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POLAROGRAPHY OF MOLTEN SALTS

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16. Abstract

A Soviet chemist reports on the results obtained in the polarography of molten salts utilizing ternary electrolytes rather than the liquid capillary electrodes used by the American investigators Steinberg and Nachtreib, and showing mathematical models which consistently predict outcomes which can be proven empirically.

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POLAROGRAPHY OF MOLTEN SALTS

Y. K. Delimarskiy

1. Introduction

Diverse authors have repeatedly observed the appearance of a limiting current during the electrolysis of molten salts [1, 2, 3]. Of particular interest in this respect is the work of Karpachev, Rempel and Jordan [4], in which it was shown that during the electrolysis of incompletely dehydrated carnallite, the dependence of the cathode potential on the current density was expressed by a characteristic curve with a limiting current for hydrogen. This curve expresses not only the concentration polarizations, but also the overvoltage. /766*

The appearance of a limiting current, observed during the electrolysis of molten salts, served for a while as a basis for polarographic investigations of molten electrolytes. Initial papers in this field were published in 1948 [5, 6, 7].

The American investigators Steinberg and Nachtreib, using a mercury capillary electrode, studied the polarographic behavior of Ni^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+} in the molten ternary electrolyte $LiNO_3$-$NaNO_3$-KNO_3. These authors showed that a mercury capillary electrode proceeds in fused electrolytes (at temperatures below 160°C) just as in agueous solution. All equations which hold for the mercury capillary electrode in aqueous solutions were applicable for work in molten electrolytes. In particular, the well known Ilkovich equation

$$i_d = K \cdot D^{1/2} \cdot c \cdot m^{2/3} \cdot t^{1/6}, \tag{1}$$

was valid, where i_d is the strength of the diffusion current, K is a constant, D is the diffusion coefficient, c is the initial concentration, m is the

*Numbers in the margins indicate pagination in the foreign text.

quantity of mercury falling from the capillary per second and t is the discharge time of one drop of mercury.

Molten electrolytes with such low melting temperatures (160°) are not used commercially, and therefore the use of the mercury electrode for the polarography of molten salts is of no practical interest. Understanding this, Steinberg and Nachtreib attempted to use molten tin and bismuth as electrode materials, but without success. The preconception that only a polarographic wave taken from a liquid capillary electrode could be theoretically interpreted sidetracked the American investigators onto an incorrect path, which made their work on the polarography of molten salts of little interest.

A totally different path of polarographic investigation of molten salts was selected by Soviet chemists who recognized that the mercury capillary electrode was clearly unsuitable for the polarography of molten salts. Based on the above mentioned work of Karpachev, Rempel, and Jordan, and the work of other authors, which established the appearance of a limiting current during the electrolysis of molten salts, the Soviet authors used ternary electrolytes in the polarography of molten salts.

This was a difficult course in the respect that theoretical bases on the use of ternary electrolytes in polarography were very obscure. /767

In 1948, we [8] published a paper in which we gave an account of the results of polarographic investigations of molten electrolytes consisting of aluminum halides and halides of other metals. The polarograms were obtained using solid platinum microelectrodes. This study was carried out with a view to the physical-chemical investigations of complex molten electrolytes.

In the same year a paper was published by Lalikov and Karmazin [5] in which polarograms were presented which described the introduction of copper and cadmium ions into a base electrolyte of molten potassium nitrate. The authors used a solid "dipping" electrode. The investigation had analytical goals; it confirmed the proportionality between the value of the limiting current and the concentration of the solution.

It is interesting to note that the first papers of Lalikov and Karmazin, Steinberg and Nachtreib and also our articles were published almost simultaneously and independently of each other.

As a result of the first papers in the area of the polarography of molten salts, the following problems must be solved in undertaking an investigation of this type.

1. A theoretical foundation for the application of solid electrodes in the polarography of molten salts.
2. An elucidation of the molecular composition of the molten electrodes.
3. A direct quantitative determination of the concentration of ions in various molten electrolytes.

The solution to these questions is governed by the laws of metallurgy since the molten salts used as electrolytes are non-ferrous and rare metals. On the other hand, pyrometallurgical processes, which form the basis for the production of the majority of heavy metals, are connected with the formation of various slags, which in their own right are molten electrolytes.

In accordance with the above enumerated problems, the polarography of molten salts was developed in three directions.

1. The development of the theory of the polarography of molten salts using solid electrodes.
2. The investigation of the electrolytic properties of molten electrolytes by the polarographic method.
3. The development of polarographic voltamperometric methods of the quantitative investigation of ions in molten electrolytes.

2. Methods of the Polarography of Molten Salts

The essential experimental methods for the polarographic investigation of molten salts must be divided into three groups.

In the first case, a mercury capillary electrode is used just as in the usual polarography of aqueous solutions. In the second case, the polarogram

is taken using the so-called "dipping" electrodes. In the third case, a solid stationary electrode is used, preferentially platinum.

