On the Validity of Inter- and Self-Diffusion Measurements in Molten Salts by Methods Applying Multiporous Fritted Discs

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A gravimetric method has been used to study interdiffusion in binary mixtures of $AgNO_3$ and KNO_3 over the range 50—75 mole % $AgNO_3$ at temperatures below 200 °C. The obtained cation diffusion coefficients are of the order of 2×10^{-6} cm² sec^{-1}, i.e. considerably lower than what might have been expected from other diffusion measurements. It has previously been found that there is a tendency for self-diffusion coefficients obtained with fritted discs to be lower than those obtained with the conventional open-end capillary technique. Some possible sources of error are discussed.

At present very little information is available on interdiffusion coefficients in molten salt mixtures. A gravimetric method, previously used at room temperature[1, 2], has been modified for work at elevated temperatures[3]. The pores of a cylindrical Pyrex glass disc (Jobling 3610/62, 20 mm POR 4) are filled with a salt mixture of one composition, whereafter the disc is suspended into a melt of another composition. The disc is hanging under an analytical balance, and the change in apparent weight is followed continously. It is possible to calculate the interdiffusion coefficient provided that the cell-constant of the disc is known. The required calibration has been done by a corresponding experiment with an aqueous solution (1.0-n. KCl) with known diffusion coefficient. (It has previously been shown that the same cell constant is obtained, if the calibration is done by means of a conductivity measurement[4].) This method has been used to determine interdiffusion coefficients in mixtures of potassium and silver nitrates over the concentration range 50 — 75 mole % of $AgNO_3$ for temperatures from 162 to 200 °C. Mean experimental values interpolated to 190 °C are shown in Fig. 1. The measurements indicate that there might be a minimum near the eutectic composition, where Polyakov[5] claims to have found a minimum for both viscosity and electrical conductivity.

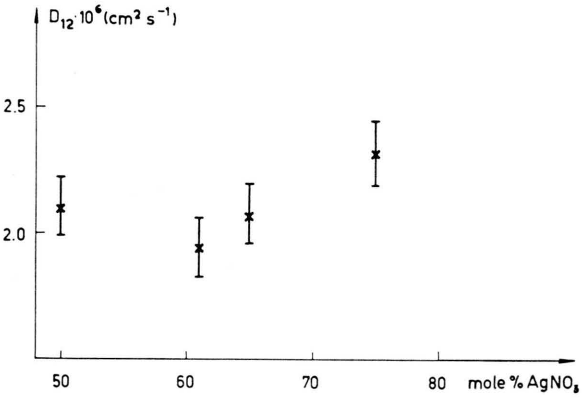

Fig. 1. Interdiffusion coefficient at 190 °C plotted versus concentration of $AgNO_3$. The indicated errors (6%) are estimated from the observed maximum spread of 3% for the calibration and 5% for the salt experiments.

A comparison with previous measurements on molten salts[6–12] shows that most inter- as well as self-diffusion coefficients are at least one order of magnitude higher than the present results. However, nearly all other measurements have been made at much higher temperatures. If the self-diffusion coefficients measured by the conventional capillary technique[13] for pure nitrates are extrapolated down to 190 °C one obtains $D_{\mathrm{K}} = 3.2 \times 10^{-6}$ and $D_{\mathrm{Ag}} = 8.5 \times 10^{-6}$ cm² sec^{-1}. At first sight this might raise the suspicion that the results obtained by the gravimetrical method are erroneous. However, this method is considered to give reliable results at room temperature[2], and the different checks made so far do not indicate that any systematic error is introduced when the temperature of operation is higher than that of calibration[14]. A similar type of discs was used by us for self-diffusion measurements in zinc bromide and thallium chloride[4, 15]. For these salts

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[14] B. R. Sundheim and A. Berlin, J. Phys. Chem. **68**, 1266 [1964], have recently studied the apparent conductivity of fused $AgNO_3$ and $TlNO_3$ in fritted Pyrex glass discs over the temperature range 213—318 °C. Our inter-diffusion measurements were made far below the temperature, 280 °C, up to which they found a normal conductivity for $AgNO_3$ (although not for $TlNO_3$). Above this temperature both salts showed an evident increase in apparent conductivity which was interpreted as "being due to ion exchange of the salt with the glass under the influence of an electric field". This observation might be of importance for interpreting our self-diffusion results, even if a mechanism that gives an increase in apparent conductivity hardly can be responsible also for a decrease in transport by diffusion.

