

# Double Layer Capacity Measurements in Molten Salts

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Differential double layer capacity measurements were performed on liquid mercury and lead in molten mixtures of alkali-metal nitrates and chlorides, respectively. The measurements were carried out with the help of a.c. bridge, using stationary U-shaped electrodes. The experimental results were discussed on the basis of the multi-layer model of the metal/molten salt interface.

The differential double layer capacity of the electrode|electrolyte interface provides useful information about the properties of this interface, which is necessary for better understanding of the electrode processes. Double layer capacity in mixtures of alkali-metal nitrates was studied by several authors [1–3]. There is a continuous transition between water solutions of alkali-metal nitrates and their dehydrated melts which gives a possibility to compare the properties of the electrode|electrolyte interface in water solutions and in molten salts.

The eutectic mixture of lithium chloride and potassium chloride is frequently the object of electrochemical studies in molten salts [4] because of its low melting point (361°C). This property is also advantageous in the investigation of the temperature dependence of the studied parameter. A discussion on the temperature dependence of the double layer capacity based on the presented experimental data can be found in [5]. In this work, an attempt to calculate the minimum value of the differential double layer capacity was made. The calculation is based on the multi-layer model of the electrode|molten salt interface [6–8].

## Experimental

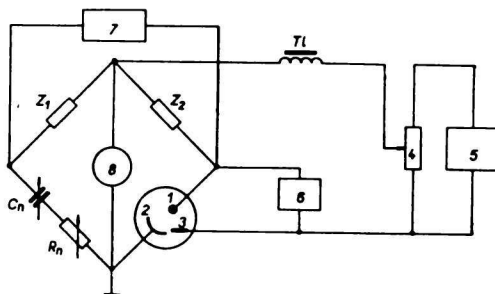
The differential double layer capacity of the studied systems was measured using an a.c. bridge. The diagram of the apparatus is presented in Fig. 1.

A slightly modified a.c. bridge "Tesla BM 400" was used (frequency range 0.2–10 kHz). In order to compensate the electrolyte and circuit resistance, an external resistance box was connected to the bridge. As the bridge indicator a selective microvoltmeter "Type 203, UNIPAN, Poland" was used. As a.c. generator, a RC oscillator Tesla (frequency range 0.025–30 kHz) was employed.

Some of the impedance measurements were carried out also in the frequency range up to 20 kHz. In this case, the bridge system consisted of a decade condenser and decade resistance box (TR-9301 and TR-9403, Fok—Gyem, Hungary). For a precise compensation of the ohmic resistance, a non-inductive potentiometer of our own construction was used.

Accuracy of the adapted a.c. bridge was tested using an electrical model of the cell. If 20 ohms resistor was connected in series with a capacitor ( $10^{-2}$   $\mu\text{F}$ –1  $\mu\text{F}$ ), the accu-

Fig. 1. The diagram of the apparatus. 1. working electrode; 2. counter electrode; 3. reference electrode; 4. varied resistor; 5. d.c. power supply; 6. electronic microvoltmeter; 7. a.c. generator; 8. bridge indicator.



accuracy of the capacity measurements was better than 0.5% in the frequency range 1–10 kHz and better than 1.5% at frequencies up to 30 kHz. It should be mentioned that the ohmic resistance of the measured system varied within the range 1–20 ohms.

In this work a stabilized power supply of d.c. designed and constructed for this purpose was used, d.c. voltage was measured by an electronic microvoltmeter with high ohmic input.

The working electrode was a stationary U-shaped electrode of similar type as that tested by *Ukšec et al.* [4]. Its surface varied within the range of 0.1–0.5 cm<sup>2</sup>. The exact diameter of the electrode capillary was measured optically and the surface was calculated as the surface of a hemisphere, corrected on the basis of *Sugden's* tables [9].

The counter electrode consisted of a platinum cylinder and its surface was much larger than that of the working electrode. In the electrical model of the cell, the working and the counter electrodes were connected in series and, therefore, the contribution of the counter electrode to the total measured capacity of the system was negligible.

Two types of reference electrodes were used. In the chloride mixtures the potential of the working electrode was measured *vs.* the reference electrode "Pb|10 wt% PbCl<sub>2</sub> + electrolyte" and in molten nitrates *vs.* the electrode "Ag|0.15 M-AgNO<sub>3</sub> + electrolyte".

The cell was placed in a resistance furnace. The temperature was measured using a Pt/Pt10Rh thermocouple and it was kept constant with the accuracy of  $\pm 1.5^\circ\text{C}$ .