As was already mentioned above, the mercury capillary electrode was used by Steinberg and Nachtreib for the polarographic investigation of molten salts. The mercury is placed in a lead glass vessel which has a capillary tip. The tip of the capillary is dipped into the molten electrolyte. A micro funnel suspended below the capillary collects the mercury, which is then weighed. The potential of the capillary electrode is determined relative to metallic mercury located at the bottom of the vessel. The potential /768 of the latter, in its turn, is determined by a potentiometer against a mercury dropping electrode. Steinberg and Nachtreib calculated the values of the electrode potentials against this standard mercury dropping electrode. A ternary alloy ($LiNO_3$--30 mole %, $NaNO_3$--17 mole %; KNO_3--53 mole %) was used as the electrolyte for the standard dropping electrode. Calomel (18g Hg_2Cl_2 in 35 g of electrolyte) was dissolved in this electrolyte. All measurements were taken in a dry nitrogen atmosphere.

In addition to the segregation potential of nickel, lead, cadmium, and zinc, these authors determined the diffusion coefficients of the corresponding ions. A fundamental inadequacy of the mercury electrode is the low boiling point of mercury. Therefore, Steinberg and Nachtreib's data, even at 160°, is in doubt since mercury forms an ash with the molten salts distorting the results of the investigation. This is not to mention that, in general, the use of mercury above 300° is impossible. In our view, a mercury dropping electrode is unpromising for polarographic investigations of molten salts.

The "dipping" solid electrode was used by Lalikov and Karmazin [9] for the polarography of molten solutions and was subsequently developed by these authors for the polarography of molten salts [5]. The "dipping" electrode is made of a platinum wire which has a gas, introduced by an internal tube, flowing over it. The gas gradually squeezes the analyzed solution out from the platinum electrode and at the moment of detachment of the gas bubble the solution again makes contact with the electrode. The polarograms obtained using such a "dipping" electrode resemble polarograms obtained with the usual mercury dropping electrode.

During slow bubbling, such large oscillations are obtained that it becomes difficult to measure the height of the wave. In order to obtain satisfactory polarograms in aqueous solutions, the rate of bubbling does not exceed 64 bubbles per minute. This same rate of bubbling is also recommended for the polarography of molten salts. The height of the polarographic wave depends on the depth of immersion of the tube as well as the rate of bubbling. During the investigation of aqueous solutions, the platinum cathode is washed with hydrogen.

As far as the molten salts are concerned Lalikov used air to wash the "dipping" electrode. On washing the platinum electrode with hydrogen or with oxygen the latter becomes the gaseous electrode. It is well known that in molten salts, platinum easily becomes the oxygen electrode. Upon the simultaneous precipitation of one metal or another onto platinum (during polarography) the determination of the precipitation potential of this metal becomes unreliable. The value of this potential will depend on many factors, namely the gas pressure on the electrode, the rate of bubbling, the chemical composition of the gas and so forth. It is very difficult to maintain all of these conditions identically when working with molten salts. The complicated hydrodynamic operating conditions of the "dipping" electrode practically do not allow a theory to be derived for the electrode. Considering all of this, there is little prospect for the polarography of molten salts using the "dipping" electrode. It is impossible to describe the polarograms using this electrode in molten salts as very reproducible.

The majority of polarographic investigations of molten salts have been carried out using stationary solid electrodes. Skobets and co-workers [10, 11] showed that with polarography using solid electrodes, stable and reproducible results are obtained if the so-called "surge" current is fixed. This affords the possibility of obtaining a polarograph which is automatically recorded /769 during the polarography of molten salts, significantly increasing the precision and sensitivity of the experimental method. In working with solid stationery electrodes, it is not necessary to take special precautions with the regeneration of the surface of the electrodes. It is quite sufficient to move the pointer of the potentiometric roll of the polarograph to the null position

(at the closed cycle of the electrolysis), in order that trace amounts of substances which precipitated onto the electrodes while taking one curve are completely dissolved at the beginning of the new run. The potential of the cathode is determined relative to the platinum anode.

The basic deficiency of solid stationary electrodes is the absence of the renewal of the pre-electrode layer of the melt. This deficiency can be overcome by the use of a rotating solid electrode. Although the latter had not been used up to this time for the polarography of molten salts, it was demonstrated by us, nevertheless that the application of a rotating solid electrode is very promising in the polarography of molten salts.

3. Analysis of the Polarographic Waves Obtained in Molten Salts Using Solid Electrodes.

As is known, the polarographic wave taken with a mercury dropping electrode has the form shown in Figure 1. The value of the limiting current i_d is proportional to the concentration of the solution and is determined by equation (1).

For the case of metals, formed from the reduction of ions, dissolved in mercury with the formation of an amalgam on the surface of the dropping electrode, the polarographic wave is described by the Gairovsk-Ilkovich equation

$$E = E_{1/2} - \frac{RT}{nF} \ln \frac{i}{i_d - i}, \qquad (2)$$

where E is the value of the electrode potential at any point of the wave; i is the value of the current strength (or density) at any point of the wave; $E_{1/2}$ is the so-called "halfwave potential", i.e., the electrode potential at the point in the wave, at which $i = \frac{i_d}{2}$; i_d is the limiting or diffusion current; $\frac{RT}{nF}$ is the prelogarithmic coefficient which has the generally accepted value in electrochemistry.

