[2] are less reliable.

Capacitance measurements were made also with different molten electrolytes and at different temperatures.[9,11] The results of these measurements can be obviously compared only in respect of the specific capacitance values, but not in respect of the potential values.

The capacitance curves for lead in melts of sodium and potassium halides are shown in Figs. 3 and 4 and those for lead in an equimolecular KCl–LiCl melt at the temperatures of 430–800°C in Figs. 5. In all systems studied the values of the minimum capacitance can be well reproduced and are characteristic. They are determined,

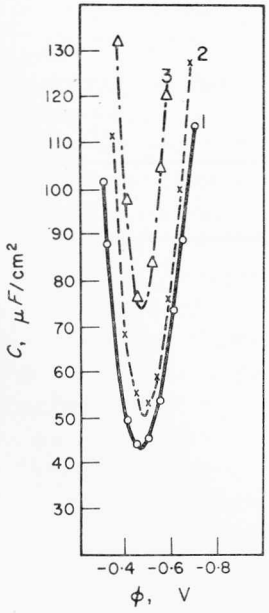

FIG. 3. Capacitance curves of a Pb electrode. 1, NaCl, 820°C; 2, NaBr, 800°; 3, NaJ, 800° C.

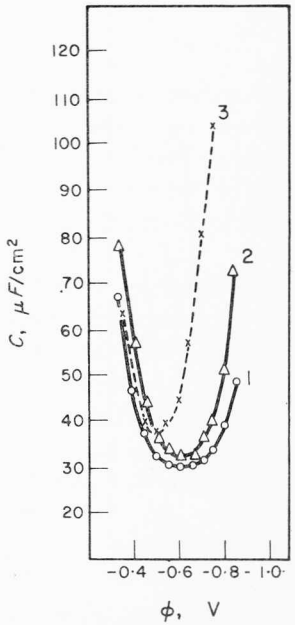

FIG. 4. Capacitance curves of a Pb electrode: 1, KCl, 800°C; 2, KJ, 800°C; 3, KCl–NaCl (1:1), 800°C.

Table 3. Minimum capacitance and the potential of the minimum on the C/φ curves for a lead electrode

Salt	°C	C_{min} $\mu F/cm^2$	φ_{min}
LiCl	800	45	−0·48
NaCl	820	45	−0·48
NaBr	800	52	−0·50
NaI	800	75	−0·50
KCl	800	28	−0·60
KBr	800	29	−0·60
KI	800	32	−0·60
CsCl	800	28	−0·57
CsI	800	33	−0·57

mainly, by the nature of the molten salt and the temperature, and do not depend markedly on the material of the cathode. This is confirmed, in particular, by the fact that the values of the minimum capacitance of aluminium, antimony and lead electrodes, measured under identical conditions (KCl and NaCl melts at 820°C) coincide.

The results of the capacitance measurements of the double layer in the case of a lead electrode, given in Table 3 and in Figs. 3–6, can be interpreted as follows. The capacitance curves in the case of a lead electrode in sodium and lithium salt melts are characterized by a relatively high minimum capacitance, a rapid change in the capacitance with the deviation of the potential from the point of zero charge and dependence

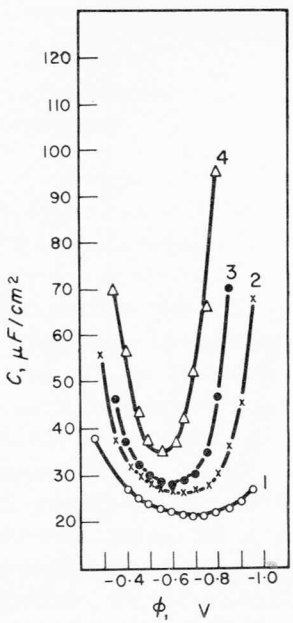

Fig. 5. Capacitance curves of a Pb electrode in KCl–LiCl (1:1) melt. 1, 450°C; 2, 600°C; 3, 700°C; 4, 800°C.

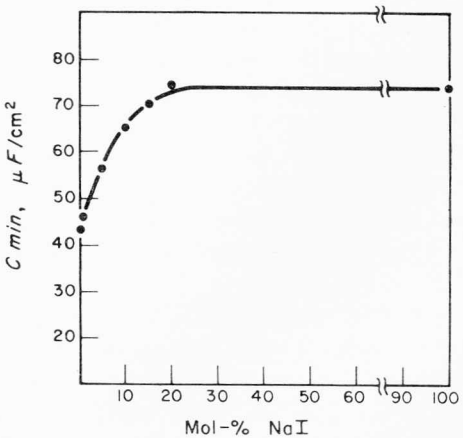

Fig. 6. Influence of NaI concentration on the double layer capacitance of lead in NaCl at 820°C.

of the minimum capacitance on the nature of the anion. The quantity C_{min} increases in the series chloride< bromide < iodide.

