

CHROM. 4247

CHROMATOGRAPHY AND ZONE ELECTROPHORESIS OF INORGANIC IONS DISSOLVED IN FUSED SALTS

V. ELECTROPHORETIC BEHAVIOUR OF SOME METAL IONS DISSOLVED IN MOLTEN PERCHLORATES*

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(Received June 27th, 1969)

SUMMARY

The mobilities of alkali metal ions in a $\text{LiClO}_4\text{-KClO}_4$ eutectic at 300° increase as their crystalline radius decreases while the opposite occurs for alkaline earth metal ions dissolved in the same solvent.

The slope of the mobility curve *vs.* ionic radius of the alkaline earth metal ions decreases in a $\text{LiClO}_4\text{-Mg}(\text{ClO}_4)_2$ melt at 300° and is completely reversed in pure $\text{Mg}(\text{ClO}_4)_2$ at 270° .

From the data obtained in molten perchlorates, as well as from results reported by other authors in molten nitrates, some general considerations and predictions on the mobility of a given cation dissolved in various fused salts having the same anion but different cations or *vice versa*, are reported and discussed.

INTRODUCTION

As shown by electrophoretic experiments in molten alkali nitrates¹⁻³ interactions between dissolved metal ions and the anions of the solvent depend very much upon the nature of the alkali metal ion of the solvent itself. These interactions decrease as the crystalline radius of the alkali metal ions of the solvent decreases. However, strong association reactions occur even in fused lithium salts as indicated by the anionic behaviour of some metal ions dissolved in these solvents¹.

To obtain a better insight on anion-cation interactions it seemed interesting to compare the electrophoretic behaviour of metal ions dissolved in fused salts having the same anion but cations of different electrical charge. The use of fused solvents other than the uni-univalent salts is restricted because many salts have melting points which are too high for electrophoretic experiments on glass fiber paper while others decompose or are very difficult to dehydrate. However, magnesium perchlorate could be used as it yields an anhydrous melt at 270° .

In this paper the electrophoretic behaviour of alkali and alkaline earth metal

* This work was supported by the "Consiglio Nazionale delle Ricerche".

ions dissolved in a molten $\text{LiClO}_4\text{-KClO}_4$ eutectic and $\text{Mg}(\text{ClO}_4)_2$ are reported and discussed.

The use of perchlorates as fused solvents has till now received very little attention; only a few papers have been published in this field⁴⁻⁷. Thus electrophoretic experiments in fused perchlorates also give more information on these solvents.

EXPERIMENTAL

KClO_4 and $\text{Mg}(\text{ClO}_4)_2$ were Merck reagents grade, while anhydrous lithium perchlorate was obtained according to a procedure described elsewhere⁴. The $\text{LiClO}_4\text{-KClO}_4$ eutectic (76% moles of LiClO_4 ; m.p. 207°) and the $\text{LiClO}_4\text{-Mg}(\text{ClO}_4)_2$ mixture (32% moles of $\text{Mg}(\text{ClO}_4)_2$; m.p. $\sim 235^\circ$) were obtained by mixing the salts in suitable quantities and drying them again under vacuum at 110°. Preliminary chromatographic controls were performed to ascertain whether precipitation of the oxides or interaction with the support occurs.

The electrophoretic experiments were performed in an apparatus similar to that described in a previous paper⁸, the experimental conditions being similar to that reported in ref. 1. The strip of glass-fiber paper was chromatographically impregnated and left for conditioning overnight. When $\text{Mg}(\text{ClO}_4)_2$ was used as electrolyte, the strip was directly impregnated by dipping it in molten $\text{Mg}(\text{ClO}_4)_2$ contained in a dry-box filled with anhydrous nitrogen.

A suitable mixture of alkali nitrates was used as catholite (alkali perchlorates cannot be employed since the alkali metals discharged at the cathode react with the solvent explosively). This mixture was controlled experimentally so that this substitution did not affect the composition of the solvent, since no trace of nitrate ions (< 0.01 mg) was found in the neighbouring vessel, into which the strip dipped.

The alkali and alkaline earth metal ions were detected radiometrically by using ^{22}Na , ^{42}K , ^{86}Rb , ^{134}Cs , ^{45}Ca , ^{80}Sr and ^{131}Ba as tracers. A Gaussian distribution of the activity was obtained by scanning the strip every 0.5 cm for alkali metal ions and every 0.2 cm for alkaline earth metal ions, owing to their lower mobility. Tl(I) ion was detected as sulphide.