Equation (2) was derived in due time using the following basic assumptions.

1. The validity of Tyurin's equation [12] for an amalgamated electrode which, using the notation of contemporary electrochemistry, has the

form
$$E = E_a^0 - \frac{RT}{nF} \ln \frac{c_a^0 \cdot f_a}{c_s^0 \cdot f_s}, \tag{3}$$
where E_a° is the normal potential of the amalgam; c_a° is the concentration of ions of the amalgam; c_s° is the concentration of ions of reduced metal at the surface of the electrode; f_a and f_s are the corresponding activity coefficients.

2. The rate of diffusion of ions is directly proportional to the difference in their concentrations in the entire solution and in the pre-electrode layer.

3. The current strength is directly proportional to the diffusion of the ions undergoing reduction. The value of the limiting current is proportional to the concentration of ions in solution.
$$i_d = k_s \cdot c_s, \tag{4}$$
where k_s is a proportionality constant.

4. The concentration of the amalgam which is formed at any point on the polarographic wave is proportional to the current strength. /770

With respect to solid electrodes which have been used rather frequently lately, in polarography their corresponding theoretical foundation is as yet unknown. This is explained by the fact that in respect to solid electrodes the generally accepted assertion, in accordance with which the diffusion towards such an electrode is not symmetrical, cannot be precisely interpreted mathematically. Nevertheless, solid electrodes turn out to be suitable on a practical level both in the polarography of aqueous solutions and in the polarography of molten salts. Considering the practical utility of solid micro-electrodes in the polarography of aqueous solutions Kohltoff and Lingaine [13] proposed an equation for the polarographic wave taken using platinum solid electrodes. This equation had the following form:
$$E = E_M^\circ - \frac{RT}{nF} \ln \frac{k_s}{f_s} + \frac{RT}{nF} \ln (i_d - i), \tag{5}$$
where E_M° is the normal electrode potential of the metal of the ion which is being reduced; k_s and f_s have the same values as in equations (3) and (4).

Equation (5) is based on the supposition that the platinum electrode is momentarily covered with a layer of the reduced metal. Such an electrode immediately behaves as a metallic electrode which had been made from the metal of the ion which is being reduced. At any point of the polarographic wave, the value of the electrode potential will depend only on the activity of the metal ions in solution.

As Kahltoff and Lingaine showed, the validity of equation (5) was experimentally confirmed by Laitinen in the reduction of lead and thallium ions (in aqueous solutions).

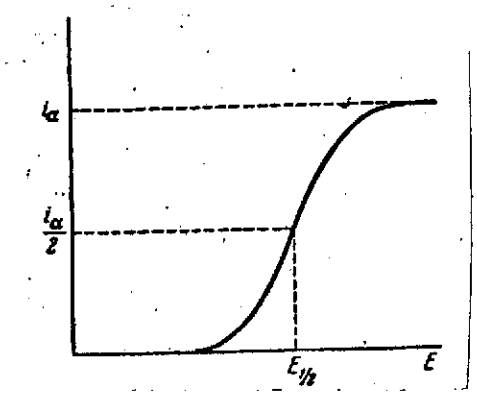

Figure 1: A Polarographic Curve Taken on a Mercury Capillary Electrode.

Analysis of polarographic waves which we obtained [14] using solid platinum electrodes for the reduction of Mg^{2+}, Zn^{2+}, Tl^{+}, Pb^{2+}, Cd^{2+}, and Ag^{+} ions in a molten potassium nitrate base electrolyte showed the complete inapplicability of equation (5) of Kohltoff and Lingaine. If the experimental data are plotted as E vs. log (i_d--i) then we obtain not a direct relationship as equation (5) requires but a parabolic curve. This is not surprising since equation (5) is based on assumptions which are known to be incorrect. As a matter of fact, it was difficult to accept at the time the polarogram was taken that the platinum solid electrode was momentarily transformed into an electrode of the metal of the ion which was being reduced. Therefore, it is incorrect to consider that the activity of the metal which is on the solid electrode is constant as equation (5) requires. On the contrary, obviously it would be more correct to consider it to be a function of the current strength. Equation (5) considers only the concentration polarization determined by the depletion of ions undergoing reduction in the pre-electrode layer of solution. If this corresponded with fact then the polarographic wave would have the form shown in Figure 2.

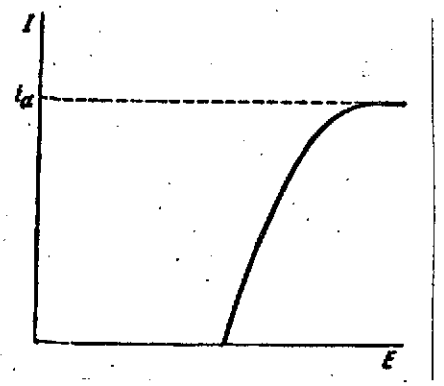

Figure 2: Curve Indicating Concentration Polarization.

