

Influence of wetting of the electrode on its effective surface Application to the study of diffusion in the melt NaCl—KCl—PbCl₂

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Using chronopotentiometric method the diffusion coefficients of Pb²⁺ ions in the melt NaCl ($t = 820^{\circ}\text{C}$, $D = 4.69 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and in the equimolar mixture NaCl—KCl ($t = 710^{\circ}\text{C}$, $D = 3.51 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) were determined. The experimental results are compared with literature data and the influence of rising of meniscus of the melt at immersed electrode on the value of apparent diffusion coefficient is discussed.

Были определены коэффициенты диффузии ионов Pb²⁺ в расплаве NaCl ($D = 4,69 \times 10^{-5} \text{ см}^2 \text{ сек}^{-1}$ при 820°C) и в эквимольной смеси NaCl—KCl ($D = 3,51 \times 10^{-5} \text{ см}^2 \text{ сек}^{-1}$ при 710°C) с использованием хронопотенциометрического метода. Экспериментальные данные сравниваются с литературными данными и обсуждается влияние поднятия мениска расплава при погруженном электроде на величину кажущегося коэффициента диффузии.

The determination of the diffusion coefficient of Pb²⁺ ions in melts is dealt with in numerous papers [1—8]. However, as it follows from Table 1, the differences between data exceed the reported error of experiment. The aim of this work is to determine the diffusion coefficient of Pb²⁺ in the melt NaCl—KCl using different types of electrodes and on the basis of critical comparison of the obtained and literature data to appreciate possible sources of errors. The melts NaCl—KCl and NaCl were chosen as model systems because the temperature region 700—850°C is interesting from the point of view of applications and temperature is the parameter which influences considerably the experimental technique used.

The theory of chronopotentiometry is sufficiently described in the literature [1, 9, 10]. For the electrode reaction controlled by linear diffusion it holds

$$j\tau^{1/2}/C = 0.5nF\pi^{1/2}D^{1/2} \quad (1)$$

where j is the current density, τ is the transition time (*i.e.* time at which the concentration of Pb²⁺ ions at the electrode approaches zero), C is the original

concentration of Pb^{2+} ions in the melt, n is the charge number of the cell reaction (in our case $n = 2$), F is the Faraday constant, and D is the diffusion coefficient of Pb^{2+} ions in the system.

If at given conditions the electrode reaction is reversible then in ideal case the time dependence of potential can be described by the relationship

$$E = E^0 + \frac{RT}{nF} \ln(D_R/D_0)^{1/2} + \frac{RT}{nF} \ln(\tau^{1/2} - t^{1/2})/t^{1/2} \quad (2)$$

The deviations from this ideal behaviour result mainly from the following reasons: charging of the double layer capacity, adsorption phenomena, and influence of oxide layers on the electrode. Bard [11] suggested to express the influence of these factors on transition time by the following equation

$$j\tau^{1/2}/C = 0.5nF\pi^{1/2}D^{1/2} + \frac{C_{dl}\Delta E}{C\tau^{1/2}} + \frac{Q_{ox}}{C\tau^{1/2}} + \frac{nF\Gamma}{C\tau^{1/2}} \quad (3)$$

where C_{dl} is the mean double layer capacity in the potential interval ΔE , Q_{ox} is the charge needed for dissolution or formation of the oxide layer on electrode surface, and Γ are the moles of electroactive species adsorbed at unit surface of the electrode. In literature many methods for elimination of the effects influencing transition time are described. The theoretical treatment of this problem is based on the elimination of charging capacity currents. However, as it follows from eqn (3) besides the capacity currents there are also other effects influencing transition time. For correction of these effects it is substantial that all correction terms in eqn (3) can be expressed as $B/C\tau^{1/2}$. The survey of different corrections is summarized in [12]. In this work we used for determination of transition time from $E-t$ plot the method ascribed to Reinmuth [12] which has a simple theoretical background and satisfies semiempirical eqn (3).

It should be mentioned that because of complexity of phenomena influencing transition time the reliable results can be obtained from chronopotentiometric curves just then when the different methods used for determination of transition time yield principally the same results. From eqn (3) it follows that at low concentration of electroactive substance the disturbing effects play more important role and they cause increase of apparent diffusion coefficient. On the other hand increasing of the concentration of the electroactive substance enhances its part in electrical conductivity, which also is to be avoided. The simple criterion of the assumption that the transport of electroactive species to the electrode is controlled by the linear diffusion is the independence of the quantity $j\tau^{1/2}/C$ on applied current density. This criterion is in the system studied fulfilled and therefore the correct determination of diffusion coefficient depends on the correct determination of the surface of electrode (which knowledge is necessary for determination of current density) and of the concentration of electroactive substances.