The purification of reagents was performed with greatest care. Mercury of the grade "for polarography" was double-distilled before use. The purity of lead was 99.9999% (Koch-Light Laboratories Ltd.). Analytical grade alkali-metal nitrates and chlorides were used. These chemicals were purified by methods recommended in the literature [10]. Before the measurements, a pre-electrolysis was performed in order to minimize the residual current. The pre-electrolysis was carried out with platinum wire net electrodes. However, the currents of order of 1  $\mu\text{A}$  were still observed in the end of the electrolysis, the voltage being 1.5 V.

## Results and Discussion

The dependence of the differential double layer capacity on the potential of the working electrode for Hg|LiNO<sub>3</sub>–NaNO<sub>3</sub>–KNO<sub>3</sub> eutectic mixture and Pb|LiCl–KCl eutectic mixture systems are presented in Figs. 2 and 3. The measurements were carried out at different temperatures. On the basis of these experimental data, the temperature dependence of the differential double layer capacity was discussed [5].

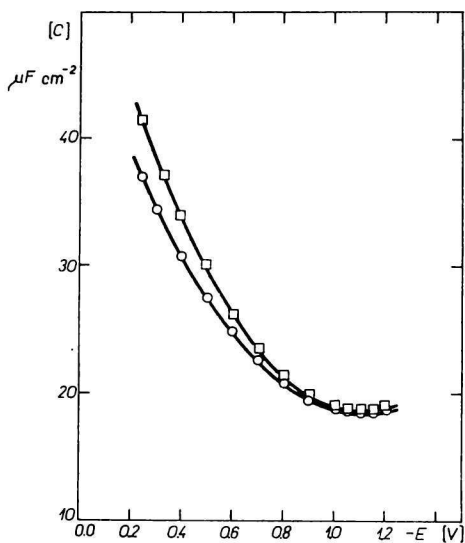


Fig. 2. The dependence of the differential double layer capacity  $C$ , for  $\text{Hg}|\text{LiNO}_3 - \text{NaNO}_3 - \text{KNO}_3$  system on the polarizing potential.

□ 140°C; ○ 200°C.

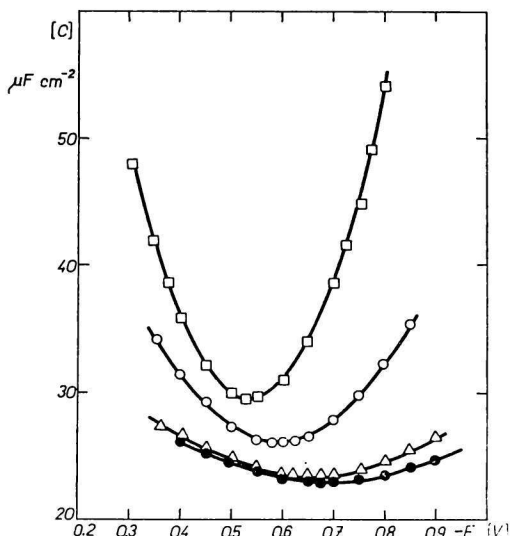


Fig. 3. The dependence of the differential double layer capacity  $C$ , for  $\text{Pb}|\text{LiCl} - \text{KCl}$  system on the polarizing potential.

● 400°C; △ 500°C; ○ 600°C; □ 700°C.

In this paper, an attempt to calculate the minimum value of the differential double layer capacity,  $C_{\min}$ , for the studied systems was made. The calculation was based on the multi-layer model of the metal|molten salt interface proposed by *Bukun* and *Ukše* [8]. The capacity calculated on the basis of this model is the integral double layer capacity; however, one should take into account that, close to the point of zero charge, the integral and differential double layer capacities are almost equal. The multi-layer models of the electrode|molten salt interface are based on the assumption that the short range order is preserved after the melting of salts. The distribution of the electrical charge at the electrode has a character of a damped oscillation function. In the first layer, there is a charge of the opposite sign with respect to the electrode, but its absolute value is larger than that on the electrode. In the second layer, the charge is of the same sign as on the electrode, but its absolute value is lower than that in the first layer, etc. In the fourth or fifth layer the influence of the charged electrode is weaker and the layer structure of the melt is disturbed.