Experiments do not confirm this. The polarographic waves obtained using solid electrodes in molten salts both by us and by other authors have the form shown in Figure 1, i.e., they have a point of inflection. These curves resemble polarographic waves obtained using a mercury dropping electrode. /771

All this stimulated us to reject the interpretations of the polarographic properties of solid electrodes which had been expressed by Kohltoff, Lingaine, Laitinen, and other authors and to attempt to bring some other interpretations to bear on the polarographic waves which are obtained by using such electrodes.

E. Skobets [10, 11, 15, 17], carrying out a breadth of investigations on the polarographic properties of solid electrodes, paid significant attention to the renewal of the pre-electrode layer and to the motion of the diffusion front in the depth of the solution. As is known [18], for conditions of nonstationary diffusion, the strength of the diffusion current is determined by the equation

$$i = \frac{n \cdot F \cdot \sqrt{D}}{\sqrt{\pi \cdot t}} (c_s - c_s^{\circ}), \qquad (6)$$

where D is diffusion coefficient of the ions being reduced; c_s is the concentration of ions in the entire solution; c_s° is the concentration of ions in the pre-electrode layer; t is the time.

The validity of equation (6) for solid electrodes in aqueous solutions was experimentally tested and confirmed by Skobets and Kavetski [19] and in molten salts by Markov and Berenbloom [20].

Thus for solid electrodes there must be a true dependence which is expressed by equation (4).

The experimental data obtained by us and also by other authors confirmed the validity of equation (4) for a limiting current observed during the electrolysis of molten salts using solid electrodes.

With respect to the theoretical equation of the polarographic wave obtained using solid electrodes during the electrolysis of molten salts, one can be guided by the following considerations.

During the polarographic plot, the platinum solid electrode onto which metal ions are being reduced is not covered by a continuous layer of this metal, but instead forms an alloy with its surface. The formation of surface alloys makes it possible for the atoms of the reduced metal to diffuse into the platinum. Considering that the polarography of molten salts takes place at comparatively high temperatures it is possible to assume that the rate of diffusion is significantly increased since it is known that the temperature dependence of the diffusion coefficient of solid metals is determined by the equation:

$$D = A \cdot e^{-\frac{E}{RT}}. \tag{7}$$

At high temperatures the diffusion of metal atoms in platinum can be compared to the diffusion of metal atoms into mercury which takes place with the usual polarography in aqueous solution. Because of the formation of surface alloys, the activity of the metal of the ion which is being reduced onto the platinum can not be a constant value and will depend on the current strength. As Frumkin [18] showed, the concentration (c_M) of the metal, precipitated onto the surface of the electrode must be related to the concentration of metal ions in solution c_I (in our case with the molten electrolyte) by the equation:

$$\frac{c_M}{c_I} = \sqrt{\frac{D_I}{D_M}}, \tag{8}$$

where $D_i D_M$ are, respectively, the diffusion coefficients of the ions in solution and metal atoms in the electrode (in the platinum).

On the basis of our experiments on the polarographic investigation of ions in a molten potassium nitrate base electrolyte, the value c_I can be taken as 10^{-2} mole % [14]. According to the work of Steinberg and Nachtreib [8], the diffusion coefficient of ions in molten potassium nitrate have values of

the order of 10^{-6} cm^2/sec. For the metals which we have investigated, data for the diffusion coefficients in platinum are not known. Berrer [21] presented data for the diffusion coefficients of a series of metals (Pb, Zn, Cd, and others) in silver and copper. The activation energy for the diffusion of various metals in silver had a value of the order of 20,000 to 22,000 cal./atom. Taking the same activation energy for the diffusion in platinum, i.e., 22,000 cal./atom, and calculating the diffusion coefficient of metals at 613 K from this value, we then obtain a value of the order of $10^{-12}cm^2$/sec. Substitution of all these metals into equation (8) gives a value of 10 atom %. At higher temperatures the value of c_M will be significantly lower.

As a result of the cleaning of the electrode and electrochemical reactions leading to decomposition of the surface of the platinum, the diffusion coefficient at the surface layer must be higher than $10^{-12}cm^2$/sec.

In the calculation which was carried out, we used the diffusion volume as the coefficients. However in our case undoubtedly it is not a volume diffusion that takes place in the decomposed surface layer but a boundary and even a surface diffusion. Unfortunately there are no data in the literature on the diffusion coefficients of various metals in the surface layer of platinum. However, a comparison of the volume and the boundary coefficients of diffusion obtained for other metals shows that the latter is 100 times greater than the former. The coefficients of surface diffusion are even higher [22]. If this relationship is correct for our case then we can use a value of the order of $10^{-10}cm^2$/sec. for the coefficient of boundary diffusion. We then obtain a value for c_M of 1 atom %. Thus the initial concentration of metal in the surface layer of the platinum electrode will be significantly lower than our calculated value.

