

Diffusivity of lead(II) ions in a system of molten chlorides

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The diffusion coefficients of Pb(II) ions in the system NaCl–KCl–PbCl₂ were measured by chronopotentiometric method at 720, 760, 800, 840, and 880°C. The corresponding mean diffusion coefficients were in the range of $(6.8–14.8) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The activation energy of diffusion in this temperature range had the value of $12.4 \pm 1.0 \text{ kcal mol}^{-1}$.

For the application of galvanotechniques in molten salts it appears useful to study the diffusivity of Pb(II) ions in the system NaCl–KCl–PbCl₂ in the region of low PbCl₂ content. From among the methods available for this purpose chronopotentiometry was chosen. From the recorded curves $E-t$ (where E is the potential of the measured electrode, t is the time) the transition time τ is obtained, which is in relationship with the diffusion coefficient (*i.e.* with the quantity of diffusivity) of the studied ions by means of the well-known Sand equation [7]

$$\tau^{1/2} = \frac{nF\pi^{1/2} \cdot D_{\text{ox}}^{1/2} \cdot C_{\text{ox}}^0}{2i}$$

where nF = number of Faraday charges in the electrode reaction,

π = Ludolfian number,

D_{ox} = diffusion coefficient of the oxidized form of the electroactive species ($\text{cm}^2 \text{ s}^{-1}$),

C_{ox}^0 = concentration of the oxidized form of the electroactive species in the bulk of the melt (mol cm^{-3}),

i = current density on the microelectrode (A cm^{-2}).

Experimental

Superpure NaCl, KCl, and PbCl₂, anal. grade, were used in the experiments. For measurements the mixture of constant composition of 49.67 mole % NaCl, 49.67 mole % KCl, and 0.66 mole % PbCl₂ was chosen. This value represents 1×10^{-4} mole PbCl₂ per gram of an equimolar mixture of NaCl and KCl. About 20 g of this mixture was placed into a Pt crucible. For melting and maintaining the system at the given temperature a silit resistance furnace was used. The temperature in the system was measured with a Pt/Pt–Rh(10%) thermocouple and showed a maximum deviation of $\pm 5^\circ\text{C}$. The electrical circuit for registration of the curves “potential–time” consists of an electric

cell, a constant current supply and a recorder of the measured curves. The electrolytic cell contains a Pt disc microelectrode with the area of $5 \times 10^{-3} \text{ cm}^2$, sealed into a pipe of VYCOR glass. The counter electrode was realized with a Pt crucible, standard size No. 3, to which a contact of Pt sheet is welded. This contact is led out of the furnace through the cover. The crucible serves not only as a counter electrode, but at the same time also as an electrolytic cell. The ratio of the areas of both the electrodes is adapted in the way that the current density on the microelectrode is 8000 times greater than that on the counter electrode (crucible), so that this one behaves as a reference electrode without any polarization and practically with constant potential.

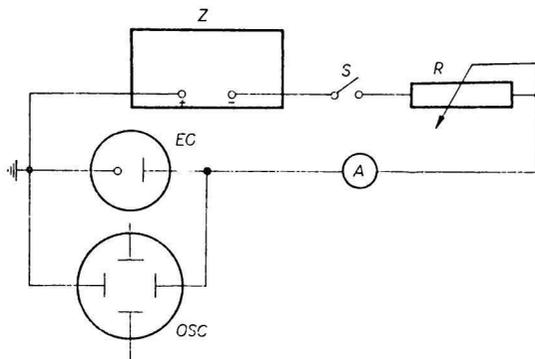


Fig. 1. Circuit diagram used in the described measurements.

Z — d.c. power supply; S — switch; R — resistor divider to 100 Ω ; A — milli-ampmeter; EC — electric cell; OSC — oscilloscope.

For constant current supply a laboratory source TR 9102 ORION EMG, Budapest, with a resistor divider was used, limiting the current pulse magnitude. The response of the system to the current pulse is recorded and gives the mentioned curves "potential—time" on the screen of the oscilloscope for slow processes TESLA OPD 280. A time-mark generator forming a part of this oscilloscope makes possible the time calibration of the curves in 100 ms marks. The same generator may be used also for calibration of the potential axis (Fig. 1).

The temperature dependence of the diffusion coefficient of the Pb(II) ion was studied in the temperature range of 720–880°C. This range is wide enough for the determination of the activation energy of the running process.

Every experimental point of this dependence is the average of 30 parallel measurements. After stabilization of the chosen temperature for each of the measurements a constant current pulse was passed through the cell to evoke an electrode process. The current density of the pulses was in the range of 0.15–0.3 A cm⁻². The potential change of the microelectrode against that of the counter electrode is shown on the screen of the oscilloscope, being there photographically recorded. Upon finishing every measurement, the surface of the Pt microelectrode was mechanically renewed according to *Laitinen* [12].

In order to obtain the transition time values from the curves "potential—time" the method according to *Thallmayer* [17] was applied for their calculation, having been more convenient for our purposes.

