THE DETERMINATION OF TRANSPORT QUANTITIES IN MOLTEN SALTS WITH THIN LAYER ELECTROPHORESIS AND DIFFUSION ON FRITTED CERAMIC OXIDES

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INTRODUCTION

The investigation of isothermal transport processes in molten salts has been the object of much research in recent years*.

Porous plug methods[3-9] have usually been used for determining transport numbers in fused systems.

Ionophoretic techniques have been also utilized for these determinations. As supporting media for the molten salt in the electromigration experiments, use has been made of asbestos[10], borosilicate glass fiber[11-15] and alumina powder[16].

We have used thin layers of fritted porous ceramic oxides (Al_2O_3, MgO, ZrO_2) fixed on impermeable (zero opened porosity) fritted ceramic oxide strips (Al_2O_3, ZrO_2).

These supporting media for ionophoretic experiments have the following characteristics:

(1) The thickness of the oxide layer can be varied. The quantity of salt per unit of area can thus be varied and the optimum working conditions for the system under investigation chosen.

(2) The refractory characteristics and chemical inertness of these strips permit their use with corrosive salts and at high temperature.

(3) The high temperature of the preparation procedure leads to a small specific area and to the support surface being in an inactive state. Exchange reactions or chemisorption with the molten system cannot take place.

The present work deals with the application of this ionophoretic technique to the determination of ionic mobilities in molten salts. The determination of self-diffusion (tracer-diffusion) coefficients with the zone diffusion method is also described.

In addition, the characteristics of electrophoretic methods as applied to the investigation of molten salts are critically discussed.

EXPERIMENTAL

Preparation of the support

Ceramic oxide (Al_2O_3, ZrO_2) sintered strips (10 to 30 cm long, 0.5 to 2.0 cm wide and 0.2 cm thick), especially prepared by Degussa A.G., are used. These sintered strips have a zero open porosity as determined with a mercury porosimeter.

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* For a review relative to the techniques utilized for the determination of transport quantities, and for the significance of these transport quantities see refs. 1 and 2.

The fritted layers are obtained by means of a flame spraying technique. The strips are sanded on one side and then exposed to a flux of molten ceramic particles. In the case of alumina a Metco Spray apparatus is used, while with zirconia and magnesia a Metco Plasma Jet is employed for spraying the molten particles on zirconia strips.

The flame spray gun is driven automatically to give a homogeneous distribution of the sintered ceramic material. The characteristics of the thin layer can be varied greatly depending on the procedure. The porosity depends particularly on the spraying distance, while the thickness of the layer on the number of passages.

It is possible to obtain layers from a few milligrams per square centimeter to several tenths.

Apparatus

The strip is connected *via* quartz fibers, "alumina paper"* or small ceramic strip bridges to two reservoirs (3–10 c.c. in volume) containing the ionic melt.

Working electrodes (Pt, W, etc.) are fixed in the reservoirs. In some cases (for homogeneity control) auxiliary Pt wire electrodes are fixed on the strip.

The assembly is introduced into a tubular furnace (100 cm long), equipped for controlled atmosphere operation, whose temperature is maintained constant over 30 cm ($\pm$ 2° up to 500°). The temperature of the strip under working conditions is measured by means of a thermocouple placed near the strip.

Impregnation of the strip

The impregnation is achieved by capillary action: it proceeds at a variable rate (normally 2–5 cm per h) depending on the salt, the temperature and the characteristics of the strip. Usually, in order to reach equilibrium conditions, the strip is left for conditioning overnight.

When the rate of impregnation is fast, it can lead to hydrodynamic flow during the electromigration experiment and consequently to an erroneous displacement of the labelled zone. This hydrodynamic flow during the transport experiment, which depends on the viscosity of the melt and on the interfacial surface tension of the system, can in some cases appreciably influence the measurement.

These effects can be minimized if care is taken to equalize the salt levels in the reservoir or if the electromigration is performed after the equilibrium conditions have been reached.

The equilibrium quantity of salt on the strip is usually between 5 and 30 mg/cm². This corresponds to a weight ratio of the salt to the thin ceramic layer of 0.3–2.

Homogeneity control

The homogeneity of the layer is checked by measuring the resistance** between auxiliary electrodes (platinum wires, diameter 0.2 mm) placed on the impregnated strip: the linearity of the plot resistance *vs.* strip length can be verified. The fritted

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* The "alumina paper" is prepared by fritting a poorly sanded alumina strip. The porous layer formed on the strip does not adhere.
** These determinations were carried out by applying a potential difference of about 30 V between the working electrodes in the reservoirs, measuring the potential drop between the auxiliary electrodes with an electrometer (Keithley 610 A), and recording the current intensity (Sargent recorder mod. MR). In some cases an LKB a.c. (1 or 2 kc/sec) Bridge was used.

thin layers as prepared by the method described above are very homogeneous if the sanding of the strip has been done properly.

