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High temperature voltammetry on gold electrodes in halide melts

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The voltammetric behaviour of Fe^{2+}, Mn^{2+} and Cr^{2+} in molten NaCl, NaF and Na_3AlF_6 has been studied using a gold wire as the working electrode. The metal ions studied behaved reversibly and the reduction product dissolved into the gold substrate. Diffusion coefficients were calculated from the voltammetric peak currents.

1. Introduction

Halide melts are commonly employed in high temperature electro-winning of metals such as aluminium and they are also of interest in coating and surface treatment technologies [1–3]. Relatively little information exists in the literature on the electrochemical behaviour of trace impurities present in such melts [4]. In a previous paper [5] it was suggested that the solid gold electrode is a suitable substrate for voltammetric investigations of low concentration ionic species dissolved in melts. The purpose of the present study is to use voltammetry on solid gold electrodes to measure the diffusion coefficients of Fe^{2+}, Mn^{2+} and Cr^{2+} at high temperatures (800–1000° C), in chloride and fluoride melts of industrial interest.

2. Experimental procedure

The experimental apparatus is shown in Fig. 1. A silica container (5) of 14 cm inner diameter and 55 cm length protected inside by a nickel sheath (4) was placed in a tubular 5 kW furnace (Varian type 1097) whose temperature was controlled to ± 2° C by a Eurotherm power control unit. The furnace assembly could be moved up or down while the water cooled brass flange (12) remains in a fixed position. The flange holds the electrodes, the optical observation system (10) and the crucible holder (8). Up to four pyrolytic boron nitride crucibles could be placed on the holder. They were successively brought into position by rotating the holder. Nickel heat shields were used to minimize temperature gradients in the vertical plane. The cell assembly is vacuum tight and can be filled with inert gas. The temperature of the melt is measured with a Pt/Pt–Rh thermocouple.

The working electrode was a gold wire (1 mm diameter) inserted in a silicon nitride tube (4 mm o.d., 2 mm i.d.). A Teflon fitting was placed at the top of the tube to provide a gas-tight connection. The tube was then slipped into a larger alumina tube (8 mm o.d., 5 mm i.d.) fixed on the top flange, so that the working electrode could be withdrawn during an experiment and salt pellets could be introduced into the melt prior to measurements. The immersed length of the electrode was limited to 1 cm by means of a pyrolytic boron nitride ring. The wetted electrode area was 0.32 ± 0.01 cm^2.

The counter-electrode was a 1 mm tungsten wire immersed in the melt to a depth of about 20 mm.

Most experiments were performed with a reference electrode made of a nickel wire immersed in the melt. The potential of this electrode was stable to ± 10 mV during the course of a run but its potential depended on melt composition. In some experiments the Inconel tube of the thermocouple immersed in the pure solvent was shielded from the electrolyte by a hot-pressed boron nitride tube and used as reference.

All chemicals employed were analytical grade except for the cryolite which was hand-picked natural Greenland cryolite (Kryolitselskabet,

