THE CAPACITANCE OF A DOUBLE ELECTRIC LAYER ON MERCURY IN MELTS AND CONCENTRATED SOLUTIONS OF NITRATES

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We measured the differential capacitance of the double electric layer on mercury in melts and concentrated aqueous solutions of nitrates from alkaline metals over a wide range of concentrations and temperatures. It was demonstrated that in molten nitrates, as in halides, the dependence of capacitance on potential takes the form of smooth curves with a minimum close to the zero charge point. When water is added to these systems and its concentration subsequently increased, the curves first show a plateau and then a maximum. The regularities governing the maximum are roughly of the same kind as those described previously for perchlorates.

There has been substantial research on the double electric layer on the boundary between the electrodes and dilute solutions of electrolyte [1, 2]. Over the past few years considerable attention has also been focused on the state of the interface between electrodes and melts.

A large number of papers have dealt with experimental determination [3-5] and theoretical analysis [6, 7] of the capacitance of the double layer on the boundary between liquid metals and molten salts. Dependence of capacitance on potential in halide melts on various metals takes the form of symmetric curves close to parabolas, with a minimum close to the zero charge point, and the absolute values of the capacitance, even at the minimum, are much greater than that in aqueous solutions. In molten halides there was observed an increase in capacitance as the temperature rose. It is suggested [5, 7] that these differences between melts and water solutions are associated with the formation, close to the metal, of alternating-sign ion layers with an attenuating charge.

But there is still a definite gap in the studies on capacitance in the region of highly concentrated solutions, even though the first report on capacitance measurements in concentrated nitrate solutions appeared ten years ago [3]. It is only very recently that there have been published papers on capacitance measurement with a mercury electrode in concentrated LiCl [8] and in concentrated $NaClO_4$, $Ca(ClO_4)_2$ and $CaCl_2$ solutions [9].

In our work we measured the differential capacitance of the double electric layer on a mercury drop electrode in melts and concentrated water solutions of alkaline metal nitrates.

Our choice of the subject for study was governed by the fact that the nitrates of alkaline metals in the fused state are ideal ionic liquids, and form with water extremely concentrated solutions. The literature only contains sporadic data on double layer capacitance on mercury in the molten eutectic $LiNO_3$–$NaNO_3$–KNO_3 [3] and in $NaNO_3$ [1] and KNO_3 solutions [10]. The low melting points of nitrates mixtures and high boiling points of concentrated nitrate solutions made it possible to make measurements in solutions and melts over the same temperature range and to trace the smooth transition from solution to melt.

PROCEDURE FOR MEASUREMENT

The capacitance was measured with a dropping mercury electrode by the method advanced by Grahame [11], in which we record the time between detachment of the drop and the balancing of the bridge, and from the known

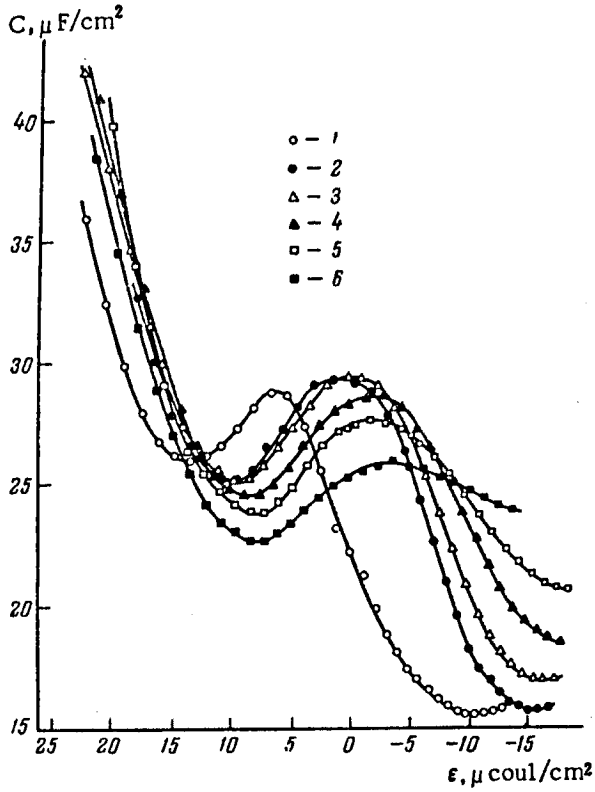


Fig. 1. Capacitance of the double layer in $LiNO_3$ solutions at 60°C: 1) 0.1; 2) 1; 3) 2; 4) 4 M; 5) $LiNO_3 \cdot 6H_2O$ (~7M); 6) $LiNO_3 \cdot 3H_2O$ (~11M).