Maximum permissible power during electrophoresis

The maximum power permissible during an electrophoretic experiment can be determined either by placing a thermocouple directly in contact with the strip, or by checking the linearity of the current tension curve.

It has been observed that at the same temperature the maximum power that can be dissipated without increase of temperature is almost independent of the quantity of salt on the strip.

Thus it is possible to give some guide limits of power dissipated for several salts without increasing the temperature more than 2° (Table I).

Above these limits it was verified that the temperature of the central zone becomes higher than the ends of the strip.

TABLE I

Salt	Temperature (° C)	Dissipation (W/cm²)
NaNO₃	350	0.1
KNO₃	350	0.3
CsNO₃	450	0.3
TlNO₃	300	0.05
AgNO₃	250	0.05

Electromigration and diffusion experiments

The electrophoretic cell, equilibrated overnight at the temperature of the experiment, is cooled rapidly and then the radioactive tracer (a quantity usually smaller than one mg) placed on the strip. The temperature is brought back to the initial value.

For a migration experiment the strip is left at this temperature for only a few minutes and then scanned radiometrically to determine precisely the position of the starting point.

The strip is now ready for the experiment. For the migration a stable potential difference of up to 10 V/cm is applied to the working electrodes for 0.5 to 4 h. This produces a displacement of the marked zone of several cm. The current intensity is usually 5–30 mA.

To determine the diffusion after placing the tracer, the strip is disconnected from the reservoirs and left at the temperature of the experiment for up to 10 h. The diffusion zone is several cm long. After the experiment the strip is again scanned.

Determination of the labelled zone of the electromigration and diffusion experiments

The position of the maximum of the activity curve after an electromigration experiment is determined by scanning the strip, which is placed under a G.M. counter with a narrow window.

The determination of the diffusion coefficients requires not only the knowledge of the position of the maximum but also that of the form of activity distribution curve. After a diffusion experiment a more precise method is used: the strip is scanned

with a G.M. counter adapted with a high density material collimator in direct contact with the strip, having a window from 0.5 to 1 mm. The collimator having a thickness of only 1 mm generally has a partial transparency and this is corrected for by scanning the strip with a windowless collimator.

Calculation of the transport parameters from the experiment

The radiometric determination of the displacement of the labelled zone and the coulometric determination of the quantity of electricity passed in the cell permits the evaluation of the ionic mobility of the labelled species provided that the conductivity and density of the molten electrolyte are known.

The equation used is:

$$u = \frac{x}{d} \cdot \frac{p \cdot l}{q} \tag{1}$$

where

  x = the specific conductance of the electrolyte;
  d = the density of the electrolyte;
  p = the weight of ionic melt per unit of length of support;
  l = the displacement of the radioactive zone;
  q = the quantity of electricity passed through the cell.

This equation accounts for the obstruction of the particles of the porous support to the ionic migration. To obtain it, starting from the usual definition of the zone mobility, a correction parameter (which is the inverse of the obstruction factor as defined by CRAWFORD AND EDWARD[17]) must be used:

$$K = \frac{R_p \cdot x \cdot p}{d} \tag{2}$$

where R_p is the electrical resistance of the impregnated strip per unit length.

The solution of the diffusion equation corresponding to our experimental conditions of a line source at the time $t = 0$, is the solution of the equation corresponding to the one-dimensional infinite diffusion case[18].

Experimentally, the slope of log activity from the radiometric scanning *versus* the square of the linear distance from the centre of the Gaussian curve (Fig. 2) is equal to $-1/4D't$ (Fig. 3), where D' is an apparent diffusion coefficient, and t the duration of the experiment*.

If the EDWARD[19] relation between the K factor defined in equation (2) and the ratio of the real ionic path, l, in the porous support to the linear one, l', is used:

$$K = \left(\frac{l}{l'}\right)^2 \tag{3}$$

then:

$$D = KD' \tag{4}$$

where D is the self-diffusion coefficient of the labelled species.

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* This method of evaluating the diffusion coefficients is essentially similar to that of ARNIKAR AND CHEMLA[10].

Thus the ionic mobilities can be determined without the explicit knowledge of K, but for the determination of the diffusion coefficient this factor must be measured.

SOME APPLICATIONS

Some typical experiments relative to the determination of ionic mobility and diffusion coefficients in molten nitrates, together with some results relative to the investigation of the mobility of transition metals in molten nitrate–chloride systems will now be presented.