On the other hand using the formula for linear migration of metal atoms into platinum as a result of diffusion one can calculate the depth of penetration of atoms into the surface layer of the electrode during a single polarographic run using the known equation [21]:

$$\Delta x = 2a\sqrt{D \cdot t}, \tag{9}$$

where Δx is the linear displacement; D is the diffusion coefficient; t is the time; and coefficient a depends on the relative concentration of diffusing substances in the two layers separated from each other by the distance Δx, i.e.,

$$a = f\left(\frac{c}{c_x}\right).$$

We may calculate the depth of penetration of the precipitated metal atoms into the electrode providing that its concentration is a factor of 100 smaller, i.e., $c_x = 0.01$ c. For such a relation between c and c_x the value of a according to Kavalki [23], is equal to approximately 0.5.

In polarographic experiments (in molten salts) t = 100 sec. Taking D = 10^{-12} cm^2/sec. we obtain for Δx [from equation (9)] the value of 10^{-5}cm. The /773
depth of penetration is approximately 500 atomic layers; it is 2,000 atomic layers if we take the value 10^{-10} cm/sec. for the coefficient of boundary diffusion.

All these considerations give a completely competent point of view which was expressed by us earlier, in correspondence with which a surface alloy is formed on the solid platinum cathode, during the polarography of molten salts.

On the basis of the above expressed physical picture, we have attempted to elucidate what sort of mathematical equation can be used to describe the polarographic wave measured from solid electrodes in molten salts.

Considering the formation of a surface alloy on the solid electrode one can calculate the electrode potential according to an equation analogous to the Tyurin equation

$$E = E_M^0 - \frac{RT}{nF} \ln \frac{a_M}{c_s^0 \cdot f_s}, \tag{10}$$

where E_M° is the "normal" electrode potential of the alloy; a_M is the activity of the metal diffusing into the electrode; c_S° is the concentration of ions of metal undergoing reduction in the pre-electrode layer; f_S is the activity coefficient for these ions. Considering equation (6), one can write

$$i = k_s(c_s - c_s^0), \tag{11}$$

where k_S is a constant; c_S is the concentration of ions in the entire volume of solution, c_S° is the concentration of ions in the pre-electrode layer.

From equations (4) and (11) we find $$c_s^0 = \frac{i_d - i}{k_s}. \quad (12)$$

Earlier we assumed that the activity of the metal precipitating onto the platinum electrode in its surface layer depends on the current strength, and this dependence is determined by the relation: $$a_M = k_a \cdot i, \quad (13)$$

where k_a is a constant.

Substituting the values a_M and c_s^0 from equations (12) and (13) into equation (10), we obtain

$$E = E_M^0 + \frac{RT}{nF} \ln f_s - \frac{RT}{nF} \ln k_a - \frac{RT}{nF} \ln k_s - \frac{RT}{nF} \ln i + \frac{RT}{nF} \ln (i_d - i). \quad (14)$$

Collecting all the constant values into one constant

$$E_M^0 + \frac{RT}{nF} \ln f_s - \frac{RT}{nF} \ln k_a - \frac{RT}{nF} \ln k_s = \text{const}, \quad (15)$$

we finally obtain

$$E = \text{const} - \frac{RT}{nF} \cdot \ln \frac{i}{i_d - i}. \quad (16)$$

Equation (16) is identical to the equation of Gairovsk and Ilkovich.

Polarograms obtained by us [14] for the reduction of Mg^{2+}, Zn^{2+}, Tl^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Ag^{+} ions onto a solid platinum electrode in a molten potassium nitrate base electrolyte are fully described by equation (16). A straight line relationship is obtained in graphs of $E - \lg \frac{i}{i_d - i}$. /774

A plot is presented in Figure 3 for the reduction of silver ions. Analogous plots were obtained for all the remaining ions which we investigated.

Equation (16) requires that the prelogarithmic coefficient $\frac{RT}{nF}$ be equal to the reciprocal of tan alpha, where a is the slope of the line constructed in the coordinates $E, \lg \frac{i}{i_d - i}$.

The experimental data [14] which we have obtained fundamentally confirmed this as is seen from Table 1 in which the values are presented both as found from experiment and as calculated theoretically using the fact that $\frac{\Delta E}{\Delta \lg i / i_d - i}$,

$$\frac{\Delta E}{\Delta \lg i / i_d - i} = \frac{2,3 \cdot RT}{nF}. \quad (17)$$

The data in Table 1 were obtained at a temperature of 340°.

For all of the ions except magnesium, the pre-logarithmic coefficients found from the plot of the experimental data are in satisfactory agreement (considering the specific work with molten salts) with theoretically calculated values.

In contrast to the polarographic waves obtained in aqueous solutions with the mercury dropping electrode, the waves taken in molten salts are not completely symmetrical. Therefore, the constant in the equation (16) does not have the same constancy that is observed for the half wave potential using the mercury dropping electrode. However, as the experimental data demonstrate this constant is almost independent of the concentration and on the whole remains relatively constant; it conditionally can be called a "half wave potential". This confirms experimental data taken from earlier published works [14] and which is presented in Table 2.