Determination of the surface of working electrode

From the analysis of experimental techniques used for the determination of diffusion coefficient of Pb^{2+} [1—8] it followed that one of the reasons for discrepancy between results obtained by different authors could be using of different types of electrodes. In this work three types of working electrodes were tested:

- platinum wire \varnothing 1 mm, sealed in Vycor glass;
- platinum wire \varnothing 1 and 2 mm immersed into melt. Depth of the immersion was changed. This type of electrode is cylindrical, but at given conditions the diffusion can be considered linear [13];
- platinum plate (surface ca. 75 mm^2) hanged on platinum wire \varnothing 0.3 mm.

In the two latter cases the rising of melt on the electrode was considered because it significantly changes the electrode surface.

Let us consider the wire of diameter r which is immersed in melt the density of which is ρ and surface tension γ . Then as a result of capillary forces the melt wets the wire and its meniscus rises to a definite height, h , if the contact angle, θ , is finite (Fig. 1). In the case of plate (which is the limit case of wire having infinite diameter) it holds [14]

$$h = \sqrt{\frac{2\gamma(1 - \sin \theta)}{g\rho}} \quad (4)$$

The rising of meniscus for the case of finite diameter of wire was derived on the basis of the following consideration. The force W which holds the column of rising liquid equals

$$W = 2\pi r \gamma \cos \theta \quad (5)$$

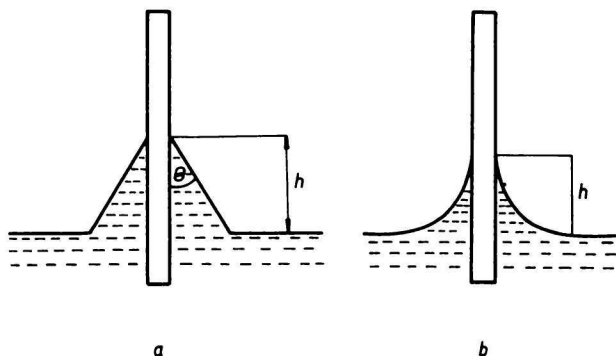


Fig. 1. Models of wetting of the immersed wire.

If we chose an arbitrary shape of meniscus we can calculate its weight which depends on the geometrical shape of meniscus and the height h . The height h must be chosen so that the weight of rising liquid equals the force W obtained from eqn (5). We solved the task numerically for two shapes of meniscus (Fig. 1a, b) and different diameters of wire. In the case of infinite diameter the results were compared with analytical solution of the problem (eqn (4)). The height h calculated from a model was then corrected (normalized) according to the relation

$$h = h_m h_a(r = \infty) / h_m(r = \infty) \quad (6)$$

where h_m is the height of rising obtained for a given model, $h_m(r = \infty)$ is the height for infinite diameter and h_a is the height of rising calculated from eqn (4). Both models of meniscus shape give practically the same dependence of rising of liquid vs. diameter of wire. For the case of equimolar melt NaCl—KCl at 710°C the plot h vs. r is in Fig. 2. The contact angle θ was approximately 30° and it was determined experimentally using heating microscope.

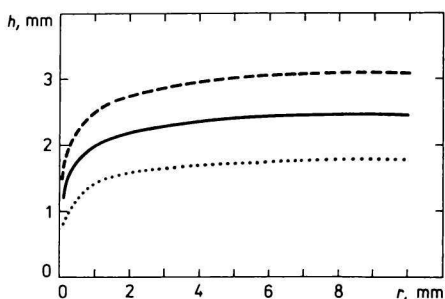


Fig. 2. Height of rising liquid as a function of wire diameter.

----- model a in Fig. 1;
 model b in Fig. 1;
 ——— corrected height of rising according to eqn (6).

The correction of electrode surface calculated from the height of meniscus with definite θ does not take into account a possibility of covering of the surface over the height h by a thin film of liquid or the change of wetting angle θ and surface tension with the change of the potential of electrode.

The experimental results indicate that these factors can partially influence the quantity h .

The second way of correction of wetting of the electrode is based on the following procedure.