RESULTS AND DISCUSSION

Table I shows the electrophoretic mobilities of the alkali and alkaline earth metal ions, and thallium(I) dissolved in fused $\text{LiClO}_4\text{-KClO}_4$ at 300°. Measurements of mobility of other inorganic ions such as Pb(II) , Cd(II) , Co(II) , Ni(II) and Cu(II) were not carried out because chromatographic experiments showed that these ions did not travel with the front of the solvent, thus suggesting the low solubility of their oxides*.

Owing to the lack of knowledge of electroosmotic flow in molten media, mobility data could represent the apparent, rather than the true mobility of the species under examination.

As shown in Fig. 1 the mobilities of alkali metal ions decrease as their crystalline

* The attempt to hinder the formation of metal oxides by adding ammonium perchlorate as acid to the molten solvent (according to the report in our previous paper¹) was unsuccessful, since ammonium perchlorate decomposes very quickly at this temperature.

TABLE I

ELECTROPHORETIC MOBILITIES ($\text{cm}^2/\text{V sec}$) OF ALKALI, ALKALINE EARTH METAL IONS AND THALLIUM IN MOLTEN $\text{LiClO}_4\text{-KClO}_4$ AT 300°

Ion	$u \times 10^4$	Crystalline ionic radius (\AA)
Na(I)	3.6 ± 0.1	0.97
K(I)	3.0 ± 0.1	1.33
Rb(I)	2.6 ± 0.1	1.47
Cs(I)	2.4 ± 0.1	1.67
Tl(I)	2.7 ± 0.1	1.15
Ca(II)	0.45 ± 0.01	0.99
Sr(II)	0.80 ± 0.01	1.12
Ba(II)	1.22 ± 0.01	1.34