Evaluation of the measurements

The experimental study of diffusion conditions in molten salt systems is a great technical problem, since it is difficult to reach a reliable reproducibility of the results [6]. This problem follows from the character of the used method, as well as from the different behaviour of the molten salts. It is known that with increasing temperature also that portion of results increases, which is beyond the allowed dispersion for the method under

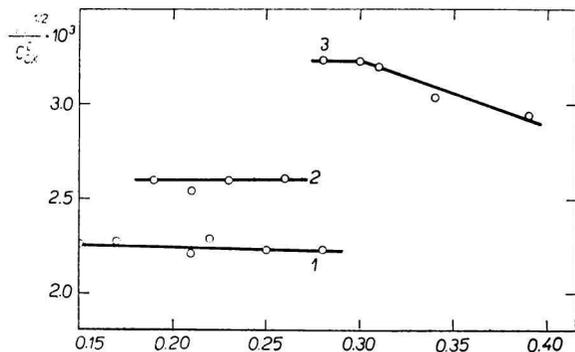


Fig. 2. Dependence of the transition time constant on current density in the system NaCl—KCl—PbCl₂.
1. 720°C; 2. 800°C; 3. 880°C.

consideration. In applying the chronopotentiometric method to the study of diffusivity in systems of aqueous electrolytes the reproducibility is up to 3% [7], while for molten salt systems it is much poorer. Better reproducibility could be attained, however, with increased number of the repeated measurements. Since in the present work the system under consideration lies in the temperature region up to 880°C, we decided for 30 parallels for one point of the temperature dependence. This decision proved right, since the reproducibility did not exceed 2.5%. (Reproducibility here means the ratio of the mean square deviation σ to the average value of the diffusion coefficient \bar{D} in percent.)

The results were evaluated by the least-square method with a computer MINSK 22; the transition time τ was calculated for every measurement as well as the transition time constant $i\tau^{1/2}/C_{ox}^0$ using the Sand equation [7]. The mean square deviation of the

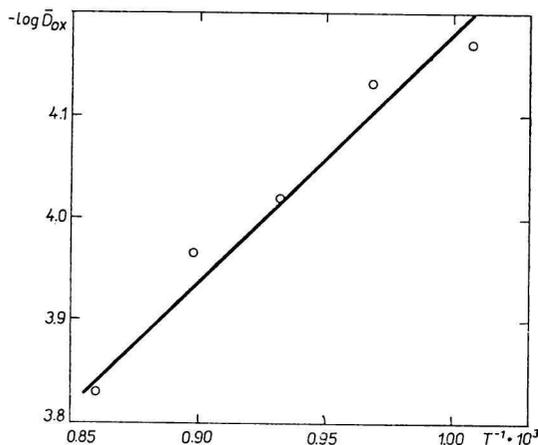


Fig. 3. Dependence of the diffusion coefficient of the Pb(II) ion in the system NaCl—KCl—PbCl₂ on the temperature: 720, 760, 800, 840, and 880°C.

Table 1

Temperature dependence of the diffusion coefficient of the Pb(II) ion

Temperature [°C]	$\bar{D} \cdot 10^5$ [cm ² s ⁻¹]	$-\log \bar{D}$	10 ³ /T	i [A cm ⁻²]	$(i \tau^{1/2}/C_{ox}^0) \cdot 10^{-3}$ [A cm ⁻² s ^{1/2} mol ⁻¹ g]	σ_{\pm}
720	6.8 ± 0.1	4.17	1.007	0.15	2.26	0.01
				0.17	2.27	0.04
				0.21	2.21	0.02
				0.22	2.29	0.03
				0.25	2.23	0.03
				0.28	2.23	0.04
760	7.4 ± 0.1	4.13	0.97	—	—	—
800	9.5 ± 0.2	4.02	0.93	0.19	2.60	0.04
				0.21	2.54	0.04
				0.23	2.60	0.05
				0.26	2.61	0.03
840	10.7 ± 0.2	3.96	0.9	—	—	—
880	14.8 ± 0.4	3.83	0.87	0.28	3.23	0.04
				0.30	3.23	0.08
				0.31	3.2	0.01
				0.35	3.04	0.04
				0.39	2.94	0.09

diffusion coefficient values for one point of the temperature dependence is at the lowest temperature of the range (720°C), *i.e.* 2%; at the highest temperature (880°C) it is 2.5% from the average value of the diffusion coefficient for the given temperature. The mean square deviation for the transition time constant at 720°C is 1.8%, at 800°C 1.5%, and at 880°C 2.5–3% of the average value.

From the results of the measurements the dependence of the transition time constant $i \tau^{1/2}/C_{ox}^0$ on current density may be constructed. This dependence serves as a criterion and allows to determine whether the process is controlled by the diffusion of the studied ion, or is partly influenced by both the rate of the electrode reaction and that of the diffusion [7]. This dependence is shown in Fig. 2 for three temperatures: 720, 800, and 880°C, respectively.

The temperature dependence of the diffusion coefficient of the Pb(II) ion in the considered temperature range is shown in Fig. 3 and in Table 1. From the logarithmic dependence of the diffusion coefficient of the given ion on the inverse temperature, the activation energy of the process was found to be 12.4 ± 1.0 kcal mol⁻¹.