The values listed in Table 1, from graphs of E vs. $\log \frac{i}{i_d - i}$, correspond to the value with $\log \frac{i}{i_d - i} = 0$.

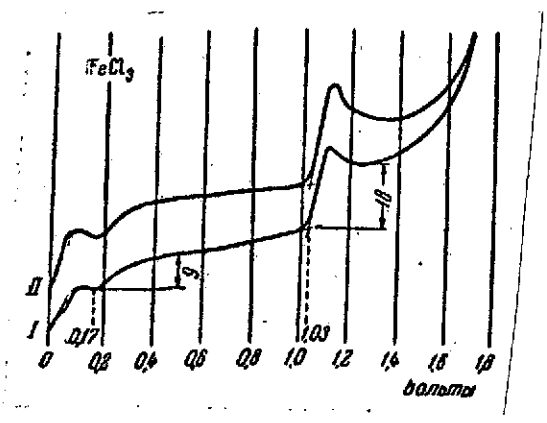

Figure 3: The Dependence of the Potential on Log $\left(\frac{i}{i_d - i}\right)$. A Solution of $AgNO_3$ in $NaNO_3$, Concentration -- 0.015% Mole. $\tan \alpha = 0.121$.

In fairness, Equation (16) was demonstrated by Rempel [25] who investigated the electrolytic yield of hydrogen from incompletely dehydrated molten carnallite. Using a solid molybdenum cathode, Rempel obtained a limiting current and a polarographic wave for hydrogen which is described beautifully by this equation.

Chovnik's [26] experimental data are also in excellent agreement with equation (16). Later Panchenko [27] carried out a polarographic investigation on magnesium chlorides (in a base electrolyte of molten potassium chloride), which confirmed both the /775

validity of equation (16) and the better agreement of the experimental values of the slopes with the calculated values.

Table 1.

Ions	$\frac{\Delta E}{\Delta \lg i/i_d - i}$ from experimental data	$2{,}3 \cdot \frac{RT}{nF}$ (calculated data)	$\frac{\Delta E}{\Delta \lg i/i_d - i} - \frac{2.3 \cdot RT}{nF}$
Mg^{2+}	0,098	0,060	+0,038
Zn^{2+}	0,080	0,060	+0,020
Tl^{+}	0,107	0,120	—0,013
Pb^{2+}	0,068	0,060	+0,008
Cd^{2+}	0,060	0,060	0,000
Ni^{2+}	0,074	0,060	+0,014
Co^{2+}	0,062	0,060	+0,002
Cu^{2+}	0,074	0,060	+0,014
Ag^{+}	0,121	0,120	+0,001

Note: Commas indicate decimal points.

Table 2.

Concentration in Mole % \ Ions	Values of the constnat in equation (16) in volts					
	Zn^{2+}	Cd^{2+}	Co^{2+}	Ni^{2+}	Ag^{+}	Tl^{+}
0,030	1,26	1,08	—	1,02	0,87	—
0,045	—	1,08	0,95	—	0,90	1,18
0,060	1,28	1,08	0,96	1,04	0,92	1,20
0,075	—	1,08	0,96	—	0,90	—
0,090	1,30	—	—	1,04	—	1,20
Average value of the constants.	1,28	1,08	0,96	1,03	0,89	1,19

Note: Commas indicate decimal points.

Thus one can regard to a significant extent that the applicability of equation (16) is well grounded for the polarographic waves obtained in molten electrolytes using solid electrodes just as with the Gairovsk - Ilkovich equation. The point of view expressed above does not exclude other possible interpretations of the nature of the polarographic waves obtained using solid electrodes in melts. Further investigations in this area can resolve this question.

3. The Polarographic Investigation of the Electrochemical Properties of Molten Electrolytes.

In the polarographic investigation of molten salts, the following items are generally taken into consideration: the elucidation of the nature and

properties of the ions in the molten electrolyte, a study of the behavior of these ions and an elucidation of the molecular composition of the molten salts.

In addition to our investigations [7, 14, 24], the works of Rempel [25], Chovnik [26, 28], and Panchenko [27] are also relevant here. In our first paper, we investigated metal chlorides and bromides in the base electrolyte $AlCl_3$ -- NaCl and $AlBr_3$ -- NaBr respectively.

During the determination of the concentrations, the polarographic waves and also the potential for the generation of the metals was obtained. The dependence of the nature of the polarograms on the concentration of ions indicates that there is complex formation in the melts. /776

For example, polarograms for ferric chloride (Figure 4) showed that the reduction of Fe^{3+} ions takes place stepwise:

$$a)\quad Fe^{3+} + e \rightarrow Fe^{2+},$$

$$b)\quad Fe^{2+} + 2e \rightarrow Fe.$$

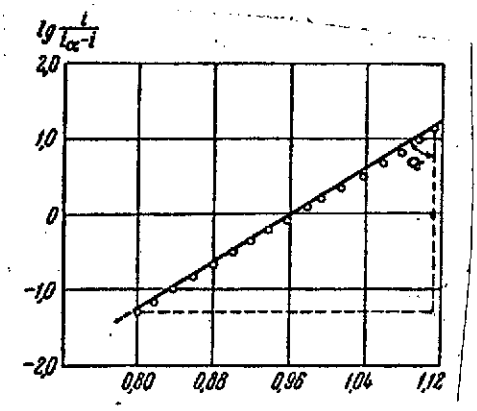

Figure 4: Polarogram for a Solution of $FeCl_3$ in NaCl -- $AlCl_3$.