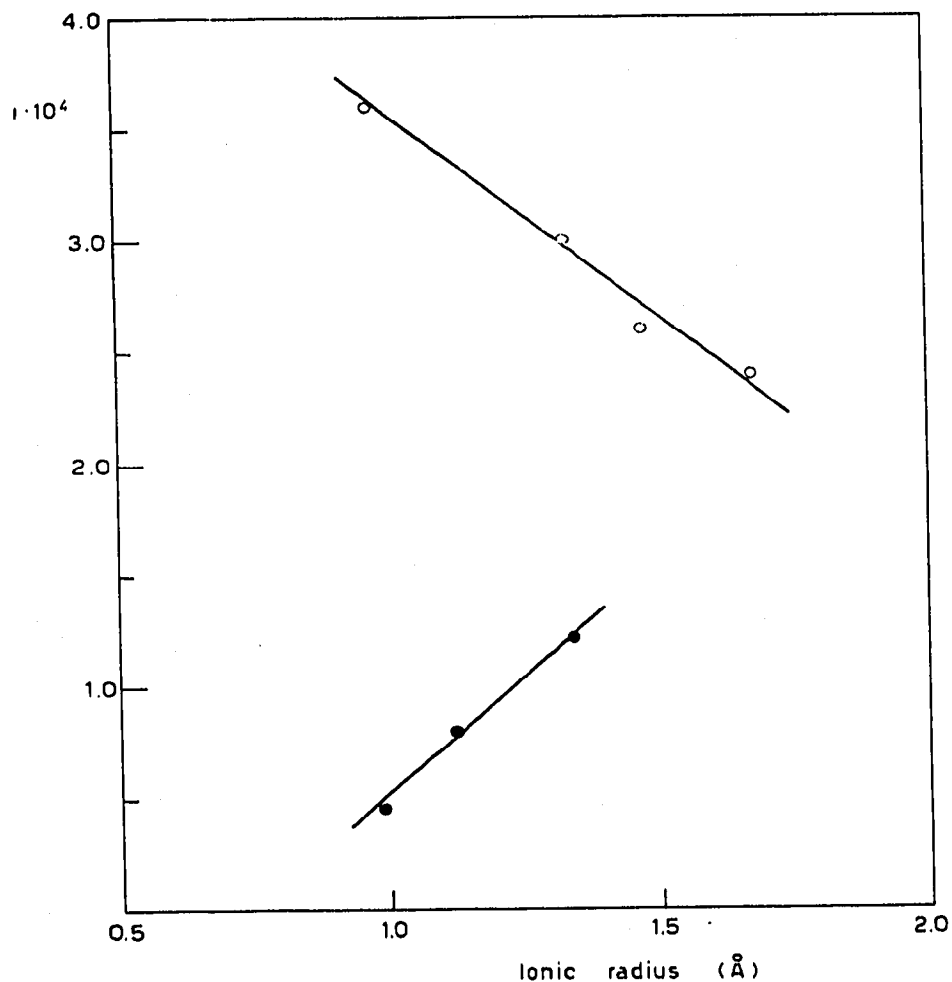


Fig. 1. Electrophoretic mobilities ($\text{cm}^2/\text{V sec}$) of Na^+ , K^+ , Rb^+ and Cs^+ (circles) and Ca^{2+} , Sr^{2+} and Ba^{2+} (black dots) in a molten $\text{LiClO}_4\text{-KClO}_4$ eutectic at 300° as a function of crystalline ionic radius.

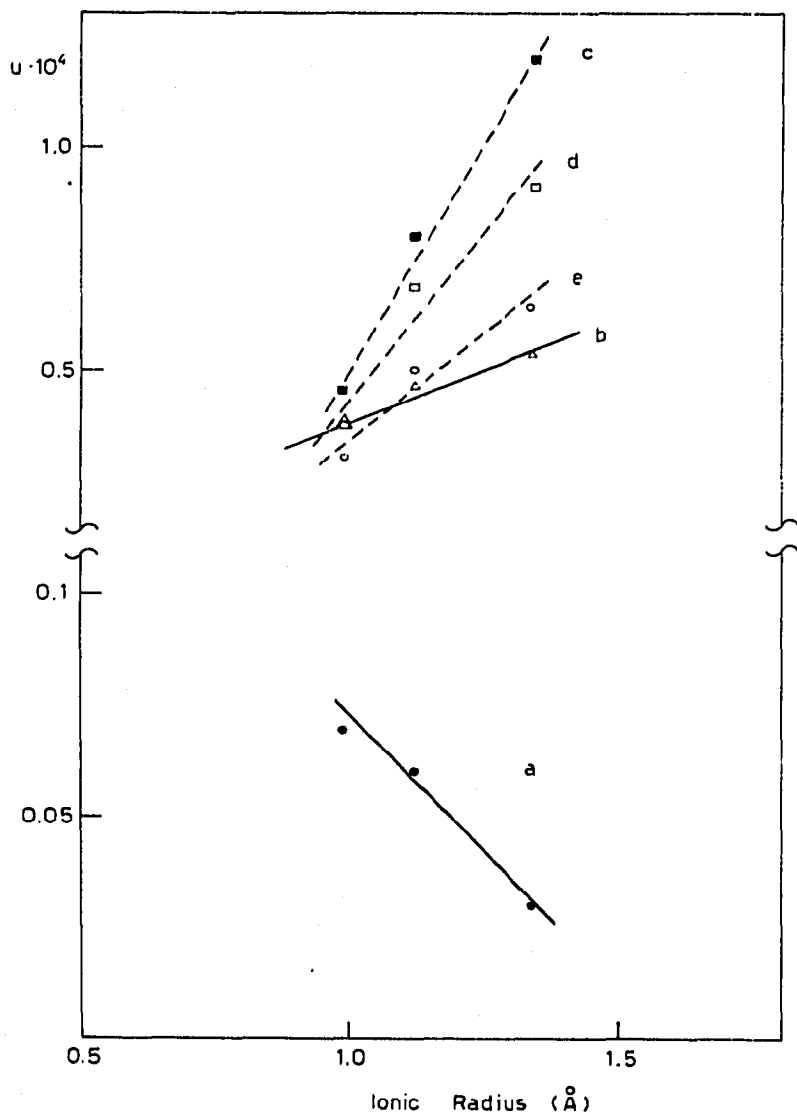


Fig. 2. Electrophoretic mobilities ($\text{cm}^2/\text{V sec}$) of alkaline earth metal ions, as a function of crystalline ionic radius, in various molten media. (a) Pure $\text{Mg}(\text{ClO}_4)_2$ at 270° ; (b) LiClO_4 - $\text{Mg}(\text{ClO}_4)_2$ mixture at 300° ; (c, d, e) LiClO_4 - KClO_4 eutectic at 300° , 270° and 240° respectively.

radius increases while the opposite occurs for the alkaline earth metal ions (an analogous trend was also observed by FORCHERI⁹ in molten nitrates).