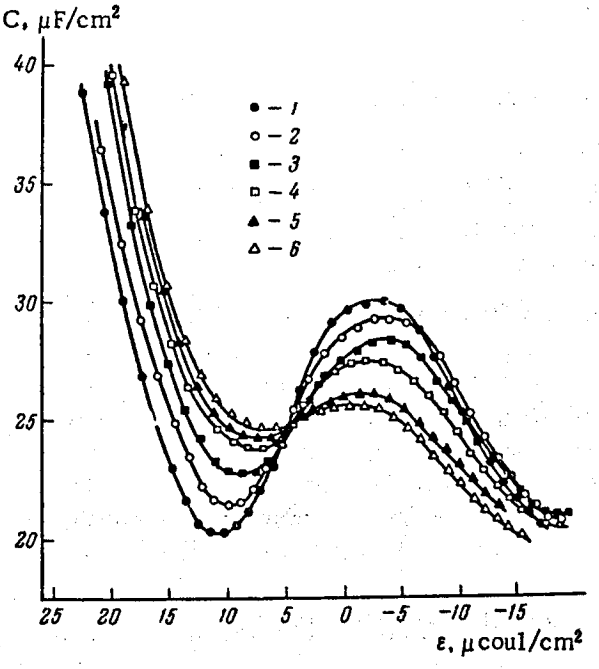


Fig. 2. Capacitance of the double electric layer in a $LiNO_3 \cdot 6H_2O$ solution at different temperatures: 1) 4; 2) 20; 3) 40; 4) 60; 5) 80; 6) 95°C.

rate of emission of the mercury calculate the surface of the mercury drop at the moment the bridge balances. The measurements were made at 5000 cps (in a 0.1 M solution at 1000 cps). The relative error in measurement did not exceed 2.5%. The measuring cell was similar to the one described in the literature [12]. The capillary was made of molybdenum glass, which is far more resistant to the action of hot concentrated solutions and melts of nitrates than ordinary laboratory glass. As the counterelectrode we used a platinum foil cylinder 1 cm in diameter and 1.5 cm high. The end if the capillary was placed in the middle of the cylinder. As already pointed out [12], the nonuniformity of the current distribution in an electrode system of this kind hardly has any effect on the results provided the frequency is not too high. In our measurement current dispersion was observed at 20 cps, evidentally due to screening of the mercury drop by the capillary.

As the comparison electrode in the experiments with the solutions we used a silver half-element Ag ‖ 0.15 M $AgNO_3$ and $LiNO_3 \cdot 3H_2O$, and for those in melts one with Ag ‖ 0.15 M $AgNO_3$ in the appropriate melt. The potential of this electrode at 40° according to our measurements was +0.424 V as against the normal calomel half-cell. The electrolyte was thermostated in the cell by means of a water ultrathermostat (up to an accuracy of 0.2°) or an oil one (up to an accuracy of 0.5°). A highly important condition for working with a mercury drop electrode at elevated temperatures is to thermostat the mercury in the capillary since the viscosity (and therefore the emission rate) of the mercury is strongly dependent on temperature. In our experiments the whole of the cell was placed in an air thermostat with an electric heating system, the temperature of which (equal to the electrolyte temperature) was maintained with an accuracy up to 1°.

The solutions were made with doubly distilled water from chemically pure recrystallized salts. It was demonstrated by separate experiments that secondary crystallization had no effect on the results of the capacitance measurements.

The results are shown in the form of capacitance versus charge. The zero charge potentials were measured by two methods: either from the maximum on the drop period versus potential curves, or from a jet-type electrode. The surface charges were calculated from the C vs. φ curves (C = capacitance and φ = potential) by graphic integration.

RESULTS AND DISCUSSION

Fig. 1 shows differential capacitance curves in $LiNO_3$ solutions. As can be seen, when the concentration increases, the path of the curve varies smoothly. All the curves have a marked "hump" typical of this type of curve plotted in not very dilute aqueous solutions [13, 14].