[15] C.-A. Sjöblom, Z. Naturforschg. **18 a**, 1247 [1963].

a comparison with results from other capillary methods is possible. For $ZnBr_2$ three methods gave about the same temperature dependence for the cation self-diffusion coefficient (D^+), but a plot shows a considerable displacement of the curves, the fritted disc giving D^+ values nearly a factor of two lower than those obtained with the conventional capillary with an open end, here called the A-S (ANDERSON-SADDINGTON) method. The results obtained with a long capillary fall inbetween, see Table 1. For TlCl there are two independent investigations with the A-S method [16, 17], both in good agreement with each other, but in conflict with the disc method. Thus the latter gave a much more pronounced temperature dependence. For both cation and anion the two methods give the same diffusion coefficients at about 535 °C, but a hundred degrees lower the disc method gives values that are about 70% of those obtained by the A-S method, cf. Table 1. It has recently been claimed that the self-diffusion coefficients previously obtained with the A-S method should be reduced considerably [9]. This would reduce the discrepancies between the A-S method and the disc method. However, at the present stage all methods used so far for diffusion measurements in melts should be viewed with some suspicion. In comparison with other capillary methods disc methods are characterized by numerous irregular capillaries of small dimensions and a very large glass surface exposed to the melt. If the small dimensions of the capillaries and pores have a reducing effect on the diffusion within the disc, this should mean that "wall effects" have a much larger range in melts than in aqueous solutions. For some A-S experiments with molten metals the self-diffusion coefficient seems to decrease with decreasing capillary diameter [18], but it has been suggested that such observations are due to disturbance by convection in the capillaries [19, 20]. The "capillaries" in fritted discs are narrow compared with those used in the A-S method, 10 μm might be taken as a typical diameter of a pore, but this is still a large distance compared with the dimensions of the diffusing units, even if these are assumed to be globules consisting of perhaps a hundred atoms [21]. The other typical property of the discs is the large glass area exposed to the melt. If an exchange of ions takes place between the two phases, this could explain why the disc methods give low diffusion coefficients [14]. However, it seems unlikely that both anions (Br^-, Cl^-) and cations (Zn^{2+}, Tl^+) are involved to the same extent in exchange reactions. The self-diffusion measurements with the disc have shown for both $ZnBr_2$ and TlCl that the ratio D^+/D^- remains constant over the whole investigated temperature range, and that this ratio is about the same whether the disc or the A-S method is used. We consider this as a strong indication that reactions between the melt and the glass are negligible at least for the two halides in question. There has so far not appeared any experimental support for assuming a priori that methods using fritted discs are inferior to other diffusion methods tested, or that "low" inter- and self-diffusion coefficients are erronous. We hope that our results obtained with the gravimetric method will stimulate the development of new methods for diffusion measurements in melts. Comparisons with new methods are urgently needed for settling the question of the reliability of the methods used so far.

Salt	$ZnBr_2$		TlCl			
Diffusing ion	Zn	Zn	Tl	Tl	Cl	Cl
Temp. °C	450	550	450	550	450	550
D_{AS}/D_{DH}	1.90	1.81	1.52	0.95	1.40	0.93
D_W/D_{DH}	1.24	1.40				

Table 1. Comparison of self-diffusion coefficients obtained by different methods [4]. Subscripts indicate AS ANDERSON-SADDINGTON, W WALLIN, DH DJORDJEVIC-HILLS (fritted disc).

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