Self-Diffusion in Molten Lead Bromide

C.-A. Sjöblom and J. Andersson

Department of Physics, Chalmers University of Technology, Gothenburg, Sweden

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The self-diffusion coefficients of both ions in molten $PbBr_2$ have been measured with a modification of the porous-frit technique [1-3]. The results can be described with Arrhenius relations:

$$D_{Pb} = 7.4 \times 10^{-4} \exp(-6500 \pm 900)/R\,T \qquad (380-540\ ^\circ C),$$
$$D_{Br} = 8.3 \times 10^{-4} \exp(-6100 \pm 700)/R\,T \qquad (380-555\ ^\circ C).$$

D is expressed in $cm^2\,s^{-1}$, R in $cal \cdot mole^{-1}\,degree^{-1}$ and T in degrees Kelvin. The relative merits of different experimental techniques are discussed and a comparison between the (experimental) external transport number and the corresponding calculated quantity using Laity's "new formalism" is made.

Relatively few diffusion studies have been made on high temperature liquids such as pure molten salts due to experimental difficulties. This is very unfortunate since there is a great need for more accurate data as an aid in developing a theory for transport in ionic melts. Finding a way to correlate the diffusion mobilities and electrical mobilities of the ions in a pure molten salt would be a step in this direction. The proper definition of ionic mobility in a pure molten salt is of course a problem of its own but it has been found [4, 5] that the external transference numbers [6] in conjunction with the so-called "new formalism" developed by Laity [7] can be used with remarkable accuracy to correlate diffusion and electrical mobility in all monovalent salts studied up till now [4-7], and also one divalent salt $ZnBr_2$[4]. $PbCl_2$ deviates from this pattern having a transference number of only 0.23 for the lead ion at 560 °C. Since the corresponding transference number for the lead ion in $PbBr_2$ is 0.35 it was considered valuable to measure the self-diffusion coefficients of both ions in lead bromide in order to see if the two lead salts behave similarly in this respect. The porous-frit technique [1-3] is particularly suitable for this work since one of the ions (Br^-) has radioactive isotopes with short half-lives only.

Experimental

BDH laboratory reagent lead bromide was further purified by recrystallization from hot 0.01 M HBr solution and dried at 150 °C for more than 48 hours. $PbBr_2{}^{82}$ was obtained from Aktiebolaget Atomenergi, Studsvik, and $Pb^{210}(NO_3)_2$ from NEN, Boston, Massachusetts.

D_{Pb} and D_{Br} were determined in separate runs, using different techniques for the radio-analysis. The analysis of Pb^{210} was similar to the procedure used by Angell and Tomlinson [8] who utilized the strong β-radiation of the daughter Bi^{210} and counted the samples in a liquid Geiger counter. The samples were counted about three weeks after the runs when the initially pure Pb^{210} sample had come to equilibrium with the Bi daughter. The amount of lead in each sample was determined electrolytically as peroxide [9] and the specific activity of each sample was calculated.

The analysis of $PbBr_2{}^{82}$ was performed in an entirely different way. It was possible to measure the total γ-activity of the cell with a scintillation counter before and after each run, since Pyrex glass frits with a thickness of only 2 mm were used. The frit was allowed to cool down and was mounted behind a circular lead diaphragm with the flat surfaces of the frit parallel to the nearest face of the scintillation crystal. The distance between the frit and the center of the crystal was about 15 cm and the frit could be replaced with an accuracy of better than ± 0.3 mm. The error introduced by this procedure was thus negligible. The cells were used up to three times in the D_{Br}-experiments since careful tests showed that the frit was unaffected by lead bromide melting and solidifying inside it.

The experimental set-up has been described elsewhere [2]. The furnace was blanketed with argon gas in order to minimize the effect of water vapor in the atmosphere. Commercial Pyrex glass frits, JOBLING 3610 /62,20 mm POR 4 were used. The effective length of each frit was determined by the gravimetric diffusion

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technique[10] developed by Wall and coworkers. The present procedure is desribed by Sjöblom[11], the only difference being that 0.5-m KCl solution is diffusing out into 0.075-m KCl solution. The average frit thickness was 2.2 mm and the corresponding effective thickness about 2.7 mm. The labyrinth factor (the correction factor with which the experimental diffusion coefficient is to be multiplied) ranged from 1.3 to 1.9[12].

The container for the radio-active salt was filled with salt for several experiments and the frits were inserted and removed through a port in the furnace top without changing the furnace temperature. The experiments could thus be performed in a rapid succession when the temperature had reached equilibrium at the chosen value. The temperature was measured with a Croydon potentiometer type P 3 using a calibrated thermocouple and it was constant to better than ±0.5 °C. When a cell was re-used it was already partly filled with active salt. Before next experiment it was replaced into the radioactive melt for a time long enough to allow the activity to be evenly distributed through the frit again (about 10 times the actual diffusion time was considered adequate). The diffusion times were very short (200 – 350 seconds) due to the thin frits.

Results and Discussion

The results are given in Fig. 1. They can be summarized by least-squares fitting in two Arrhenius equations (all stated errors are standard deviations):

$$D_{\mathrm{Pb}} = 7.4 \times 10^{-4} \exp(-6500 \pm 900)/R\,T \quad (380-540\,^{\circ}),$$

$$D_{\mathrm{Br}} = 8.3 \times 10^{-4} \exp(-6100 \pm 700)/R\,T \quad (380-555\,^{\circ}\mathrm{C}).$$

The standard errors of estimate in the ${}^{e}\log(D \times 10^{6})$ vs. $10^{3}/T$ plots are about 4.5%.