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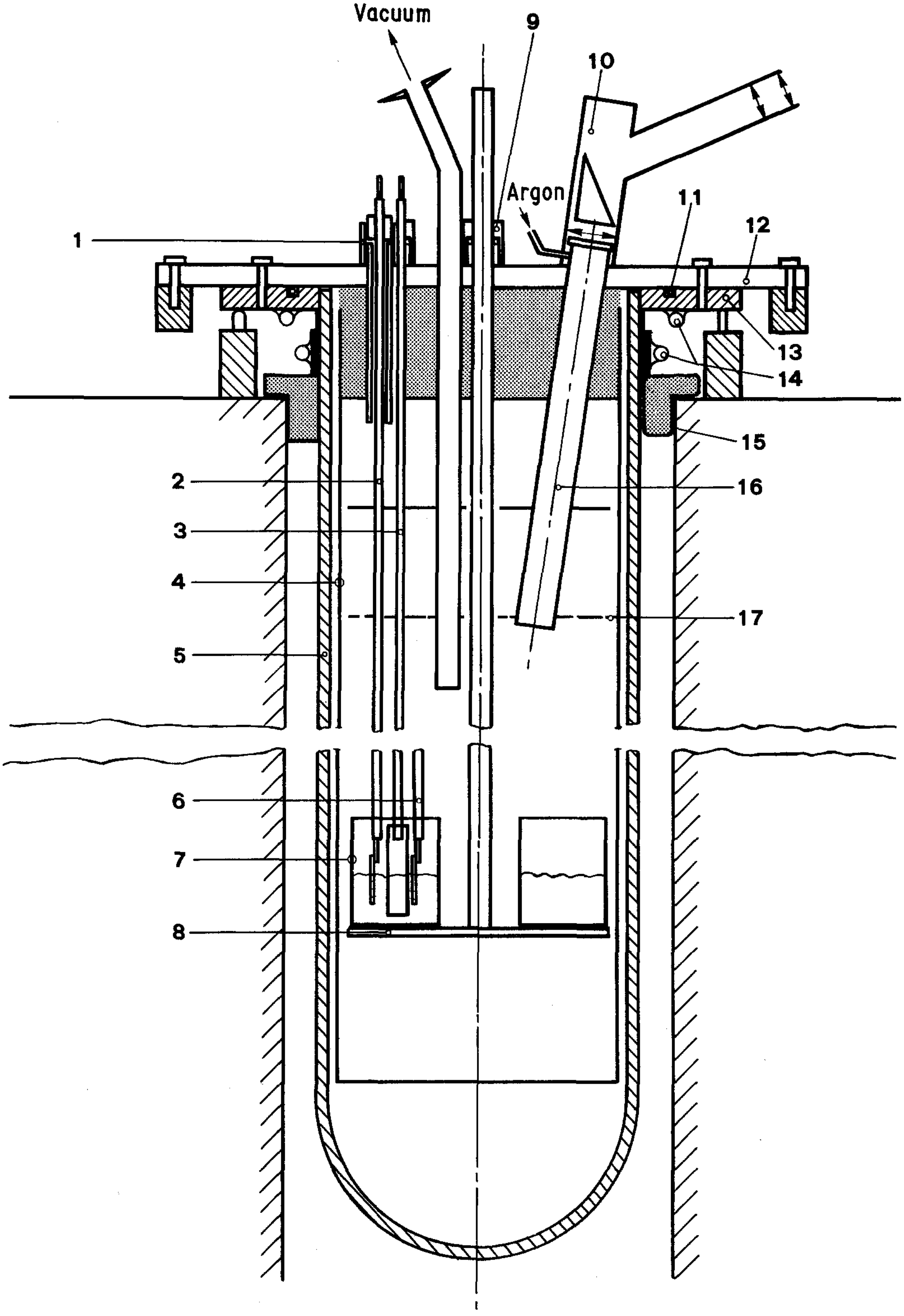

Fig. 1. Furnace assembly. 1. Fitting, 2. working electrode, 3. reference electrode, 4. nickel sheath, 5. silica container, 6. counter-electrode, 7. boron nitride crucible, 8. stainless steel holder, 9. fitting, 10. optical observation system, 11. O-ring, 12. brass top flange, 13. brass fixture, 14. water cooling, 15. insulating wool, 16. stainless steel tube, 17. nickel reflector plates.

Øresund DK). The heavy metal ions Mn^{2+}, Fe^{2+} and Cr^{2+} were added as fluorides or chlorides pressed into pellets. Voltammograms of the pure melts were used to ascertain that no significant cross-contamination occurred between cells during a series of experiments. A potentiostat (Amel 551) with a function generator (Amel 566) was employed. Voltammograms were recorded with a digital oscilloscope (Nicolet Explorer II).

In a typical experiment aimed at the determination of the diffusion coefficient, a voltammogram was first determined in the pure solvent to estimate the magnitude of residual currents for various scan rates (normally 1, 2, 5, 10 and 20 $V s^{-1}$). A predetermined amount of metal salt was then introduced in the form of pellets. After the voltammograms had been recorded at various scan rates, an additional amount of metal salt was introduced and the voltammetric measurements were repeated. For each scan rate, the difference in peak current corresponding to the concentration increase was determined and plotted as a function of the square-root of the scan rate. From the slope of several curves, typically 3 or 4, the average value of the diffusion coefficient was calculated as described below. The concentration range studied extended from 5×10^{-6} mol cm^{-3} to 2×10^{-5} mol cm^{-3}. Most solutions employed were stable for the duration of an experiment. However, in the case of Fe^{2+} in cryolite at 1000° C, a slow decrease in concentration was observed. For this reason, measurements were taken at different times and extrapolated to the time of introduction of the pellets.