Discussion

The diffusivity of the Pb(II) ion in molten nitrates and halogenides was studied by several authors [2, 5, 8–10, 13–15, 19]. Their results concerning the diffusion coefficient of this ion in the same molten systems are, however, rather contradictory. This is apparently caused by the fact that those authors did not reach the conditions, when the process was controlled solely by diffusion. Our measurements were performed in the open atmosphere and were compared with the results of the authors who had obtained them under the same conditions, namely in the system NaCl–KCl–PbCl₂ and in the open atmosphere. *Delimarskii* [8] did not mention the temperature dependence of the diffusion coefficient of the considered ion in his work, therefore we could not compare

Table 2

Comparison of previously published data of diffusion coefficient and activation energy of diffusion of Pb^{2+} ion with this work

Electrolyte	Ion	Temperature [°C]	$D \cdot 10^5$ [$\text{cm}^2 \text{s}^{-1}$]	E_d [kcal mol ⁻¹]	Reference
$\text{NaNO}_3 - \text{KNO}_3 - \text{Pb}(\text{NO}_3)_2$	Pb^{2+}	264	0.23	—	[10]
$\text{LiCl} - \text{KCl} - \text{PbCl}_2$	Pb^{2+}	380–735	8.9 ± 2	9.5	[17]
$\text{LiCl} - \text{KCl} - \text{PbCl}_2$	Pb^{2+}	450	1.7	—	[9]*
$\text{LiCl} - \text{KCl} - \text{PbCl}_2$	Pb^{2+}	450	2.18	7.9	[12]
$\text{KCl} - \text{PbCl}_2$	Pb^{2+}	Not reported	—	11.54	[14]
$\text{NaCl} - \text{KCl} - \text{PbCl}_2$	Pb^{2+}	700–800	2.40–4.40	12.5	[15]*
$\text{NaCl} - \text{KCl} - \text{PbCl}_2$	Pb^{2+}	695–924	3.05–6.14	3.5	[13]
$\text{NaCl} - \text{KCl} - \text{PbCl}_2$	Pb^{2+}	800	4.3	—	[2]
$\text{NaCl} - \text{KCl} - \text{PbCl}_2$	Pb^{2+}	710	7.0	—	[8]
$\text{NaCl} - \text{KCl} - \text{PbCl}_2$	Pb^{2+}	680–760	6.4	10.2	[19]
$\text{NaCl} - \text{KCl} - \text{PbCl}_2$	Pb^{2+}	720–880	6.80–14.8	12.4 ± 1.0	[18]

* Data obtained by polarography in molten salts.

our results with his in this point. But comparison was possible with the results found by Yanagi [19], who made his measurements in nearly the same temperature range. As it may be seen from Table 2, those authors who measured the diffusion coefficient of the $\text{Pb}(\text{II})$ ion in the same systems of molten halogenides show sufficient agreement in their results. Our value of the activation energy, *i.e.* $12.4 \pm 1.0 \text{ kcal mol}^{-1}$ is somewhat higher than the value $10.2 \text{ kcal mol}^{-1}$, calculated from the activation heat published by Yanagi [19]. According to Jost [20] the activation energy may be calculated by the relation

$$E_d = \Delta H^* + RT,$$

where E_d = activation energy of diffusion,

ΔH^* = activation heat,

T = average temperature of the given range.

As Fig. 2 shows, in our measurements we reached the state, when the diffusion kinetics had the controlling influence, though at 720°C also another type of kinetics was observed. At 880°C a break appeared on the straight line at the current density above 0.3 A cm^{-2} . This is probably due to exceeding the limit of current densities, below which the transport of the ions is still provided solely by diffusion, while beyond it, it also may be caused by natural convection. This influence is apparently supported also by higher temperature in the system leading to greater effects of the thermic drops and thereby to those caused by differences in the melt density in different points of its volume.

A confrontation of the data of phase diagrams, density, viscosity, electric conductivity, and transference numbers of the ions in the molten system $\text{NaCl} - \text{KCl} - \text{PbCl}_2$ [11, 16] evidently shows that this is a complicated system probably containing the complex anions PbCl_4^{2-} and PbCl_3^- , respectively, which are the decomposition products of still more complicated unstable anions or structure units. This conception is suggested by several authors [1, 4] and some of them do not exclude even the presence of the auto-complex ions PbCl^+ .

The ions Pb^{2+} or PbCl^+ , respectively, on the one hand, and the complicated complex

anions as PbCl_3^- , PbCl_4^{2-} , and Pb_2Cl_5^- on the other hand, are in the molten salt apparently in equilibrium. The exhaustion of the positive Pb-containing particles by their discharge on the cathode leads to the disintegration of these complicated complex ions, thus evoking the generation of new Pb^{2+} ions.

Since it may be expected that the rate of disintegration of these complexes under the given conditions is comparable to the rate of diffusion, we may explain the relatively high value of the activation energy [3].

Therefore the process under discussion appears to be limited not only by the rate of diffusion, but also by that of the disintegration of the mentioned complex ions or of some still unknown type of solvated ions.

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