The "activation energies"[13] for diffusion of cations and anions in lead bromide are thus equal within the experimental accuracy. This fact is in agreement with the results for all investigated molten salts. Both self-diffusion coefficients and activation energies are very close to the values for lead chloride obtained by Perkins, Escue, Lamb, and Wimberley[14] and independently by Angell and Tomlinson[8] (and the values of D^{+} are smaller than those of D^{-} at corresponding temperatures for both lead salts and also for zinc bromide[3]).

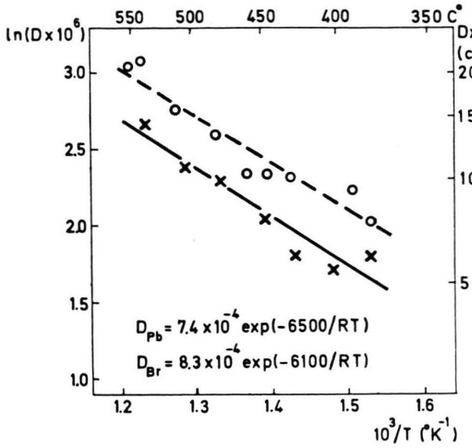

Fig. 1. The self-diffusion coefficient of the cation, D_{Pb}, (×), and the anion, D_{Br}, (○) in molten PbBr_2. The lines correspond to the equations quoted in the figure and the text.

The self-diffusion coefficients and the equivalent conductance can be used to calculate the "external transport number"[5, 6] for the salt if the "new formalism"

$$t_{+} = \tfrac{1}{2}(\Lambda/F^{2} + z_{+}\,D_{+}/R\,T - z_{-}\,D_{-}/R\,T)/(\Lambda/F^{2})$$

by Laity[7] is assumed to be valid. The result of a calculation for lead bromide is given in Table 1. It can be seen that neither the magnitude nor the temperature dependence of the transport number can be correctly described by the theoretical equation. (The equation gives good agreement in both these respects for zinc bromide[4].) A more comprehensive comparison between experimental and theoretical transport numbers is made in Ref. [4].

In this work an attempt has been made to utilize the strong sides of the porous-frit method without seriously increasing its weaknesses. As noted elsewhere[8] it is best suited for applications under difficult experimental conditions where the potentially higher accuracy of the ordinary capillary method (developed by Anderson and Saddington[15, 8]) cannot be realized. When the isotope Br^{82} is used a short diffusion time is important particularly if a whole series of experiments is to be performed. In the present form the porous-frit technique can be used with isotopes having a half-life shorter than

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Temperature (°C)	External transport number $t_{Pb^{++}}$ Experimental [5]	Theoretical
400	0.38	0.61
450	0.37	0.62
500	0.36	0.62
550	0.34	0.64

Table 1. The external transport number of the lead ion in molten lead bromide as a function of temperature. The experimental values are measured by Laity and Sjöblom [5] and the theoretical values are calculated according to the Eqs. (4.5) and (2.2) in Ref. [6] using density data by Lorenz, Frei and Jabs [16] and by Boardman, Dorman and Heymann [17] and conductivity data by Harrap and Heymann [18].

one hour for β-active isotopes (provided the chemical analysis is reasonably esay) and shorter than 30 minutes for γ-active isotopes. This fact represents an important improvement over conventional capillary techniques using diffusion times of the order of 20 – 70 hours. This advantage is of course obtained at the expense of a certain decrease in accuracy. The gravimetric calibration of the frits has a spread of $\pm 3\%$ (see for instance Ref. [11]) due to the minute weight changes involved in the process. The diffusion times are very short but they can be determined to better than 2% since the manipulation of the cell in the furnace is very simple. The immersion errors can be minimized for the same reason. The flow rate of salt past the frit was 5 mm/sec (corresponding to a stirring speed of 20 rev/min). Thus there is no reason to believe that the end-errors are more serious in this technique (although they might be in part responsible for the somewhat higher spread in the data compared to the conventional capillary technique).

As far as the technique is concerned it can be concluded that it has been developed into a method capable of measuring diffusion coefficients with reasonably good precision and well suited for difficult experimental conditions. It is also very easy and straightforward to work with and requires no complicated auxiliary apparatus. No accuracy is sacrificed if the total radio-activity of the frit before and after the run is measured with a scintillation counter instead of determining the specific activity of liquid samples of the active melts. Careful tests show that the effective length of the frits is unaffected by lead bromide melting and solidifying inside the frits (this is of course a property of this particular salt since an attempt to do the same thing in zinc bromide or silver nitrate would certainly fail).

The experimental external transport number of the Pb^{++} ion in molten lead bromide is 0.36 at 500 °C while the "theoretical" value is 0.62. It is probable that the doubly charged Pb^{++}-ion is preferentially bound to the glass-salt interface in the porous-plug transport number experiment. This view is supported by the fact that the result of such an experiment can be changed by applying an external potential to the frit [5]. The flow-corrected formalism works well for monovalent salts and also for a divalent salt such as zinc bromide [4] which is considered as having a complex structure in the melt. Cadmium chloride has a position in between in this respect being a divalent salt but partially "associated" to $CdCl^+$-ions. Thus the experimental and theoretical values of the external transference numbers can be expected to agree reasonably well and this is also the case.

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