3. Results and discussion

Figures 2 and 3 show voltammograms for Fe^{2+} and Mn^{2+}, respectively, in cryolite at 1015° C. An Inconel reference electrode was employed in this case. The shape of the voltammograms corresponds to that predicted by theory for a reversible electrode reaction involving two dissolved species [6]. As a consequence, the peak potential is independent of the scan rate, and the reoxidation current referred to the cathodic sweep baseline is approximately equal to the reduction current. According to the theory developed by Nicholson and Shain [6], the peak current for a reversible reduction–oxidation process at a temperature T is given by

$$I_p = 4.64 \times 10^6 n^{3/2} T^{-1/2} A C_o D_o^{1/2} v^{1/2}. \quad (1)$$

Here I_p is the peak current (A), n is the charge number, T the absolute temperature, A the electrode area (cm^2), C_o the bulk concentration of the reacting species (mol cm^{-3}), D_o the diffusion coefficient (cm^2 s^{-1}) and v the scan rate (V s^{-1}).

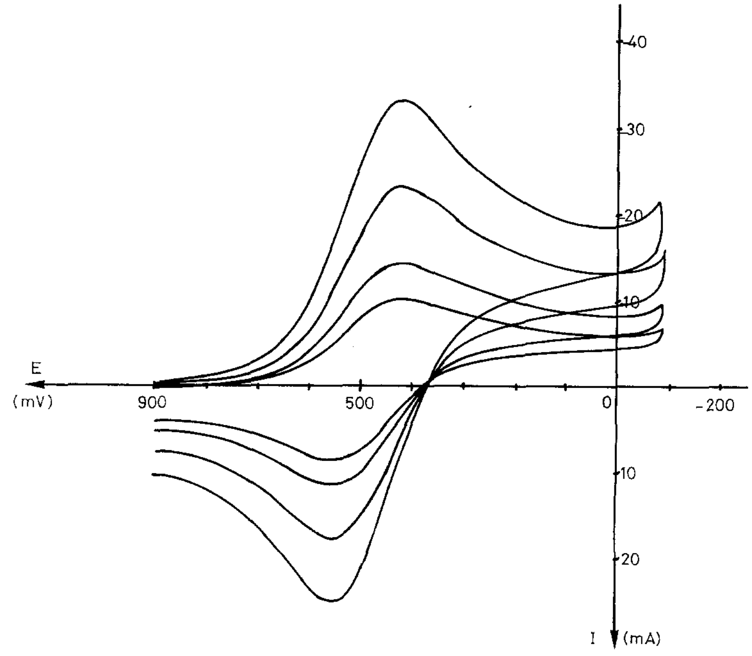

Fig. 2. Voltammogram of cryolite containing 1.58×10^{-5} mol cm^{-3} of FeF_2 at 1015° C. Working electrode: gold wire (area: 0.32 cm^2). Reference electrode: Inconel/cryolite in a hot-pressed boron nitride container. Scanning rates : 1, 2, 5, 10 V s^{-1}.

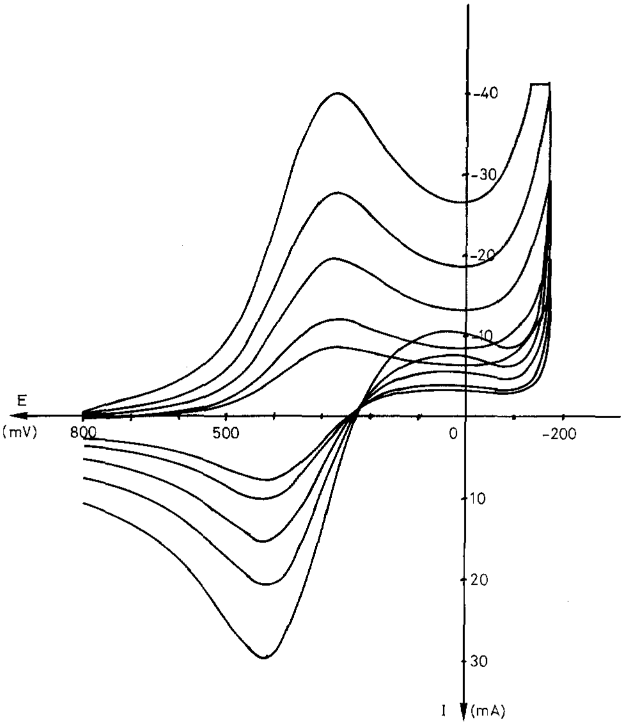

Fig. 3. Voltammogram of cryolite containing 1.146×10^{-5} mol cm^{-3} of MnF_2 at 1015° C. Working electrode: gold wire (area: 0.32 cm^2). Reference electrode: Inconel/cryolite in a hot-pressed boron nitride container. Scanning rates: 1, 2. 5. 10. 20 V s^{-1}.

