

CHROM. 4400

CHROMATOGRAPHY AND ZONE ELECTROPHORESIS OF
INORGANIC IONS DISSOLVED IN FUSED SALTSVI. THE ELECTROPHORETIC BEHAVIOUR OF SOME INORGANIC ANIONS
IN ALKALI NITRATE AND PERCHLORATE MELTS*

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(Received October 1st, 1969)

SUMMARY

The electrophoretic mobilities of some inorganic anions dissolved in molten LiNO_3 at 300° , $(\text{Li-K})\text{NO}_3$ eutectic at 160° , $(\text{Na-K})\text{NO}_3$ mixture at 250° and $(\text{Li-K})\text{ClO}_4$ eutectic at 300° are reported and discussed.

In $(\text{Li-K})\text{ClO}_4$ eutectic, all the anions examined, except ClO_4^- , move towards the cathode or stay at the point of application. This is probably due to a strong cation-anion interaction, according to the BLANDER¹¹ model of molten salts, occurring between the Li ions of the solvent and the dissolved anions.

From the differences between the mobilities of the chloride and bromide ions in the solvents examined, an approximate scale for the associating power of the cations of these solvents could be established.

INTRODUCTION

The electrophoretic behaviour of inorganic anions dissolved in molten salts¹⁻⁴ has, until now, received very little attention.

Some indication concerning the type of the interaction occurring in fused salts can be deduced⁵⁻⁷ from determination of the mobilities of tracer cations; hence measurements of the mobilities of tracer anions should permit a better understanding of these interactions.

The behaviour of the tracer anions was investigated by zone electrophoresis, a technique already used in tracer cation mobilities studies^{1, 5, 8}. Various fused alkali nitrates and molten $(\text{Li-K})\text{ClO}_4$ eutectic were used as electrolytes in order to investigate the influence of the cations and anions of the solvent on the mobilities of the tracer anions.

* This work was supported by Consiglio Nazionale delle Ricerche.

EXPERIMENTAL

LiNO_3 , NaNO_3 , KNO_3 and KClO_4 were Erba RP products. NO_2ClO_4 was supplied by K & K Laboratories; anhydrous LiClO_4 was obtained according to a procedure described previously⁹. The salts were finely powdered, 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°), $\text{LiClO}_4\text{--KClO}_4$ (76:24) (m.p. 207°) and then dried again at 110° .

The electrophoretic experiments were performed in an apparatus similar to that described in a previous paper¹; the experimental conditions were similar to those reported in ref. 8, the cathodic and anodic reservoirs being separated from the central vessels, where the strip dipped.

To avoid explosive reactions when $(\text{Li--K})\text{ClO}_4$ eutectic was employed as solvent, a suitable alkali nitrate mixture was used as catholite.

Cl^- , Br^- and ClO_4^- were detected radiometrically by using ^{36}Cl , ^{82}Br and $^{36}\text{ClO}_4$ tracers, the distribution of their activities on the glass fiber paper being obtained by scanning each 0.5 cm of the strip.

The colorimetric detection of other inorganic anions was made by cutting the strip in several portions of 0.5 cm and dipping them in aqueous solutions of suitable reagents.

RESULTS AND DISCUSSION

Table I shows the electrophoretic mobilities* of some inorganic anions dissolved in various fused nitrates and $(\text{Li--K})\text{ClO}_4$ eutectic.

TABLE I

ELECTROPHORETIC MOBILITY ($\text{cm}^2/\text{V sec} \cdot 10^{-4}$) OF INORGANIC ANIONS IN VARIOUS FUSED SOLVENTS

<i>Ion</i>	<i>(Li--K)ClO₄</i> <i>T = 300°</i>	<i>LiNO₃</i> <i>T = 300°</i>	<i>(Li--K)NO₃</i> <i>T = 160°</i>	<i>(Na--K)NO₃</i> <i>T = 250°</i>
NO_3^-	3.3 (+)	—	—	—
NO_2^-	2.4 (+)	—	—	—
CrO_4^{2-}	0.8 (+)	0.0	0.3 (—)	0.8 (—)
$\text{Cr}_2\text{O}_7^{2-}$	0.8 (+)	0.0	0.3 (—)	0.8 (—)
ClO_4^-	0.7 (—)	—	—	—
ClO_3^-	—	0.5 (—)	0.3 (—)	0.65 (—)
BrO_3^-	0.45 (+)	0.15 (—)	0.15 (—)	0.3 (—)
IO_3^-	0.8 (+)	0.1 (+)	0.0	0.1 (—)
Cl^-	0.9 (+)	0.65 (—)	0.4 (—)	1.0 (—)
Br^-	0.1 (+)	1.1 (—)	0.6 (—)	0.8 (—)
I^-	—	—	0.7 (—)	0.75 (—)

(+) Movement towards cathode.

(—) Movement towards anode.

The most striking feature is that, in a $(\text{Li--K})\text{ClO}_4$ eutectic, all the species examined, except ClO_4^- , travel towards the cathode, or stay at the point of application. The cationic behaviour was also confirmed for nitrate, electrophoresis experiments

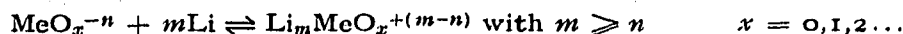
* As already pointed out⁸, lack of knowledge concerning the electroosmotic flow in molten media, precludes our knowing for certain whether the values represent the true mobility of the species under examination.

being carried out for a period of several hours. After 10 h of electrolysis it was noted that no traces of nitrate ion (< 0.01 mg) had migrated from the cathodic vessel containing the nitrate mixture to the neighbouring vessel into which the strip dipped*.

