

CHROMATOGRAPHY AND ZONE ELECTROPHORESIS OF INORGANIC IONS DISSOLVED IN FUSED SALTS

IV. ELECTROPHORETIC BEHAVIOUR OF INORGANIC IONS IN FUSED ALKALI NITRATES*

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Zone electrophoresis in molten salts has been employed in recent years either to determine ionic mobilities¹⁻⁹, or to obtain some information on the nature of the ionic species in these ionic solvents¹⁰⁻¹², or to perform some analytical separation of inorganic ions^{13,14}.

However, up to the present, most of the work has been restricted to determination of the mobilities of alkali metal ions^{1-9,12} while very little experimental work has been reported on the electrophoretic behaviour of other inorganic ions^{10,11,13,14}. With regard to the electromigration of inorganic ions in fused alkali nitrates, it must be emphasized that most of the multivalent ions give insoluble oxides in these solvents and therefore the measurements have been restricted to inorganic ions whose oxides are soluble in fused nitrates^{10,13}. To extend the electrophoretic studies to other inorganic metal ions, oxide precipitation has been avoided by adding to fused nitrates a suitable amount of NH_4NO_3 which is a strong oxygen ion acceptor.

REAGENTS AND ANALYTICAL PROCEDURES

Finely powdered LiNO_3 (Erba RP), KNO_3 (Erba RP), NaNO_3 (Erba RP) were dried at 110° and mixed in the molar proportions: $\text{LiNO}_3:\text{KNO}_3 = 43:57$ (m.p. 132°), $\text{NaNO}_3:\text{KNO}_3 = 50:50$ (m.p. 220°) and then dried again at 110° before use. A suitable amount of NH_4NO_3 (10 % by weight), previously dried at 110° , was added to the molten solvent. The glass fibre paper (Whatman GF 82) was purified by dipping in aqueous HNO_3 (1:1) and rinsing with distilled water. After this purification the strips were dipped in a concentrated aqueous solution of KNO_3 in order to increase the wettability by the fused solvents as described elsewhere¹⁵ and then dried at 160° .

The solutions of the metal ions ($\approx 10^{-2} M$) were prepared by dissolving the metal nitrates (Erba RP) in the molten solvent containing NH_4NO_3 . Europium nitrate was prepared by dissolving Eu_2O_3 (Johnson-Matthey Co., London) in hot conc. HNO_3 and evaporating to dryness.

Metal ions were detected by spraying suitable reagents on to the glass fibre strips. $\text{UO}_2(\text{II})$ and $\text{Eu}(\text{III})$ were detected by fluorescence spot tests^{16,17}. $\text{Cs}(\text{I})$ was determined radiometrically by using ^{137}Cs as tracer.

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APPARATUS

Chromatographic and electrophoretic experiments were performed in apparatus similar to that described in a previous paper¹¹.

In this work double vessels were used at the cathode and the anode to avoid any contamination of the strip by the electrolysis products.

The average potential gradient ($2.5-4.0 \text{ V cm}^{-1}$) was measured by two platinum wires wound around the supporting glass plate with the paper strip. The electric current was maintained in the range 60-100 mA; in this way only small differences between the temperature of the strip and of the surrounding atmosphere were found.

The strip was chromatographically impregnated and left for conditioning overnight. A Cary 14H Spectrophotometer was employed for adsorption measurements.

RESULTS AND DISCUSSION

As discussed in a previous paper¹¹, before determining the electrophoretic behaviour of a given ion, it must be ascertained whether the ion interacts with the support or an insoluble precipitate is formed. A simple control can be performed by chromatographic experiments under the same experimental conditions employed in the electrophoretic studies. In this way it was found that by adding 10% by weight of NH_4NO_3 to the fused nitrates all the ions examined travel freely with the solvent front and therefore neither precipitation nor interaction occurs. Table I shows the electrophoretic behaviour of some inorganic ions in molten alkali nitrates.

TABLE I

ELECTROPHORETIC MOBILITY ($\text{cm}^2 \text{ V}^{-1} \text{ sec}^{-1} \cdot 10^4$) OF INORGANIC IONS IN MOLTEN NITRATES
(+) = Movement towards cathode; (—) = movement towards anode.