The dimensionless potential corresponding to the peak current is

$$\phi_p = \frac{nF}{RT}(E_p - E_{1/2}) = -1.109 \qquad (2)$$

Here E_p is the peak potential and $E_{1/2}$ the polarographic halfwave potential which is defined by

$$E_{1/2} = E^0 + \frac{RT}{nF}\ln\left(\frac{D_R}{D_o}\right)^{1/2}. \qquad (3)$$

The dimensionless potential corresponding to the reoxidation peak is given by

$$\phi_{PR} = \frac{nF}{RT}(E_{PR} - E_{1/2}) = 1.131. \qquad (4)$$

The experimentally determined value of $E_{PR} - E_p$ in Figs. 2 and 3 is approximately 0.13 V, in close agreement with the theoretical value of 0.125 V calculated from Equations 2 and 3 for $T = 1288$ K, assuming $n = 2$.

The reduction–oxidation waves observed in chloride melts for Fe^{2+}, Mn^{2+} and Cr^{2+} ions are all similar to those shown in Figs. 2 and 3, i.e., they are reversible. On the other hand, reduction of Cr^{2+} in fluoride melts exhibited a more complex behaviour which will not be discussed any further here.

The shape of the voltammograms of Figs. 2 and 3 corresponding to reversible charge transfer involving two dissolved species suggests that the deposited metal dissolves readily into the gold substrate. To test this hypothesis, gold wire electrodes were cathodically polarized at a constant potential for 10 min at 1015° C in cryolite melts containing Mn^{2+} or Fe^{2+} ions. A charge of 16 C cm^{-2} was passed. After removal from the melt a thin layer of nickel was cathodically deposited on them from an aqueous solution. They were embedded in a casting resin and cut across the exposed electrode surface. After mechanical polishing, the samples were analysed by X-ray microprobe. Figure 4 shows the concentration depth profiles of Fe and Mn. The data confirm that the deposited metal diffuses into the substrate. The diffusion coefficient of Fe in Au at 1015° C reported in the literature is 7.3×10^{-9} cm^2 s^{-1} [7]. The value for Mn is probably of the same order of magnitude. To estimate whether the observed profile corresponds to this value, one can evaluate the thickness of the Fe or Mn diffusion layer and compare it to that estimated theoretically. The latter is approximately given by

$$\delta \approx (\pi D t)^{1/2}. \qquad (6)$$

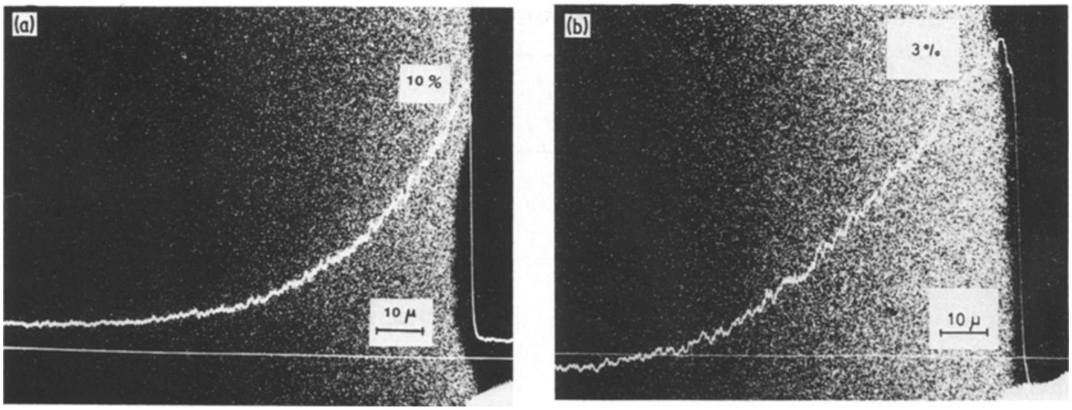

Fig. 4. Microprobe analysis on a cross-section of a gold electrode submitted to a prolonged cathodic polarization at 1015° C in cryolite melts containing Fe^{2+} or Mn^{2+}. (a) Concentration profile of Fe (white curve) as a function of the distance to the surface. (b) Concentration profile of Mn as a function of the distance to the surface.