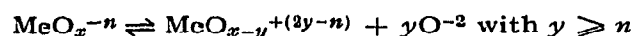
Simple chromatographic tests on all species showing zero mobility showed that this behaviour was not due to interaction with the support.

The cationic behaviour of inorganic anions in molten perchlorates could be explained by the following two hypotheses:

(a) Strong interactions occur between the tracer anions and the cations of the melt, according to the equilibrium



(b) A positively charged group is stable in this solvent, according to the Lux-Flood equilibrium



It must be noted that the oxygen ion formed in eqn. (b) can give rise to stable association, as reported by KOHLMÜLLER¹⁰, with the lithium ions of the solvent, shifting equilibrium (b) towards the right. Thus, in both cases, the "cationic" behaviour of inorganic tracer anions is probably due to the strong associating power of Li^+ .

Concerning the equilibrium (b), an attempt was made to introduce the species NO_2^+ (the Lux acid corresponding to NO_3^-) directly into a well-dried perchlorate melt by using nitronium perchlorate. The introduction of this salt immediately gave rise to gaseous products and the successive analysis showed no traces of nitrate or nitrite ions in the melt. It thus seems that NO_2^+ is not very stable in fused perchlorates and that the formation of positively charged species is probably due to equilibrium (a).

A similar equilibrium holds for tracer cations dissolved in fused salts as already discussed by LANTELME AND CHEMLA and in our previous papers in order to explain the behaviour of alkali metal ions in fused nitrates⁶ and perchlorates⁵, or the anionic mobilities of transition metal ions in molten $(\text{Li-K})\text{NO}_3$ ⁸.

The behaviour of the perchlorate ion in $(\text{Li-K})\text{ClO}_4$ eutectic suggests that this anion is the one which interacts least with the Li^+ of the solvent among all the anions examined. This is in good agreement with the well-known poor complexing power of perchlorate anion in aqueous solution.

The differences between the mobilities of chloride and bromide ions, measured in the various fused solvents, are reported in Table II.

One can see that in nitrate solvents containing Li^+ , bromide also moves faster towards the anode than chloride, while, according to the Stokes' law, the opposite should be expected. Furthermore, in this case the electrophoretic behaviour is affected by association reactions though not so evidently as in a perchlorate solvent.

The interaction of the halide anions with the cations of the solvent can be related, according to the BLANDER model¹¹, to the coulombic effect which is greater the smaller the distance of closest approach in the cation-anion pair.

* In this way, the use of nitrates as catholite was fully justified, since no variation in the composition of perchlorate solvent occurs.

TABLE II

DIFFERENCES BETWEEN THE ELECTROPHORETIC MOBILITY ($\text{cm}^2/\text{V sec} \cdot 10^{-4}$) OF CHLORIDE AND BROMIDE IONS DISSOLVED IN VARIOUS FUSED SOLVENTS

Solvents	U_{Cl^-}	U_{Br^-}	Δu
(Li-K)ClO ₄	0.9 (+)	0.1 (+)	+0.8
LiNO ₃	0.65 (-)	1.1 (-)	+0.45
(Li-K)NO ₃	0.4 (-)	0.6 (-)	+0.2
(Na-K)NO ₃	1.0 (-)	0.8 (-)	-0.2

(+) Movement towards cathode.
 (-) Movement towards anode.

When the Li⁺ of the solvent is substituted by the less associating Na⁺ (Table II last column) the ionic interactions are weakened and the anionic mobility of chloride becomes greater than that of bromide*.

With respect to the electrophoretic mobilities of inorganic oxyanions the situation is more complicated and comparison of the results obtained in various solvents is difficult. Data reported in Table I, seem to indicate that the interactions of these species with the cations of the solvent are due rather to polarization forces, as suggested by FÖRLAND¹², than to coulombic effect.

Unfortunately, the lack of data, such as ionic radius and polarizability of the oxyanions examined, does not allow us to attempt quantitative considerations. On the other hand we think, according to the LUMSDEN formulation¹³, that both coulombic and polarization effects have to be considered to explain the interactions among the tracer anions and the cations of the solvent.

Probably the anion under investigation will be greatly affected by both, depending upon its own particular shape. The results obtained seem useful in order to have a scale for the interacting power of Li⁺ with inorganic anions.

As reported previously⁵, a relationship between this quantity and the molar concentration of Li⁺ in the melt cannot be deduced easily when the anion of the solvent is changed.

Since the electrophoretic behaviour of the tracer anions depends upon the relative interaction of the ions with the cations of the solvent, it would seem possible to correlate the values of the differences between the mobilities of chloride and bromide** dissolved in various melts (Table II) to the amount of "free" Li ion. The data obtained suggest that the "activity" of Li⁺ is higher in a (Li-K)ClO₄ eutectic than in pure LiNO₃, in good agreement with data obtained for the solubility of ammonia in these media¹⁴. Thus, a first approximate*** scale of the interacting power of the cations of the melt can be deduced from the mobility differences (which are not affected by the eventual electroosmotic flow).

This scale could be useful in order to have, among different fused salts, a first comparison criterion, which, till now, has never been stated unambiguously.

* For a more detailed discussion on the dependence of the electrophoretic mobilities of a given tracer ion on the cations and the anions present in the melt see ref. 5.

** These anions were selected since they should exhibit less complex interactions with the cations of the solvent than the other species examined.

*** Variations in viscosity and temperature should be also be taken into account, but in our case they cannot cause a reversal of the sign of the mobility differences.

ACKNOWLEDGEMENT

The authors wish to express their thanks to Professor G. ALBERTI for many helpful discussions.

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