According to [8] the minimum of the double layer capacity,  $C_{\min}$ , is determined by the expression

$$C_{\min} = \frac{\varepsilon}{4\pi a_1} \cdot \frac{1 - \beta}{1 - k\beta}, \quad (1)$$

where  $C_{\min}$  is the minimum value of the double layer capacity,  $\varepsilon$ , is the dielectric constant,

$$k = \frac{a_1 + a_2}{a_1}, \quad (2)$$

$a_1$  and  $a_2$  being the mean ionic radius and the mean ionic diameter, respectively.

$$\beta = \left( \frac{V_1}{V_s} \right)^{2/3} - 1, \quad (3)$$

$V_1$  and  $V_s$  being the molar volume of the melt at temperature  $T$  and the molar volume of the salt at temperature 0 K, respectively.

$$a_2 \cong 2a_1, \text{ and therefore } k \cong 3.$$

The term

$$C_k = \frac{\varepsilon}{4\pi a_1} \quad (4)$$

corresponds to the capacity of the first layer, assuming that it is an equivalent of a plate capacitor.

The physical meaning of the coefficient  $\beta$  can be seen from the following consideration: assuming that the metal|electrolyte interface is formed only by two layers, from the condition of electroneutrality it follows that

$$q_{Me} + q_2 = -q_1, \quad (5)$$

where  $q_{Me}$  is the charge of the electrode and  $q_1$  and  $q_2$  are charges of the first and the second layers, respectively.

Between the charges  $q_{Me}$ ,  $q_1$ ,  $q_2$ , there are the following relations

$$q_1 = -q_{Me} - \beta q_{Me}; \quad q_2 = \beta q_{Me}. \quad (6)$$

According to [8] the coefficient of "overcharging"  $\beta$  is in relation to the free volume of the melt and this relation can be expressed by the equation (2).

The estimation of  $C_{min}$  values in LiCl-KCl and LiNO<sub>3</sub>-NaNO<sub>3</sub>-KNO<sub>3</sub> eutectics is based on the following assumptions:

1. The capacity of the electrical double layer does not depend on the material of the electrode; it depends only on the nature of the electrolyte.
2. Dielectric constant was accepted to be 3 [10, 11]. (It is a composite electronic and ionic dielectric constant.)

Table 1

Calculation of  $C_k$  for different ionic radii

	Ionic radius, or half interionic distance [Å]	$C_k, \mu\text{F cm}^{-2}$ , based on	
		$\varepsilon = 3$	$\varepsilon = 1.7$
Li <sup>+</sup>	0.60	44.2	25.1
Na <sup>+</sup>	0.95	27.9	15.8
K <sup>+</sup>	1.33	20.0	11.3
Cl <sup>-</sup>	1.81	14.7	8.3
NO <sub>3</sub> <sup>-</sup>	2.20	12.1	6.8
$\frac{r_{K^+} + r_{Cl^-}}{2}$	1.57	17.0	9.6
$\frac{r_{K^+} + r_{NO_3^-}}{2}$	1.76	15.1	8.6

In Table 1, the values of  $C_k$  calculated from the equation (4) are summarized for different thicknesses of the plate condensers corresponding to the ionic radii of ions. In this table also the values  $C_k$  based on  $\epsilon = 1.7$  are presented, this corresponding to the value obtained on the basis of Fajans' ionic polarizabilities (for alkali-metal chlorides) or approximately to the value obtained on the basis of infrared spectra and refractivity (for alkali-metal nitrates).

Table 2

Calculation of the minimal double layer capacity

Salt	Temperature [°C]	$\frac{1 - \beta}{1 - 3\beta}$	$C_{\min}, \mu\text{F cm}^{-2}$	
			calculated ( $\epsilon = 3$ )	found
KNO <sub>3</sub> in eutectic mixture LiNO <sub>3</sub> —KNO <sub>3</sub>	200	1.0	15	18.5
KCl in eutectic mixture LiCl—KCl	400	1.5	25	23.0
KCl	800	2.0	34	28.8

From comparison of the experimental values of  $C_{\min}$  (23.04  $\mu\text{F cm}^{-2}$  at 400°C in LiCl—KCl eutectic mixture, 18.49  $\mu\text{F cm}^{-2}$  at 200°C in LiNO<sub>3</sub>—NaNO<sub>3</sub>—KNO<sub>3</sub> eutectic mixture) with those given in Table 1, it follows that the thickness of the first layer should be greater or approximately equal to the ionic radius of the potassium ion.

In Table 1, also the values based on the assumption that the thickness of the first layer equals to the arithmetical mean of the cathodic and anodic radii are presented.

The values of  $C_{\min}$  calculated from the equation (1) are presented in Table 2.

The calculations presented in this paper were obtained under simplified conditions which are not necessarily satisfied in the real systems. From this point of view, the presented calculations of  $C_{\min}$  should be considered as a first approximation to the solution of this problem.

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