Setting $t = 480\,s, D = 7.3 \times 10^{-9}\,cm^2\,s^{-1}$, one obtains $\delta \approx 33\,\mu m$. The experimental value obtained by linearly extrapolating the gradient at the electrode surface to the bulk concentration is $\delta \approx 25\,\mu m$ for iron and $\delta \approx 60\,\mu m$ for Mn. It may therefore be concluded that the order of magnitude of observed diffusion rates of Fe and Mn in the gold electrode is in agreement with the literature values.

According to Equation 1 the measured peak current in the cathodic sweep is proportional to the square-root of the scan rate. This is borne out by experiment as illustrated in Fig. 5 which shows the reduced peak current difference $\Delta I/\Delta C$ for two Fe^{2+} and two Mn^{2+} concentrations in cryolite melt as a function of $v^{1/2}$. Average values of the diffusion coefficients calculated from the slope of 3 or 4 of these curves are given in Table 1 for various melts and temperatures. It follows that at a temperature of 1015° C, the diffusion coefficients of Fe^{2+} and Mn^{2+} in NaF and Na_3AlF_6 are about equal while their value in NaCl is roughly twice as high. The observed difference between fluoride and chloride melts may in part be due to the different viscosities.

In aqueous solution, the Stokes–Einstein equation (Equation 6) is widely used to relate the diffusion coefficient, D_i, of minor ionic species to viscosity [8].

$$D_i = \frac{kT}{a\eta r_i} \qquad (6)$$

Here r_i is the effective ionic radius, η is the viscosity and a is a constant which for spherical particles has a value of 6π. The transposition of the Stokes–Einstein equation to the description of diffusion processes in molten salts is complicated by ionic interactions and complex formation,

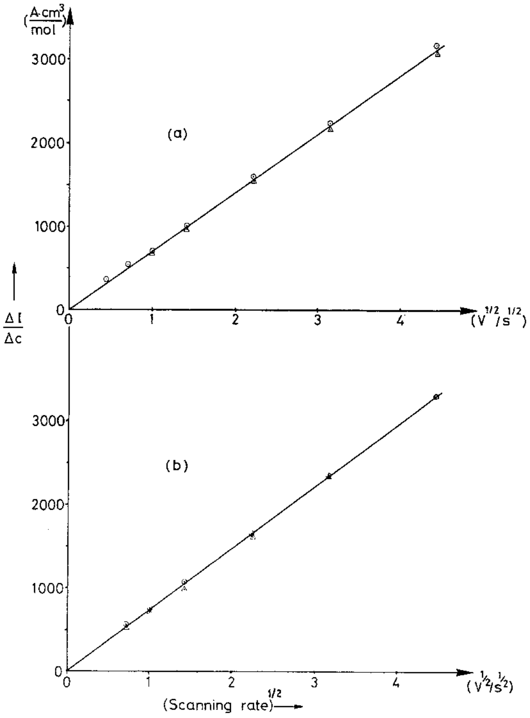

Fig. 5. Variation of peak current for Fe^{2+} and Mn^{2+} reduction with scan rate; cryolite 1015° C; $A = 0.32\,cm^2$. (a) Introduced Mn^{2+} concentration: (⊙): 1.33×10^{-5} mol cm^{-3}, (⚠): $1.26 \times 10^{-5}\,mol\,cm^{-3}$. (b) Introduced Fe^{2+} concentration: (⊙): $1.37 \times 10^{-5}\,mol\,cm^{-3}$, (⚠): $9.55 \times 10^{-6}\,mol\,cm^{-3}$.