Let us consider that the surface of an electrode can be divided into two parts:

— geometrical surface A calculated without taking into account the influence of wetting or the effects caused by nonlinear diffusion at the tip of electrode ($A = 2\pi rl + r^2$ where l is the depth of immersion without wetting),

— surface b which depends on wetting ($b = 2\pi rh$); this correction can cover also the influence of nonlinear diffusion at the tip of the electrode and the effect of

a thin film over the meniscus. As the surface b does not depend on the immersion l then from eqn (1) it follows

$$\frac{I\tau^{1/2}}{C(A+b)} = \text{constant}, \quad k; \quad \frac{I\tau^{1/2}}{C} = kA + kb \quad (7)$$

where I is the total current. Therefore if we plot $I\tau^{1/2}/C$ vs. A we obtain a straight line. The correction b of the geometrical surface of electrode can be calculated from its slope k and ordinate at $A=0$. Diffusion coefficient can be calculated directly from the slope k , or according to eqn (1) where the real electrode surface $(A+b)$ is to be used for calculation of current density.

Experimental

Preparation of electrolyte

The electrolyte was prepared from NaCl and KCl (anal. grade) calcined at 600°C and dry PbCl₂ of anal. grade. The concentration of Pb²⁺ ions in the melt was changed in the range (3—9) × 10⁻⁵ mol cm⁻³. An exact concentration of Pb²⁺ ions in the electrolyte was determined for each series of experiments by complexometric analysis by titrating lead with solution of EDTA using Xylene orange indicator [15].

Apparatus

The electrolytic cell was formed by sinter-corundum crucible placed in the shaft of furnace. Temperature was measured by Pt—Pt10Rh thermocouple and it was maintained constant with precision ± 1°C. The working electrode (cathode) was formed by Pt microelectrode with surface ca. 0.8 mm² (Pt wire sealed in Vycor glass), by Pt wire of diameter 1 and 2 mm, Mo wire of diameter 0.5 mm or by Pt plate (thickness 0.3 and 0.5 mm). The electrodes were fixed in holder which enabled to move the electrodes using micrometric screw and therefore to change precisely their surface. The geometrical surface of Pt wire electrodes changed in the region 5—100 mm² and of the Mo wire electrode in the region 2—25 mm². The surface of Pt plate electrodes was ca. 50 mm², the precise surface being measured by means of a microscope. The auxiliary electrode was formed by platinum spiral and the reference electrode was formed by Pt wire placed in the distance of 1 mm from the working electrode. Total current passing through the cell was in the limits 1—100 mA and transition times changed in the region 0.01—1 s. As a source of constant current potentiostat Ple-60 VPZ-SVÚOM was used. The potential response was registered using the X-Y recorder HP 7004B or storage oscilloscope Tektronix type 434 equipped with Polaroid camera. Time base was in both cases calibrated using signal generator Wavetek type 112.

Results and discussion

Transition time is determined with precision better than 2.5% and total current passing through the cell with precision better than 1%. Therefore for the correct determination of diffusion coefficient it is necessary to know the exact surface of the working electrode and the concentration of electroactive substance.

The requirement on the knowledge of an exact concentration seems to be trivial. However, one should take into account the evaporation of PbCl_2 during preparation of the melts from pure components. For our experimental arrangement when the total weight of the sample was ca. 60 g, 0.5—1 g PbCl_2 was weighed in and from this amount ca. 0.13 g evaporated, which influenced considerably the resulting concentration of electroactive species. When lead electrodes are used there is a danger of their oxidation, which results in an increase of the concentration of electroactive species. We added into 60 g of the melt NaCl — KCl ($t = 700^\circ\text{C}$) a 4 g piece of lead and we found after 1 h 0.11 wt % Pb^{2+} in the melt. Therefore if lead working electrode is used one should check very carefully if in its vicinity (which is the most important from the point of view of electrochemical reaction) the concentration of Pb^{2+} ions does not increase, which would result in apparent decrease of diffusion coefficient.

From the discussion of the effect of wetting on electrode surface it could seem that all problems disappear if a microelectrode formed by platinum wire sealed in suitable material is used. In this work we tested Pt microelectrode sealed in Vycor glass. We found that the reproducibility of results obtained with this electrode was rather poor and diffusion coefficients approached the highest values reported in literature. This phenomenon could not be explained by leakage of the electrolyte between metal and glass. Observation of the microelectrode using metallographic microscope and X-ray microanalyzer showed that lead and alkali metals deposited on the electrode during its cathodic polarization react with glass. Optically it can be observed as a dark ring formed around the wire. We suppose that this layer can be electrically conductive, at least at higher temperatures, and thus the real surface of electrode increases. One should realize that for an electrode of diameter 1 mm its increase by 5% results in increase of apparent diffusion coefficient by about 20%. Therefore one should be careful while using this type of electrode at high temperatures.