The opposite behaviour of the alkali and alkaline earth metal ions can be related to the presence of the Li ion in the solvent. This ion, owing to its small crystalline radius, interacts more strongly than the other alkali metal ions with the anion of the solvent. Thus, in molten LiClO_4 or in fused systems with high concentrations of Li ions, the interactions of Na^+ , K^+ , Rb^+ and Cs^+ with the anion of the solvent are weak and their mobility decreases with their increasing crystalline radius. On the other hand, the higher electrical charge of the alkaline earth metal ions makes them more reactive than the Li ion. Since interaction is stronger the smaller the alkaline earth metal ion, the mobility decreases as their crystalline radius decreases.

Taking into account the behaviour of the alkali metal ions in alkali nitrates², a decreasing mobility with increasing crystalline radius can also be expected for

TABLE II

ELECTROPHORETIC MOBILITIES ($\text{cm}^2/\text{V sec} \cdot 10^{-4}$) OF ALKALINE EARTH METAL IONS DISSOLVED IN LiClO_4 - $\text{Mg}(\text{ClO}_4)_2$ MIXTURE AT 300° AND PURE $\text{Mg}(\text{ClO}_4)_2$ AT 270°

Ion	LiClO_4 - $\text{Mg}(\text{ClO}_4)_2$ (300°)	$\text{Mg}(\text{ClO}_4)_2$ (270°)
Ca (II)	0.37 ± 0.01	0.07 ± 0.01
Sr (II)	0.47 ± 0.01	0.06 ± 0.01
Ba (II)	0.53 ± 0.01	0.03 ± 0.01

alkaline earth metal ions in a solvent whose cation interacts with its own anion more strongly than with the tracer alkaline earth metal ions. To test this hypothesis, one of the smaller, *i.e.* the more interacting alkaline earth metal ions, was selected as cation of the solvent, and electrophoretic experiments were performed either in pure $\text{Mg}(\text{ClO}_4)_2$ at 270° or in LiClO_4 - $\text{Mg}(\text{ClO}_4)_2$ mixture at 300° .

The values obtained are reported in Table II. In Fig. 2 these data are plotted vs. ionic radii of the ions. Data obtained in LiClO_4 - KClO_4 at 240° , 270° (Table III) and 300° are also reported for comparison (dashed curves). These temperatures were selected since the comparisons among different fused systems (in our case LiClO_4 - KClO_4 eutectic and pure $\text{Mg}(\text{ClO}_4)_2$) are usually made at the same fixed number of degrees above their melting points or at the same ratio between working temperature and melting point.

It can be seen from Fig. 2:

(a) That the mobilities of alkaline earth metal ions in the LiClO_4 - KClO_4 eutectic increase with temperature; however, the slope of the mobility curves of these ions is not greatly affected by temperature changes;

(b) When pure $\text{Mg}(\text{ClO}_4)_2$ is employed a reversal of the slope is obtained, in agreement with our previous expectations;

(c) When LiClO_4 - $\text{Mg}(\text{ClO}_4)_2$ is employed the slope of the mobility curves is lowered with respect to that obtained in LiClO_4 - KClO_4 , but not reversed, owing to the low concentration of Mg^{2+} .

It must be pointed out that the different behaviour of the alkaline earth metal ions in LiClO_4 - KClO_4 and in $\text{Mg}(\text{ClO}_4)_2$ cannot be ascribed to viscosity differences between these solvents, since variations in viscosity can increase or decrease, but not reverse the slope of the mobility curves. Thus the inversion of the slope of the mo-

TABLE III

ELECTROPHORETIC MOBILITIES ($\text{cm}^2/\text{V sec}$) OF ALKALINE EARTH METAL IONS IN MOLTEN LiClO_4 - KClO_4 AT 240° AND 270°

Ion	$u \times 10^4$ (240°)	$u \times 10^4$ (270°)
Ca (II)	0.30 ± 0.01	0.37 ± 0.01
Sr (II)	0.50 ± 0.01	0.68 ± 0.01
Ba (II)	0.64 ± 0.01	0.91 ± 0.01

ility curves must be ascribed to the different interacting forces of the cations of the solvents.