The capacitance curves of a lead electrode in the melts of potassium and caesium halides are characterized by a relatively low minimum, a slight change in the capacitance with deviation of the potential from the point of zero charge and a very slight dependence of the minimum capacitance on the nature of the anion.

The character of the capacitance curves of a lead electrode in molten equimolar LiCl–KCl and NaCl–KCl mixtures is intermediate between those of the capacitance curves for corresponding individual salts (Fig. 4).

When the corresponding iodide is added to molten sodium chloride (or lithium chloride) the capacitance of the double layer increases rapidly, and in melts containing *ca* 20 mol per cent iodide already attains the limiting value corresponding to pure NaI (or LiI), Fig. 6.

With increasing temperature of the salt melt, the capacitance rises (Fig. 5), the temperature coefficient of the minimum capacitance ($\alpha_{min} = dC_{min}/dT$) essentially depending on the nature of the salt (Table 4), so that for lithium and sodium halides α_{min} is 3·3 times as large as for potassium and caesium halides.

TABLE 4. TEMPERATURE COEFFICIENT OF C_{min}

Salt	Temperature range °C	α_{min} $\mu F/cm^2/100°C$
LiCl	700–800	11·0
NaCl	820–860	11·0
KI	730–820	3·3
CsCl	680–800	3·3
KCl–NaCl	700–800	5·0
KCl–LiCl	450–800	5·0

It follows from the above that the molten halides of alkali metals may be divided into two groups according to their influence on the double layer capacitance of the lead electrode. In melts of lithium and sodium salts the capacitance is large and greatly depends on the anion and on the temperature, whereas in melts of potassium and caesium salts, the capacitance is relatively small and but slightly depends on the anion and on temperature.

The character of the dependence of the double layer capacitance on the potential and the above-mentioned relations can be explained by supposing that the changes in the capacitance of the double layer are due to the deformation of ions and to the changes in the structure of the molten salts in the layer near the electrode.

A characteristic feature of sodium and lithium salts is the small value of the ratio of cation and anion radii (τ_K/τ_A); the mutual repulsion of anions is of great importance.[17] The crystalline lithium salts are characterized by a structure with the cations located quite loosely in octahedral holes formed by closely packed anions, *ie* where an anion–anion contact is realized. For crystalline sodium salts the anion–anion contact is geometrically impossible, but as the radius of the Na^+ anion is small, the mutual repulsion of anions has a marked effect upon the distance between the ions, which by some percent exceeds the sum of the ionic radii.[17] In potassium and caesium halides, the mutual repulsion of anions is not of essential importance and the ions

with opposite signs play in fact equal roles in the structure of the crystalline lattice. These differences are, probably, also important in molten salts, which may be supposed to have preserved a quasi-structure,[18] similar to the corresponding crystalline lattice.

A simple Helmholtz model in which all excess charges are supposed to be located in one plane can be hardly applicable in the case in question as it cannot explain the symmetry of the C/φ curves and the location of the capacitance minimum at the potential of zero charge. Nor can we apply the concepts of the diffuse structure of the double layer in the sense of Stern, and Gouy and Chapman, since these concepts are at variance with the high capacitance values at the minimum (20–75 μF/cm^2) and with the marked increase in the capacitance with rise of temperature.

It may be supposed that in the case of molten salts, the excess charges in the electrolyte are located several atomic layers deep. This supposition was discussed recently for the case of concentrated ionic systems by Stillinger and Kirkwood.[19] The increase in the capacitance with changing potential seems to be due to the deformation of the structure of the molten salt and not to that of the electronic shells of the ions judging from the temperature dependence of capacitance and the symmetry of the C/φ curves.

Another possible model of the double layer in molten salts amounts to the consideration of the cations and cation vacancies, which being the most mobile elements of the melt, bring about the charging of the electrolyte side of the double layer. In this model the anions are assumed to be stationary and their distribution in the double layer to be independent of the potential. This model explains the symmetry of the capacitance curves. The increase in the capacitance with rise of temperature may be caused by the increase of the mobile cations and cation vacancies.

The data available point to an essential influence of electrostatic adsorption in the field of the double layer on the properties of the latter. In particular, the rise in capacitance with increasing iodide concentration in a NaCl melt (Fig. 6) is an indication of the surface activity of I^- ions, which can, probably, expel the Cl^- ions from the double layer. There is no doubt that the adsorption results in a rearrangement of the double layer structure and in its "compression". The details of this rearrangement are not quite clear. It may be supposed that each salt is characterized by its own kind of packing in the double layer and that this packing is to a great extent determined by the ratio of the anion and cation radii.

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