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Ion-sieving properties of some inorganic ion exchangers in fused solvents

The occurrence of interactions between a solid surface (*e.g.* the support, the plug, and the walls) and fused solvents used in electrophoresis, e.m.f. and conductivity measurements, respectively, is of fundamental importance in determining the transport properties of molten salts.

The most striking example of an interaction between the support and inorganic tracer ions dissolved in fused salts can be found in the electrophoresis experiments of KETELAAR AND HONIG[1]. These authors gave a value of 0.4×10^{-4} cm²/Vsec for the mobility of the Na^+ tracer ion in fused $CsNO_3$ at 450° on glass fibre paper. This value was later corrected to 1.7×10^{-4} cm²/Vsec by electrophoresis measurements with quartz fibre paper as support[2]. The smaller mobility on glass was ascribed to an "isotopic ion exchange" between the Na^+ tracer ions in the melt and the Na^+ ions in the glass[3]. Nevertheless this explanation does not seem to be sufficient, taking into account, for example, that the mobility of Na^+ tracer ions in molten KNO_3 does not depend on the support used.

We have repeated similar experiments in our laboratory by a simple chromatographic technique, using Whatman GF 81 glass fibre paper and quartz powder dried at 500° as supports. The chromatograhpy of Na^+ tracer ion with molten $CsNO_3$ as solvent at 450° shows that this ion travels with the front when the quartz powder is used as support, whilst it stays at the point of application on glass fibre paper. We have also found that with the latter support Na^+ ions can be eluted to the front by adding 1 % of $LiNO_3$ to molten $CsNO_3$.

We think that the behaviour in $CsNO_3$ is due to the ion-exchange uptake of Na^+ by the glass fibre, the exchange being possible since the cation of the solvent is screened out at this temperature (owing to its large size, *i.e.* 1.67 Å). When ions with a suitable size for the exchange with glass (such as lithium) are dissolved in the melt, the tracer sodium ion is eluted to the chromatographic front.

The behaviour of the dehydrated quartz powder is clearly quite different, taking into account that this material should not have any ion-exchange properties in fused salts. Thus with particular supports and particular melts containing tracer ions there may be true ion-exchange processes which can strongly affect their mobility measurements depending on the selectivity of tracer ions with respect to the exchanger. In this case, the chromatographic method is a simple and useful technique for ascertaining whether or not interactions between the ions of the melt and the support are present.

In order to obtain more quantitative data on ion-sieving phenomena in molten salts some experiments were conducted with crystalline zirconium phosphate (CZP), which possesses good ion-exchange properties in molten salts up to 550° (ref. 4).

1 g each of various salt forms of this exchanger — lithium (CZPLi), sodium (CZPNa) and potassium (CZPK) — was equilibrated for ten days with 50 g of $CsNO_3$ at 450°.

The data obtained (Table I) show that, while the potassium form of the exchanger is almost completely converted into the caesium form, the lithium and sodium forms are only exchanged to the extent of 50 % (3.5 mequiv./g) by the caesium ions of the solvent.

TABLE I

DEGREES OF CONVERSION OF VARIOUS SALT FORMS OF CRYSTALLINE ZIRCONIUM PHOSPHATE IN $CsNO_3$ AT 450°

$\bar{X}_{Cs}$ = mole fraction of Cs^+ in the exchanger.

Salt form of the exchanger	$\bar{X}_{Cs}$
Li^+	0.47
Na^+	0.51
K^+	0.98

This fact was confirmed by column experiments where the solvent $CsNO_3$ at 450° is percolated through a bed of CZPLi and CZPNa. After several elutions the degree of conversion was the same as that obtained in batch experiments. On the other hand, by bringing the mixed sodium–caesium form of the exchanger into contact with molten $NaNO_3$ at 350°, the pure sodium form of CZP* was reformed. The smaller interplanar distance of CZPLi and CZPNa with respect to CZPK[5], and the large size of the caesium ion, suggest that the partial substitution of the counterions of the exchanger in the sodium and lithium forms is due to a sieving action towards the caesium ions of the solvent.

The possibility of a sieving effect on zirconium phosphate in molten salts is of great importance both from a theoretical and a practical point of view, since it is possible to study the distribution coefficients of tracer ions (as in aqueous solution) or to use zirconium phosphate in order to extract impurities dissolved in fused salts, the cations of which would be screened out by the exchanger.

Further experiments are now in progress in order to obtain a better theoretical and practical insight into ionic sieving properties of crystalline zirconium phosphate and other exchangers of the same class.

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* Owing to the crystalline structure of zirconium phosphate it was possible to confirm this behaviour by X-ray diffraction measurements.