Table 1. Values of D × 10^5 *($cm^2 s^{-1}$) for different cations in some electrolytes*

Cation	*NaCl*			*NaF*	*Na_3AlF_6*
	815°C	*915°C*	*1015°C*	*1015° C*	*1015°C*
Fe^{2+}	5.3 ± 0.3	6.7 ± 0.4	8.3 ± 0.6	4.6 ± 0.8	4.0 ± 0.4
Mn^{2+}	4.5 ± 0.2	6.4 ± 0.4	7.8 ± 0.4	4.1 ± 0.8	3.8 ± 0.4
Cr^{2+}	3.3 ± 0.4	5.1 ± 0.5	6.3 ± 0.6	–	–

a review of the early literature on the subject having been given by Reddy [9]. Systematic studies of diffusion of alkali metal cations in chloride [10] and nitrate media [11] gave a good correlation between diffusion coefficients and viscosity. More recently Ejima *et al.* [12] found a linear correlation between the value of the diffusion coefficient of Ag^+ and $kT/\eta r_i$. However, to fully describe the observed diffusion coefficients the authors had to introduce an additional constant into the Stokes–Einstein equation.

In the present study, the validity of the Stokes–Einstein equation can be tested by calculating the $\eta \times D$ product which should be constant for a given diffusing praticle at constant temperature.

From literature data [1, 4], the values of melt viscosities are 1.46, 2.4 and 0.7 cp for NaF, Na_3AlF_6 and NaCl, respectively. Qualitatively, the higher D values observed in NaCl are consistent with the lower viscosity of this electrolyte compared with NaF and Na_3AlF_6 melts.

A good agreement is not obtained with a cryolite melt for which the values of the $\eta \times D$ product are substantially higher than those obtained for NaF and NaCl. This may indicate that the effective ion diameter of the diffusing particle is smaller in cryolite than in the other melts.

The influence of temperature on the measured diffusion coefficients in chloride melts is shown in Fig. 6. Within experimental accuracy the data can be represented by an Arrhenius-type plot. The activation energies calculated by regression analysis are 26.0 ± 0.4 kJ mol^{-1} for Fe^{2+}, 31.8 ± 3.4 kJ mol^{-1} for Mn^{2+} and 36.9 ± 5.9 kJ mol^{-1} for Cr^{2+}. These values are somewhat smaller than the activation energy for viscosity which for NaCl is given by Janz [4] as 37.7 kJ mol^{-1}. Arrhenius-type behaviour for viscosity in NaF–AlF_3 melts has recently been found by Brockner *et al.* [13] and seems to be characteristic for high temperature fused salt melts. On the other hand significant deviations from Arrhenius behaviour has earlier been reported for low temperature melts [14, 15].

4. Conclusions

An experimental apparatus is described which allows for the simultaneous use of up to four crucibles, optical observation of the working

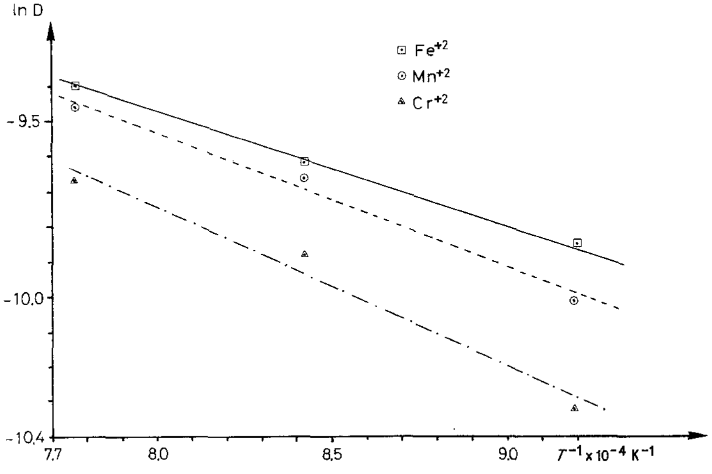

Fig. 6. Relationship between experimental diffusion coefficients and temperature for Mn^{2+}, Fe^{2+} and Cr^{2+} in NaCl.

Table 2. The calculated values of the $\eta \times D$ *product for* Fe^{2+} *and* Mn^{2+} *ions at 1015° C* ($\times 10^{-7} g\,cm^{-2}$)

Ion	*NaCl*	*NaF*	Na_3AlF_6
Fe^{2+}	5.8	6.7	9.6
Mn^{2+}	5.5	6.0	9.1

electrode and *in situ* introduction of salt pellets under an inert gas atmosphere. Diffusion coefficients of Fe^{2+}, Mn^{2+} and Cr^{2+} have been measured in high temperature chloride and fluoride melts using voltammetry. Gold has been shown to be a suitable electrode material for such a study because the deposited metals dissolve easily and diffuse into the cathode. The resulting voltammograms correspond to reversible charge transfer involving two dissolved species.

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