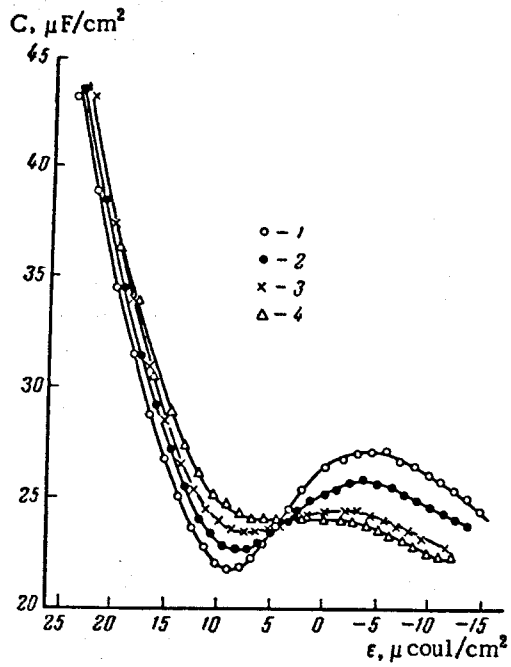


Fig. 3. Capacitance of double layer in a $LiNO_3 \cdot 3H_2O$ solution at different temperatures: 1) 40; 2) 60; 3) 95; 4) 115°.

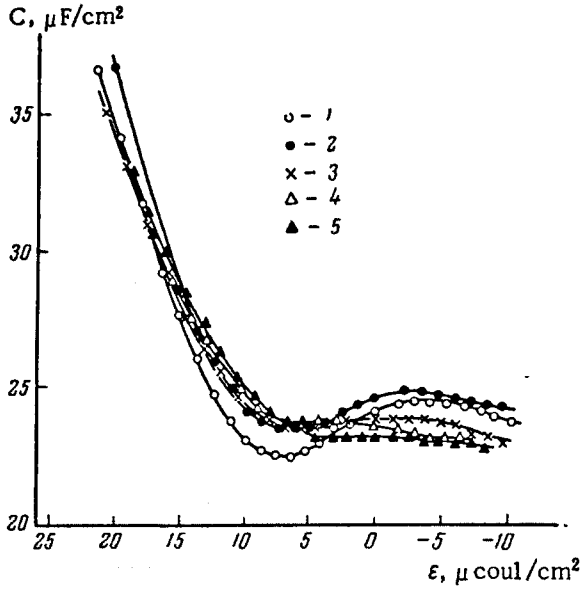


Fig. 4. The capacitance of the double layer in $LiNO_3 \cdot 2H_2O$ solutions (curves 1-4) and $LiNO_3 \cdot 1.5\ H_2O$ (curve 5): 1) 80; 2) 95; 3) 115; 4) 130; 5) 130°C.

The following changes occur as the concentration is increased:

1) the top of the "hump" shifts toward negative charges, and at $LiNO_3$ concentrations up to 2 M lies in the region of positive surface charges, and at higher concentrations in the negative charge region;

2) the capacitance corresponding to the top of the "hump" is slightly increased as the concentration is increased to 2 M, after which it drops;

3) the capacitance corresponding to the minimum on the curve smoothly declines as the concentration grows;

4) as the concentration grows the "hump" is stretched out (the interval of charges between the maximum and minimum increases while the decline in capacitance after the maximum acquires a more gentle slope).

5) at highly positive surface charges (more than +15 microcoul/cm²) the capacitance hardly depends at all on concentration, and at strongly negative ones it increases as the concentration is increased.

The shift of the "hump" toward the negative side during increase in concentration of the electrolyte was also observed in [9], where it was demonstrated that it depended on the nature of the salt. For example, during transition from 1N to 9.3 N solutions of $NaClO_4$, $Ca(ClO_4)_2$ and $CaCl_2$ the "hump" shifted 5, 15 and 5 microcoul/cm², respectively. In our measurements, during transition from 1M $LiNO_3$ to $LiNO_3 \cdot 3H_2O$ (approximately an 11 M solution) the shift was 5 microcoul/cm², although the general nature of the concentration dependence of the C v. ε curves (ε = surface charge) indicates some slight similarity between the $LiNO_3$ and $Ca(ClO_4)_2$ solutions. This similarity shows up as an appreciable drop in capacitance with concentration at not very positive surface charges (at the minimum and on the ascending branch of the "hump") andas a large difference in capacitance at different concentrations in the negative charge region.

The nature of the "hump" on the capacitance curves in water solutions is discussed in [15] and is associated with the different orientation and polarizability of the water molecules on the electrode surface at different surface charges close to the zero charge point. In [9] the assumption was put forward that in concentrated $Ca(ClO_4)_2$ solutions we observe a gradual transition from the ordinary "hump" due to orientation and polarizability of the water molecules to the adsorption-desorption maximum for the anions.