Ion	$(\text{Li-K})\text{NO}_3 + 10\% \text{NH}_4\text{NO}_3$ $t = 160^\circ$	$(\text{Li-K})\text{NO}_3 + 10\% \text{NH}_4\text{NO}_3$ $t = 250^\circ$	$(\text{Na-K})\text{NO}_3 + 10\% \text{NH}_4\text{NO}_3$ $t = 250^\circ$
$\text{NH}_4(\text{I})^*$	1.0 (+)	—	0.9 (+)
Cs(I)	1.0 (+)	1.1 (+)	0.9 (+)
Pb(II)	0.6 (+)	0.7 (+)	0.8 (+)
Cd(II)	0.3 (+)	0.35 (+)	0.45 (+)
Cu(II)	0.2 (+)	0.25 (+)	0.25 (+)
Zn(II)	0.1 (+)	0.1 (+)	0.15 (+)
Co(II)	0.0	0.2 (—)	0.0
$\text{UO}_2(\text{II})$	0.2 (—)	—	0.25 (—)
Ni(II)	0.25 (—)	0.4 (—)	0.25 (—)
Eu(III)	0.3 (—)	0.45 (—)	0.3 (—)
Cr(III)	0.2 (—)	0.4 (—)	0.6 (—)

* Experiments performed in pure $(\text{Li-K})\text{NO}_3$ solvents.

It is interesting to note that there are large differences in the cationic mobility of the various metal ions and that some bivalent and trivalent ions show even an anionic behaviour. Thus various analytical separations of inorganic ions can be expected; some of these separations such as Pb-Co-Ni and Cs-Cd-Eu have been tested experimentally with excellent results.

Regarding the anionic movement of Cr(III), spectrophotometric measurements of Cr(III) in a (Li-K)NO₃ eutectic at 160° showed that absorption peaks of Cr(III) (5800 Å) and CrO₄²⁻ (3700 Å) can be observed immediately after dissolution of Cr(NO₃)₃, then the Cr(III) peak disappears slowly while the CrO₄²⁻ peak increases. Oxidation of Cr(III) to CrO₄²⁻ by NO₃⁻ has also been observed by VAN NORMAN *et al.*¹⁰. Thus it can be concluded that the anionic mobility of Cr(III) in nitrate melts is due to CrO₄²⁻ ions which are probably formed according to the reaction:



In the other cases, it cannot be concluded from the neutral or anionic electrophoretic behaviour alone that neutral or negative complexes with nitrate ions are formed since, up to date, the extent of movement of the solvent in an electric field is unknown. The movement of the solvent in an electric field requires some consideration.

Many authors maintain that the electroosmotic flux due to a nonhomogeneous distribution of the charge at the solid-liquid interface is negligible in molten salts; however, the possibility of movement of the solvent due to differences in the ionic mobilities of cations and anions of the solvent itself must also be considered¹⁸. Therefore at present, the electrophoretic data cannot be corrected as in the case of an aqueous solution, for solvent movement and the mobility of a given ion in fused salts will include an unknown constant.

For the same reason, up to date, it is impossible to derive the sign of the species present in the fused salts from electrophoretic experiments. Thus, the present lack of information on the extent of the movement of the solvent under the action of the electric field is a serious limitation to the wider application of zone electrophoresis in fused salts studies, and it is to be hoped that in the near future an experimental determination of the movement of the solvent will be realized.

In Table I, the metal ions have been arranged according to their decreasing cationic movement. It can be seen that the movement of a given metal ion towards the cathode decreases with its electrical charge and increases with its crystalline radius, while the opposite would be expected. Clearly this phenomenon must be related to the interactions with nitrate ions. Thus the electrophoretic experiments, although not giving the sign of the species, indicate that metal ions exhibiting anionic behaviour interact with nitrate ions more strongly than those exhibiting cationic behaviour, and a relative approximate scale of these interactions can be derived by arranging the ions, as in Table I, according to their electrophoretic mobility. It can be seen that alkali metal ions of large size, such as Cs⁺, interact weakly with nitrate ions; NH₄⁺ behaves like Cs⁺, indicating that its interaction with NO₃⁻ is small.

The movement of the metal ions increases with the temperature of the alkali nitrate solvents as expected (see Table I).

The comparison between electrophoretic behaviour in (Li-K)NO₃ and (Na-K)NO₃ at the same temperature shows that the movement of Cs⁺ is higher in the (Li-K)NO₃ than in the (Na-K)NO₃ solvent, while the opposite occurs for bivalent and trivalent ions.