The second type of electrode tested was a cylindric electrode which had been often used for the study of diffusion in molten salts. The relations between transition time and diffusion coefficient for cylindric electrode are given in [13]. However, if the transition time is short enough the diffusion towards this electrode may be considered linear. The results of this work showed that it is possible to get reliable data using this type of electrode if the correction on wetting is carried out. If it is done the values of diffusion coefficient are in good agreement with those

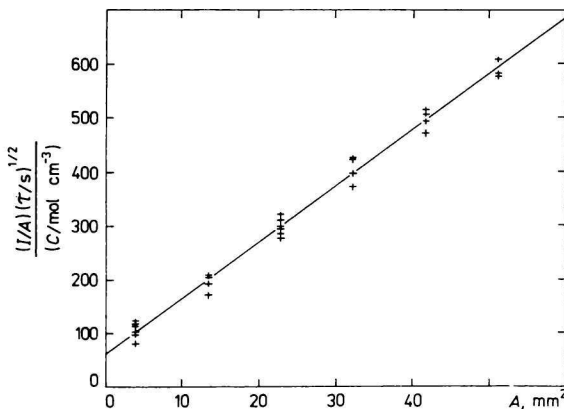


Fig. 3. Experimental dependence of the term $I\tau^{1/2}/C$ vs. geometrical surface A of electrode for Pt electrode in the melt NaCl—KCl at 710°C.

obtained using electrode formed by platinum plate. This conclusion is important because in some cases the plate electrode is difficult to be used for experimental reasons.

For illustration we present the experimental dependence of the term $I\tau^{1/2}/C$ as a function of geometrical surface of electrode (Fig. 3). The change in surface was realized by driving the Pt wire \varnothing 1 mm from melt using micrometric screw. Diffusion coefficient calculated from the slope of the straight line $I\tau^{1/2}/C = f(A)$ is $D = 3.74 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The correction of the geometrical electrode surface is 6.12 mm², which corresponds to the rise of liquid by 1.95 mm. This value is in good agreement with the value 2.0 mm estimated from Fig. 2. From this example it follows that wetting can influence significantly the surface of electrode. *E.g.*, if the electrode is immersed 10 mm its geometrical surface is 32.19 mm² and the error caused by wetting is approximately 20%. The variation coefficient of the term $j\tau^{1/2}/C$ was relatively high (6.5%). The reason for the high variation coefficient is the formation of a thin film on the electrode and/or dependence of wetting on electrode potential. After each experiment dark strips (*ca.* 0.5 mm) in the distance of 3 mm were observed. The distance 3 mm corresponds to the change in immersion of the electrode between two following sets of measurements. The dark strips, which contain KCl and NaCl as detected by X-ray microanalysis, correspond to deposition of K and Na after depletion of Pb^{2+} at the electrode surface. Width of the strips can be explained by the dependence of wetting on the electrode potential which changes considerably when the concentration of Pb^{2+} ions at the electrode approaches zero.

The results obtained using molybdenum electrode \varnothing 0.5 mm were practically the same as with Pt electrode.

The third type of electrode was formed by platinum plate of geometrical surface 75 mm^2 hanged on platinum wire of diameter 0.5 mm. In this case the correction on wetting of platinum support is lower than 4%. Variation coefficient of the expression $j\tau^{1/2}/C$ for this type of electrode was 3%.

The experimentally determined diffusion coefficients together with literature data are summarized in Table 1. From the results it follows that the plate electrode

Table 1

Diffusion coefficient of Pb^{2+} ion in the melts NaCl and NaCl—KCl

Electrolyte	Electrode	$t, ^\circ\text{C}$	$D, 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Ref.
NaCl—KCl	Pt plate	710	7.0	[2]
	Pt plate	700	6.4 ± 0.5	[3]
	Pt microelectrode	720	6.8	[4]
	Pt plate	718	3.08	[5]
	Mo wire, Pb	700	2.82*	[6, 7]
	Pt plate	710	3.51 ± 0.2	This paper
	Pt wire	710	3.70 ± 0.45	This paper
NaCl	Pt plate	831	6.41	[8]
	Pt plate	830	4.22	[5]
	Pt plate	820	4.69 ± 0.3	This paper

* The value was calculated from temperature dependence of diffusion coefficient.

yielded in the studied system the most reliable diffusion coefficient. If a cylindrical electrode formed by a wire is used it is necessary to make careful corrections on wetting of the electrode in order to obtain reliable results.

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