The appearence of this maximum is explained by the low hydration of the aniona, its strong adsorption and high activity of the electrolyte, with which there is associated a "squeezing" effect. The activity coefficients of

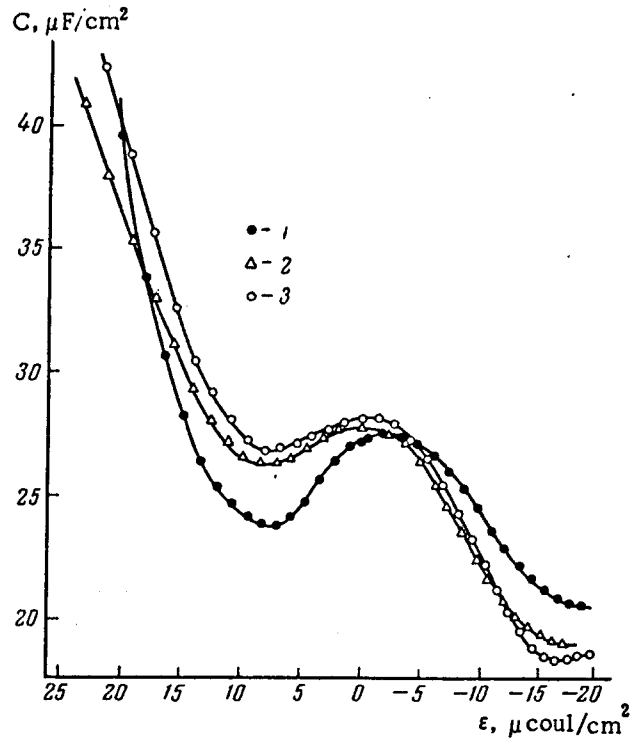


Fig. 5

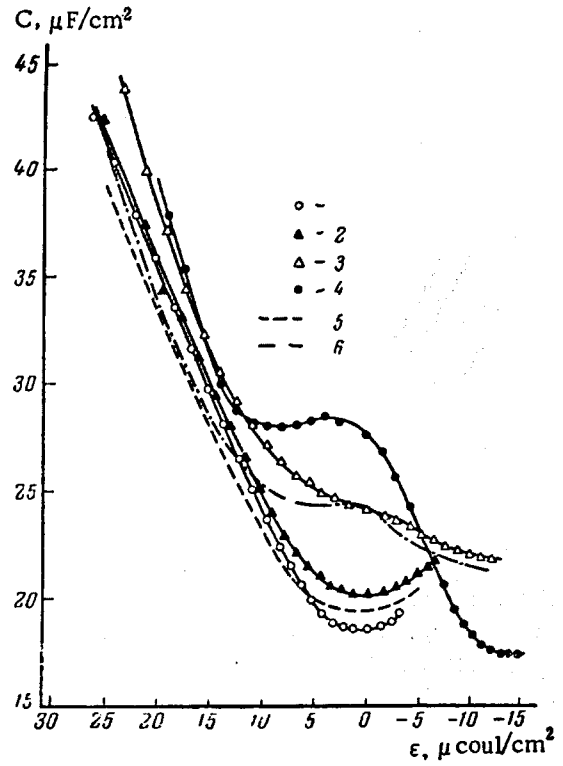


Fig. 6

Fig. 5. The capacitance of the double layer in nitrate solutions of alkaline metals $MNO_3 \cdot 6H_2O$ at 60°: 1) M = Li; 2) M = Na; 3) M = K.

Fig. 6. The capacitance of the double layer in the eutectic melt $LiNO_3-NaNO_3-KNO_3$ without water and with the addition of different amounts of water: 1) Waterless melt, t = 130°; 2) 0.1 mole H_2O per mole of nitrate, t = 130°; 3) 1.5 mole H_2O per mole of nitrate, t = 130°; 4) 2.5 M eutectic solution, t = 95°; 5) waterless eutectic melt, t = 140° [3]; 6) 1.8 mole H_2O per mole of nitrate, t = 120° [3].

$NaClO_4$, $LiNO_3$ and $Ca(ClO_4)_2$ at m = 6 are, respectively, 0.677, 1.506 and 63.7, and at m = 13 for $LiNO_3$ the coefficient is 3.20; i.e., the $LiNO_3$ occupies an intermediate position. The nature of the "hump" and its evolution as the concentration changes seem to be of the same kind and have the same causes as in perchlorate and nitrate solutions.

Figures 2-4 show differential capacitance curves for $LiNO_3$ solutions containing from 6 to 1.5 moles of water per mole of salt at temperatures ranging from 4 to 130°. As can be seen, raising the temperature and concentration is accompanied by a smoothing out of the "hump." This increase in the C vs ε and C vs φ curves has already been noted in the literature [9-11, 14]. In our own research we studied a wider concentration and temperature interval, right up to maximum possible concentrations at atmospheric pressure.