The electrophoretic values obtained in molten perchlorates for alkali and alkaline earth metal ions as well as what was previously reported in the literature for alkali metal ions in molten nitrates¹⁻³ allow us to make some general predictions about the influence of the cation and the anion of the solvent on the mobility of the dissolved metal ions.

Let us consider the following two cases:

- (1) Two or more tracer metal ions are dissolved in a given molten salt.
- (2) A given metal ion is dissolved in two or more molten salts having the same anion but different cations or *vice versa*.

In the first case the possibilities are the following:

(a) The cation of the solvent interacts with its own anion more strongly than the dissolved metal ions (*e.g.* alkali metal ions in a molten lithium salt or alkali and alkaline earth metal ions in a molten magnesium salt). In this case the interactions of the dissolved metal ions with the anion of the solvent are weak; their mobilities are thus expected to decrease with increasing crystalline radius (in agreement with Stokes' law).

(b) The cation of the solvent interacts with its own anion less than the dissolved metal ions (*e.g.* alkali and alkaline earth metal ions in a molten caesium salt). In this case, owing to the strong interaction with the anions of the solvent, the mobilities of the dissolved metal ions are expected to decrease as their crystalline radius decreases.

(c) The associating power of the cation of the solvent is intermediate to that of the dissolved metal ions (*e.g.* Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺ in a molten potassium salt). In this case the mobilities are expected to increase from Li⁺ to K⁺ and decrease from K⁺ to Cs⁺; thus the curve of mobility *vs.* crystalline ionic radius exhibits a maximum for the cation of the solvent (see ref. 2).

Predictions on the variation of the mobility of a given metal ion dissolved in different molten solvents (case 2) are more complicated since differences in the viscosity of the solvents must be taken into account. However, if the viscosity values are known, some predictions can also be made, taking into account the deviations from the product $u \times \eta = K$, obtained from Stokes' law for ideal systems. For example if we consider a given metal ion (*e.g.* K⁺) dissolved in different fused salts with the same anion (*e.g.* LiNO₃, KNO₃ and CsNO₃), the interaction of this ion with the nitrate anion will increase from KNO₃ to CsNO₃ and decrease from KNO₃ to LiNO₃. Thus the product $u \times \eta$ in the various solvents is not constant and is expected to increase as the interacting power of the cation of the solvent increases:

$$u_{\text{CsNO}_3}^{\text{K}^+} \times \eta_{\text{CsNO}_3} < u_{\text{KNO}_3}^{\text{K}^+} \times \eta_{\text{KNO}_3} < u_{\text{LiNO}_3}^{\text{K}^+} \times \eta_{\text{LiNO}_3}$$

where u^{K^+} is the mobility of the potassium ion in the system under consideration which has a viscosity value η .

As regards the mobility of a given cation in various fused solvents having the same cation but different anions the product $u \times \eta$ is expected to decrease as the interaction of the tracer cation with the anion of the solvent increases.

The mobilities of transition metal ions will probably show an even more complicated dependence on the solvent employed, owing to the possibility of them forming "true" complex ions.

We think that predictions on the mobility of a given anion in various molten salts having the same cation but different anion or *vice versa* could also be made by considering similar interactions to those previously reported for the mobility of the cations. Some preliminary experiments on the electrophoretic mobilities of various inorganic anions dissolved in a molten $\text{LiClO}_4\text{-KClO}_4$ eutectic at 300° (ref. 10), showed that all these species move towards the cathode. In some cases (*e.g.* the nitrate anion) this "cationic" mobility is very high ($3.3 \cdot 10^{-4} \text{ cm}^2/\text{V sec}$) thus justifying the use of nitrate mixtures in the cathode vessel in our electrophoretic experiments with fused perchlorates. "Cationic" mobility of the dissolved anions can be related to their stronger interaction than perchlorate anion with Li ions of the solvent. This is also in agreement with the well-known weak associating power of the perchlorate anion in aqueous solution.

In conclusion, from the knowledge on the ionic interactions, some predictions on the electrophoretic behaviour of the ionic species in molten salts can be made; on the other hand, useful information on the association reactions occurring in molten salts can be obtained from the electrophoretic mobilities of inorganic ions.

However, more exhaustive data are necessary for a more quantitative knowledge of these associations, which are of fundamental importance for the study of the properties of ionic melts.

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