As can be seen from Figure 4 the height of the potential for the second wave is twice that of the first.

We later investigated nitrates and chlorides of metals in a molten potassium nitrate base electrolyte. The nitrates of silver, zinc, cadmium and magnesium dissolve in molten potassium nitrate. Nitrates of other heavy metals (cobalt, nickel, copper) are thermally unstable and therefore one cannot obtain solutions of these metals in molten potassium nitrate. It turns out however that many metal chlorides are quite soluble in molten potassium nitrate. This affords the possibility of obtaining a nitrate molten electrolyte containing heavy metal ions of nitrates which are thermally unstable.

Table 3.

Ions	Our data		Lalikov's data		Steinberg and Nachtreib's data	
	E_M	$E_{1/2}$	E_M	$E_{1/2}$	E_M	$E_{1/2}$
K^+	−2,20	—	—	—	—	—
Na^+	−2,10	—	—	—	—	—
Mg^{2+}	−1,30	−1,38	—	—	—	—
Zn^{2+}	−1,25	−1,28	—	—	−0,88	−0,90
Pb^{2+}	−1,13	−1,18	+0,25	—	−0,47	−0,50
Cd^{2+}	−1,07	−1,08	−0,42	−0,87	−0,55	−0,57
Ni^{2+}	−1,02	−1,04	−0,65	—	−0,36	−0,37
Co^{2+}	−0,95	−0,96	−1,00	—	—	—
Cu^{2+}	−0,93	−0,94	+0,10	—	—	—
Sb^{3+}	−0,92	—	—	—	—	—
Ag^+	−0,86	−0,92	−0,03	—	—	—
Tl^+	−1,15	−1,20	—	—	—	—
$Cr_3O_7^{2-}$	—	—	−0,40	—	—	—
Hg^{2+}	—	—	±0,00	—	—	—

NOTE: E_M -- generation potential; $E_{\frac{1}{2}}$ -- half-wave potential.

Note: Commas indicate decimal points.

An investigation of the generation potentials of metals showed that for one and the same ion one obtains one and the same value independent of whether the ions are introduced into the molten potassium nitrate as the nitrate or as the chloride.

Lalikov [29] also investigated the generation potential of several metal ions in a molten potassium nitrate base electrolyte.

Data obtained from various authors on the half wave potential and on the generation potential of metals using molten potassium nitrate as solvent are presented in Table 3. These data were taken from published literature.

Steinberg and Nachtreib's values were obtained using a mercury dropping electrode against a standard calomel electrode. They do not conform with Lalikov's data nor with ours inasmuch as the latter measurements were taken relative to a platinum anode. The disagreement between Lalikov's data and ours is less clear. For the generation potential of all metals except cobalt our values are quite different from the corresponding values of Lalikov.

On the basis of the polarographic studies, it is possible to construct an electrochemical series based on the voltage of the metals in molten potassium nitrate. The metals fall in the following order:

K, Na, Mg, Zn, Tl, Pb, Cd, Ni, Co, Cu, Sb, Ag, Hg.

This series had not been known previously.

In Table 4 the generation potentials of metals from molten chlorides determined by polarography are presented.

Table 4.

Ions	Generation potentials in a NaCl--KCl--LiCl base electrolyte according to Yu. Lalikov's data (in volts)		Generation potential in a NaCl--$AlCl_3$ base electrolyte according to our data at 300° (in Volts)	Generation potential in a KCl base electrolyte according to I. D. Panchenko's data at 770°.
	$t°$	E_M		
Al^{3+}			—1,78	
Mn^{2+}			—1,63	
Zn^{2+}			—1,30	
Cd^{2+}	700	—0,30	—1,15	—1,05
Fe^{3+}			—1,03	
Pb^{2+}			—1,02	—1,10
Co^{2+}	450	—0,54	—0,86	
Cu^{2+}	445	+0,08	—0,83	
Ni^{2+}	480	—0,50	—0,78	
Sb^{3+}			—0,75	
Ag^{+}			—0,72	—0,88
Br^{3+}	460	+0,55	—0,57	

Note: Commas indicate decimal points.

Rempel [25] found a value of 1.51 V relative to the standard magnesium electrode for the generation potential of hydrogen from molten carnillite at 735°. For the slope $\frac{\Delta E}{\Delta \lg i / i_d - i} = \frac{2,3\,RT}{n \cdot F}$, taking n = 1 Rempel found a value of 0.207 instead of 0.200 as by theory. Based on this, Rempel drew a conclusion on the molecular state of hydrogen in molten carnellite.

