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Yu. M. Ryabukhin and E. A. Ukshe

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Abstract

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Yu. M. Ryabukhin and E. A. Ukshe

DIFFUSION COEFFICIENTS OF LEAD IN MOLTEN CHLORIDES

(Presented by Academician A. N. Frumkin, 11 IV 1962)

Measurements of the diffusion coefficients of ions in molten salts, besides their general theoretical significance, are extremely necessary for solving a number of problems in applied electrochemistry and metallurgy. It is natural that in recent years considerable attention has begun to be paid to this question. The methods for determining diffusion coefficients in molten salts that have found practical application reduce either to the use of radioactive isotopes or to the measurement of certain electrochemical parameters. The radioactive-isotope method was applied by Perkins et al. (1) to determine the self-diffusion coefficients of Pb^{2+} and Cl^- in $PbCl_2$. Hughes and Egan (2) determined the diffusion coefficients of Pb^{2+} and Cd^{2+} in KCl–LiCl by the polarographic method on a dropping bismuth electrode. Stein (3) measured the diffusion coefficients of Pb^{2+} by oscillographic polarography. In work (4), the diffusion coefficient of Pb^{2+} in KCl–NaCl was determined from data on the faradaic impedance. A number of investigators (5, 6) used the chronopotentiometric method to determine the diffusion coefficients of lead in melts.

The circumstance that electrochemical methods for measuring diffusion coefficients in melts had until recently still only been under development did not make it possible to obtain systematic data on the dependence of diffusion coefficients on temperature and the nature of the electrolyte. In addition, the data of individual investigators are often poorly comparable because of different experimental conditions, as illustrated by Table 1, which gives a summary of the diffusion coefficients of Pb^{2+} in chloride melts.

Table 1

Diffusion coefficients of Pb^{2+} in chloride melts (cm^2/sec)

Fig. 1

Figure 1: Fig. 1

Electrolyte	T, °C	$\Delta \cdot 10^5$	Ref.	Electrolyte	T, °C	$\Delta \cdot 10^5$	Ref.
NaCl–KCl	701	2.4	(3)	LiCl–KCl	450	1.70	(2)
NaCl–KCl	746	3.1	(3)	LiCl–KCl	450	2.18	(5)
NaCl–KCl	777	3.8	(3)	$PbCl_2$	510	1.00	(1)
NaCl–KCl	807	4.4	(3)	$PbCl_2$	546	1.13	(1)
NaCl–KCl	710	7.0	(6)	$PbCl_2$	566	1.37	(1)
NaCl–KCl	720	4.6	(4)				

Experimental data

<table>
<tr><th>Electrolyte</th><th>T, °C</th><th>Δ · 10⁵</th><th>Ref.</th><th>Electrolyte</th><th>T, °C</th><th>Δ · 10⁵</th><th>Ref.</th></tr>
<tr><td>NaCl</td><td>1003</td><td>7.40$±0.26|—|*NaCl—KCl*|924|6.14±0.63|||*NaCl*|941|6.14±0.21|—|*NaCl—KCl*|880|5.60±</td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

We used the chronopotentiometric method, whose theoretical foundations have been described in sufficient detail in the literature (5,6). To record the potential-time curves, an MPO-2 loop oscillograph with a direct-current electronic amplifier at the input was used. The measurements were carried out in an argon atmosphere. A rectangular polished platinum plate with an area of about 1 cm^2 was used as the working electrode. The anode and reference electrode was molten lead, placed in a quartz test tube connected to the main body of the melt by a capillary. In the work, salts of "chemically pure" grade, preliminarily remelted in vacuum, were used.

Fig. 1. Dependence of $\lg \Delta$ on $1/T$ for the Pb^{2+} ion in NaCl (A) (concentration of $PbCl_2$, 0.1-0.2 mol.%). B—the same in an equimolar NaCl—KCl mixture (concentration of $PbCl_2$, 0.12-0.2 mol.%). C—the same in KCl (concentration of $PbCl_2$, 0.13-0.24 mol.%). a—our data; b—calculated from equation (2); c—data of (8).

The measurement results are presented in Table 1, with the data for each temperature being the average of 3-5 measurements.

The graphs plotted in the coordinates $\lg \Delta - 1/T$ (Fig. 1) testify to the validity of Frenkel' s equation (7).

$$\Delta = \Delta_0 \cdot e^{-\frac{W}{RT}}. \qquad (1)$$

Calculation of the activation energies for diffusion of the lead ion in KCl, NaCl, and an equimolar KCl—NaCl mixture gives values of 2120, 1670, and 1410 cal/mol, respectively. Bockris and co-workers ([8]) established that the relation between the self-diffusion coefficients of the Na^+ ion and the Cl^- ion and the viscosity of the molten salt obeys the Stokes-Einstein equation:

$$\Delta = \frac{KT}{6\pi\eta r}, \qquad (2)$$

where η is the viscosity, r is the ionic radius according to Goldschmidt. An analogous regularity, as is seen from Fig. 1, holds for the Pb^{2+} ion in molten NaCl. For the calculation, viscosity values for the chlorides from ([9]) were used. However, apparently, the applicability of the Stokes-Einstein equation to the diffusion of ions in molten salts is limited to systems in which complex formation is absent, since already in the case of the KCl—NaCl melt, especially in pure KCl, there are significant deviations from equation (2)*.

* The possibility of formation of complex ions in $PbCl_2$—KCl melts was shown by a number of authors on the basis of data on surface tension, electrical conductivity, etc. ([8]).

From the work of Delahay and Berzins (10) it follows that, in the presence of a complex whose dissociation precedes the electrochemical reaction, the apparent value of the diffusion coefficient at sufficiently high current densities is related to the true value by the relation

$$\Delta_d = \Delta \cdot \left(1 + \frac{1}{K}\right)^2, \qquad (3)$$

where K is the dissociation constant of the complex.

Assuming that the true diffusion coefficient (Δ_d) can be calculated from equation (1), the dissociation constant of the lead complex in the melt can be determined from equation (3). The results of calculations of the dissociation constants of the complex in the $PbCl_2$—KCl melt, obtained using Fossit' s data on the viscosity of KCl (11), are given below.

T-ra, °C	965	942	914	863	833	811
K	10.0 ± 1.4	9.1 ± 1.4	8.3 ± 1.3	6.2 ± 1.3	5.5 ± 0.9	5.6 ± 1.1

The obtained values of the dissociation constants are, in order of magnitude, close to the data of other authors (12) for lead chloride complexes in nitrate melts.

Berezniki Branch
of the All-Union Scientific Research
Aluminum-Magnesium Institute

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