Fig. 1 represents an electropherogram of $^{137}CsNO_3$ in sodium nitrate at 350°. The two curves are the result of the readings before and after the electromigration.
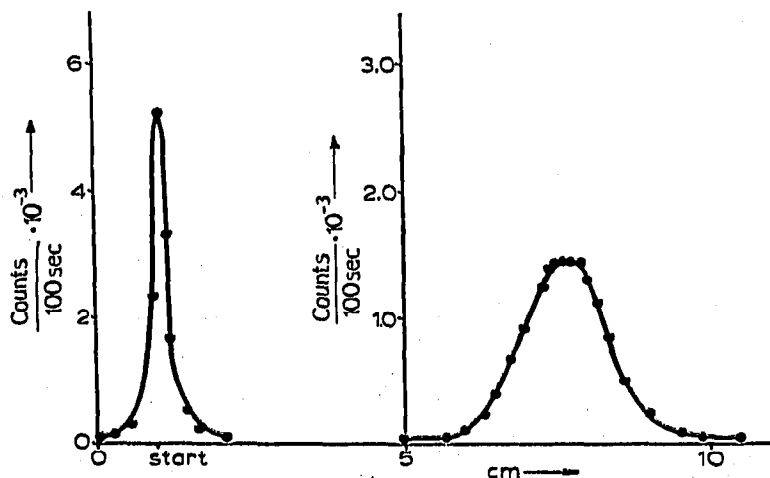

Fig. 1. Electropherogram of $^{137}CsNO_3$ in molten $NaNO_3$ on a thin layer of porous fritted alumina (thickness $\sim$ 7 mg cm^{-2}) at 330°. Conditions: applied electrical field $\sim$ 6 V cm^{-1}; current intensity $\sim$ 11 mA; time 2 h; quantity of salt per cm length of the strip, p = 5.35 mg cm^{-1}; quantity of electricity passed through the cell, q = 80.1 coulomb. The activity distribution curves have been obtained by scanning the strip for radioactivity (β counting), before and after electromigration through a lead sheet 1 mm thick with a window 0.7 mm wide, placed at 0.5 mm from the strip. The l_{Cs} value is given by the difference of the ascissae of the two maxima.

The distribution of the activity after the experiment does not show tailing or asymmetry. This permits the exclusion of the existence of chemical phenomena between the porous support and the migrating species (chemical reaction, chemisorption, or decomposition of $CsNO_3$ with formation of Cs_2O). The mobility value calculated from the formula (1), is $2.72 \cdot 10^{-4}$ cm^2 V^{-1} sec^{-1}[*].

In Fig. 2 the readings of the activity after a diffusion experiment are reported: viz. $^{22}NaNO_3$ in sodium nitrate at 325°. Curve A is obtained with a collimator of Pb, 1 mm thick, with a window of 0.5 mm. The B curve is obtained through a Pb sheet with the same dimensions but without a window. The correct diffusion profile is given by curve C[**]. In Fig. 3 the function log activity vs. the square of the linear distance from the Gaussian centre is plotted.

From the slope a value of $D_{Na} = 2.2 \cdot 10^{-5}$ cm^2 sec^{-1} is obtained (with a measured K value of 1.9). It can be compared with the value of $1.94 \cdot 10^{-5}$ cm^2 sec^{-1} of DWORKIN et al.[22] at 320°.

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[*] Specific conductivity and density interpolated from data of reference 20.
[**] For a detailed description of the counting apparatus see reference 21.

In the second case the failure of formula (1) arises from the lack of knowledge of the factor p (weight of the salt which effectively participates in the electrical transport per unit length of the strip). If p is taken as the total salt weight for unit length of the strip, the quantities measured are too large**. This point should be verified; for instance, when some pore diameters in the support are very small, part of the salt can be in cavities with small openings so that the ion exchange between the bulk might be slower than the electrical transport.

In general, it may be supposed that the transport processes of molten salts absorbed on a porous support are influenced by the pore size (or by the extension of the surface) of the support below a critical size value. The critical value lies probably in the range 1–$10^{-2}\mu$.

The ceramic supports used here have an average pore size of the order of ten microns or more. This fact and the absence of chemical interactions with molten nitrates seem to favour the method as a tool for determining the isothermal transport quantities of these systems.

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SUMMARY

The application of thin layer electrophoresis and diffusion on fritted ceramic oxides (Al_2O_3, MgO or ZrO_2) using radioisotopes for the determination of isothermal transport quantities in molten salts is described.

Some applications to the investigation of molten nitrates are presented. The characteristics of methods of this kind as applied to the study of the molten systems are critically discussed.

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