N. Chovnik [26] using the standard silver electrode and a platinum anode, investigated the anodic oxidation of divalent tin ions. The polarographic wave which he obtained is described very well by equation (16). Chovnik obtained a value of 0.31 volts relative to the silver electrode for the half wave potential. Later Chovnik [28] published the results of a polarographic investigation of the molten system of the zinc kainite type, in which the presence of stable complexes was established.

4. The Polarographic Investigations of Molten Salts for Analytical Purposes /778

Lalikov was the chief developer of the polarography of molten salts for analytical purposes. For example even in his first works [5] Lalikov demonstrated a straight line relationship between the height of the polarographic wave and the concentration for solutions of $CdCl_2$ in KNO_3. Thus the validity of the relation $i_d + K \cdot c$, was shown for molten salts and this formed the basis for polarographic analysis. Later Lalikov [30, 31[developed a polarographic method for the quantitative determination of Ag^+, Cd^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, and Co^{2+} ions in molten nitrate base electrolytes and for Bi^{3+}, Cu^{2+}, Ag^+, Ni^{2+}, Cd^{2+} and Co^{2+} ions in molten chloride base electrolytes. A polarographic method for the determination of Cu^2 and Ag^+ ions was also developed in a molten silicate base electrolyte [29, 31].

The polarographic determination of ions in nitrate salt base electrolytes can be made difficult by the low stability of the corresponding salts at the temperature at which the polarographs are taken.

For the quantitative determination of metals, the nitrates of which have a low temperature stability, Lalikov recommends the addition of acid salts to the melt, for example $KHSO_4$. However sometimes there is no possible path to obtain the nitrates of the melt containing the ions of some metals, for example Bi^{3+}, Sb^{3+}, Al^{3+} and others. This is explained by the instability not only of the nitrates but also of the sulfates of these metals which would be formed upon addition to the melt of the acid salt ($NaHSO_4$ or $KHSO_4$). It turns out to be more convenient to carry out the polarographic determination of ions in a molten chloride base electrolyte. Actually, Lalikov considers that for ions with a reduction potential below -1.0 V. the polarographic determination in molten salt base electrolytes, among which are molten chlorides, is impossible.

The average error for the polarographic determination of ions in molten chloride base electrolytes was determined by Lalikov to be 4%.

Significantly larger difficulties emerge during the polarographic determination of ions in a molten silicate base electrolyte. The high reactivity of molten silicates excludes the possibility of using ceramic in quartz

crucibles and tubes. The "dipping" solid electrode turned out to be unsuitable here so that even its author, Lalikov, renounced it. In this case Lalikov recommends the use of a solid micro-electrode.

The larger electroconductivity of molten silicates makes it more difficult to match the shunt and to extinguish the capacitor currents. The polarograms have a "creeping" character with an undecipherable appearance to the limiting currents. The determination of the height of the polarographic waves in such polarograms is rather difficult. On the basis of published results one judges that Lalikov succeeded in obtaining waves for only 2 ions in molten silicate base electrolytes: Cu^{2+} and Ag^{+}. In all cases, Lalikov constructed calibration curves which allowed the quantitative determination of ions in molten salts based on the height of the polarographic wave.

From other works devoted to quantitative polarography in molten salt base electrolytes, the investigations of Rempel and Malkov merit attention. These authors developed a polarographic method for the determination of S^{2-} ions in a molten base electrolyte mixture consisting of sodium and potassium chlorides.

The work of Rempel and Malkov is an example of anodic polarography in molten salts. A graphite rod covered with hard glass was used as the anode. The anode potential was measured relative to the standard lead electrode proposed by Artamonov [31]. A mixture of salts was used as the electrolyte: NaCl -- KCl -- /779
$PbCl_2$.

The authors found that by this polarographic method they were able to determine the sulfur content in melts in the concentration region of 10^{-4} to 10^{-5} weight %.

Rempel and Malvov's polarographic curves are described very well by equation (16). Plots of E vs. $\log \frac{i}{i_d - i}$ give a slope of 0.114 instead of the theoretically calculated value of 0.097.

6. Voltamperometric Titration

The first experiment to apply a voltamperometric titration to the investigation of molten electrolytes was carried about by Lalikov [28]. To this end,

Lalikov proposed using either the formation of the residues, insoluable in the molten salts, or an oxidation-reduction reaction, for example

$$Me(NO_3)_2 + 2KOH = MeO + 2KNO_3 + H_2O;$$
$$K_2CrO_4 + BaCl_2 = BaCrO_4 + 2KCl;$$
$$K_2Cr_2O_7 + 6NaNO_2 = 2KCrO_2 + 6NO_2 + 3Na_2O.$$

Lalikov recommends the use of the micro-dispersion method for the titration. Upon precipitation of the insoluble metal oxide, the height of the cationic wave falls. Comparing polarograms at various microdispersions one determines the equivalent current.

The utilization of the voltamperometric titration during the investigation of molten electrolytes is of very great interest to us. However, experimental material in this area is very sparse and does not allow us to make any definitive conclusions on the possibilities of the method.

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