The higher relative mobility of Cs⁺ in (Li-K)NO₃ eutectics is in good agreement with the results obtained by LANTELME *et al.*¹² and can be explained by assuming

that Li^+ ion, owing to its small crystalline radius, interacts strongly with the nitrate ions lowering their activity; thus the interaction of other alkali metal ions with nitrate ions becomes smaller and their cationic mobility increases. According to this view it is clear that the effect of Li^+ ions on the movement of a given metal ion must become less and less important as the metal ions interact more and more strongly than the Li^+ with nitrate ions. Thus the effect of Li^+ on the mobility of metal ions decreases from Cs(I) to Eu(III) (see Table I). However, the higher relative mobility towards the anode of bivalent and trivalent ions in $(\text{Li-K})\text{NO}_3$ solvents remains at present unexplained, since the difference between the viscosity of $(\text{Na-K})\text{NO}_3$ and $(\text{Li-K})\text{NO}_3$ at 250° is small^{20,21}. It could be due to a greater movement of the solvent towards the anode when the $(\text{Li-K})\text{NO}_3$ eutectic is employed and this increase of the anionic movement of the solvent could be due to the greater difference of mobility between Li^+ and NO_3^- than that between Na^+ and NO_3^- ions¹⁸. However this hypothesis can only be confirmed after the movement of the solvent in an electric field has been measured experimentally.

SUMMARY

The electrophoretic behaviour of various metal ions dissolved in molten alkali nitrates has been investigated. The movement of the ions towards the cathode is found to decrease with electrical charge and decreasing ionic radius. Some bivalent and trivalent ions even show anionic behaviour. This phenomenon has been related to the interactions with the nitrate ions. The effect of the cations of the molten solvent on the electrophoretic mobilities of the metal ions is also discussed.

REFERENCES

- 1 M. CHEMLA AND A. BONNIN, *Compt. Rend.*, 241 (1955) 1288.
- 2 J. ARNIKAR, *Thesis*, Paris (1958).
- 3 J. ARNIKAR, *Ann. Phys.*, 4 (1959) 1291.
- 4 S. FORCHERI AND C. MONFRINI, *J. Phys. Chem.*, 87 (1963) 1566.
- 5 S. FORCHERI AND V. WAGNER, *Ann. Chim.*, 56 (1966) 213.
- 6 S. FORCHERI AND A. BERLIN, *J. Chromatog.*, 26 (1967) 239.
- 7 A. KETELAAR AND E. HONIG, *J. Phys. Chem.*, 68 (1964) 1596.
- 8 E. HONIG AND A. KETELAAR, *Trans. Faraday Soc.*, 62 (1966) 190.
- 9 A. KETELAAR AND J. KWAK, *J. Phys. Chem.*, 71 (1967) 1149.
- 10 A. BAILEY AND A. STEGER, *J. Chromatog.*, 18 (1965) 374.
- 11 G. ALBERTI, S. ALLULLI AND G. MODUGNO, *J. Chromatog.*, 15 (1964) 420.
- 12 F. LANTELME AND M. CHEMLA, *Electrochim. Acta*, 10 (1965) 665.
- 13 G. ALBERTI, G. GRASSINI AND R. TRUCCO, *J. Electroanal. Chem.*, 3 (1962) 283.
- 14 H. KÜHNEL AND M. KHAN, *J. Chromatog.*, 23 (1966) 149.
- 15 G. ALBERTI, A. CONTE AND S. ALLULLI, *J. Chromatog.*, 18 (1965) 564.
- 16 G. GRASSINI AND G. ALBERTI, *Proc. Intern. Symp. Microchemical Technique*, Wiley, New York, 1961, p. 291.
- 17 G. ALBERTI AND M. A. MASSUCCI, *J. Chromatog.*, 11 (1963) 394.
- 18 B. SUNDHEIM, *Fused Salts*, McGraw-Hill, New York, 1964, p. 165.
- 19 J. VAN NORMAN AND R. OSTERYOUNG, *Anal. Chem.*, 32 (1960) 398.
- 20 C. FAWSITT, *J. Chem. Soc.*, 93 (1908) 1299.
- 21 I. MURGULESCU AND S. ZUCA, *Electrochim. Acta*, 11 (1966) 1383.