In $LiNO_3 \cdot 2H_2O$ and $LiNO_3 \cdot 1.5H_2O$ solutions at 115 and 130° the "hump" degenerates into a plateau (Fig. 4). Just as in perchlorates [9], in concentrated alkaline metal nitrate solutions the "hump" depends substantially on the cation. Fig. 5 shows curves for $LiNO_3 \cdot 6H_2O$, $NaNO_3 \cdot 6H_2O$, and $KNO_3 \cdot 6H_2O$ at 60°. As the cation increases in size the "hump" becomes less marked, and the transition from $LiNO_3$ to $NaNO_3$ causes a great change in the C vs. ε curve, while the difference in the curves for $NaNO_3$ and KNO_3 is far smaller.

It was of special interest to measure the capacitance in highly concentrated solutions and compare the results with capacitance measurements for melts. Fig. 6 shows C vs. ε curves for a eutectic melt $LiNO_3-NaNO_3-KNO_3$ and for the same composition with the addition of 0.1 and 1.5 moles of water per mole of eutectic at 130°. It can be seen that in these curves the "hump" only appears when there is a fairly large amount of water, although a slight increase in capacitance close to the zero charge point, which does not alter the nature of the curve, can be seen even when 0.1 moles of water are added. For purposes of comparison the same figure gives graphs for the eutectic $LiNO_3-NaNO_3-KNO_3$ at 140° without water and at 120° with the addition of 1.8 moles of H_2O per mole of eutectic, taken from [3]. As can be seen, these results tally well with our own data.

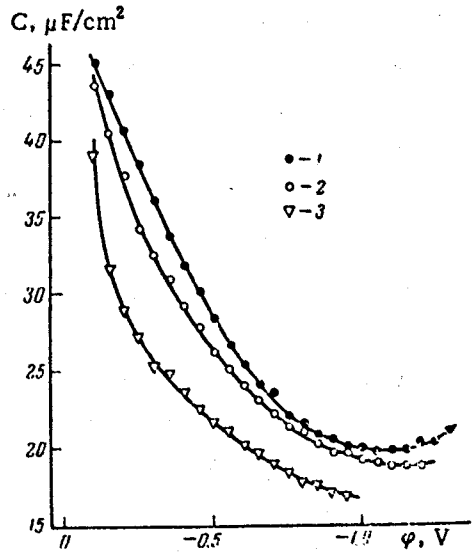


Fig. 7. The capacitance of the double layer in nitrate solutions. 1) Eutectic $LiNO_3-KNO_3$, t = 160°; 2) eutectic $LiNO_3-KNO_3$, t = 260°; 3) $LiNO_3$, t = 260°.

The relationship between capacitance and potential (or charge) in a pure melt or in a melt with the addition of water shows similarity to the earlier described capacitance curves in molten salts [5] the only difference being that with mercury it is possible to obtain only the initial segment of the cathode branch. This can been seen from Fig. 7 where we show C vs φ curves plotted for molten $LiNO_3$ at 260° and the eutectic $LiNO_3-KNO_3$ at 160° and 260°. We did not convert these curves into C vs ε curves because in the $LiNO_3$ melt it is not possible to determine the potential of the zero charge on account of the commencement of discharge. Worthy of note is the slight decline in capacitance as temperature rises. In this respect the capacitance in nitrates on mercury differs from the capacitance in chloride melts on lead [5], where over the temperature range 500-800° there was observed a substantial increase as the temperature rose, and this was explained qualitatively by the multilayer alternating structure of the ionic plates of the double layer condenser in the melts.

Thus, the measurements showed that in nitrate melts the dependence of capacitance on potential takes the form of smooth curves with a minimum close to the zero charge point, with the capacitance dropping slightly as the temperature rises. In solutions with very small amounts of water (0.1-0.3 moles H_2O per mole of salt) the behavior of the curves does not change, but there is only a slight increase in capacitance near the zero charge point when the water concentration is increased. Starting at 1.5 mole water per mole of salt we observe the occurrence of first a plateau and then a "hump," the hight of which rises as the concentration and temperature of the electrolyte declines. When the water concentration is still higher in the concentrated nitrate solutions we observe more or less the same regularities as were noted for perchlorates.

However, available data does not yet permit us to draw any firm conclusions as to the structure of the double layer in the above described systems. This is further complicated by the fact that the capacitance in dilute solutions and melts was studied basically for the case of the halides of alkaline metals, i.e., we studied systems with the simplest ions, and in the concentrated solutions we only studied the salts with complex anions. In this respect it would evidently be of interest to study the concentrated halide solutions.

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