

# SEPARATION OF INORGANIC IONS IN FUSED SALTS BY MEANS OF CHROMATOGRAPHY AND ELECTROPHORESIS ON GLASS FIBER PAPER

## III. EFFECT OF WATER, OXYGEN AND SUPPORT ON THE MIGRATION OF INORGANIC IONS DISSOLVED IN THE LiCl-KCl EUTECTIC AT 450°

G. ALBERTI, S. ALLULLI AND G. MODUGNO

*Laboratorio di Chimica della Radiazioni e Chimica Nucleare del C.N.E.N.  
and  
Centro Nazionale di Chimica dei Composti di Coordinazione del C.N.R.,  
Istituto di Chimica Generale ed Inorganica,  
Università, Rome (Italy)*

(Received November 28th, 1963)

Electromigration on glass fiber paper can be employed to obtain simply and rapidly useful information concerning the nature of ions present in fused salts, and also to perform some analytical separations of inorganic ions<sup>1-3</sup>.

Before determining the electrophoretic behaviour of an ion, it is necessary to ascertain whether the ion interacts with the support and also whether precipitation due to the ions present in the fused electrolyte could occur. This can be studied by chromatographic experiments and only when the ion travels freely with the front of the fused eutectic, can it be assumed that neither precipitation nor interaction occurs.

In this paper, the causes of precipitation of different metallic ions dissolved in the LiCl-KCl eutectic are discussed. Suitable experimental conditions for avoiding such precipitation were determined by chromatography.

### EXPERIMENTAL

#### *Preparation of dehydrated eutectic*

Finely powdered potassium chloride (Erba RP) and lithium chloride (Erba RP) were oven dried and then mixed in molar proportions of LiCl:KCl = 59:41. This mixture was dried again at 94°<sup>4</sup> and then dehydrated with anhydrous HCl in an assembly similar to that described by GRUEN AND McBETH<sup>5</sup>. The anhydrous pellets of eutectic were then stored under CCl<sub>4</sub> previously distilled over P<sub>2</sub>O<sub>5</sub>. The solutions of ions being examined were obtained by dissolving the respective anhydrous chlorides in the eutectic. Anhydrous chlorides of Th(IV), Cr(III), Co(II), Mn(II) are not readily available commercially, therefore the corresponding hydrated chlorides were dehydrated by heating in a stream of anhydrous hydrogen chloride. The chlorides were then dissolved in the fused eutectic and anhydrous hydrogen chloride was bubbled through, for approximately 1/2 h. In this way, the chlorides of all of the elements studied were perfectly dissolved in the molten eutectic.

### Apparatus

The electrophoretic experiments with non-dehydrated LiCl-KCl eutectic were performed in a furnace similar to that described in a previous paper<sup>2</sup>.

The experiments with dehydrated eutectics were performed in the stainless steel apparatus shown in Fig. 1. This apparatus consists of a cylindrical furnace, which contains an electrophoretic chamber of slightly smaller diameter than the furnace that can be tightly closed. The chamber can be easily withdrawn and transferred to a

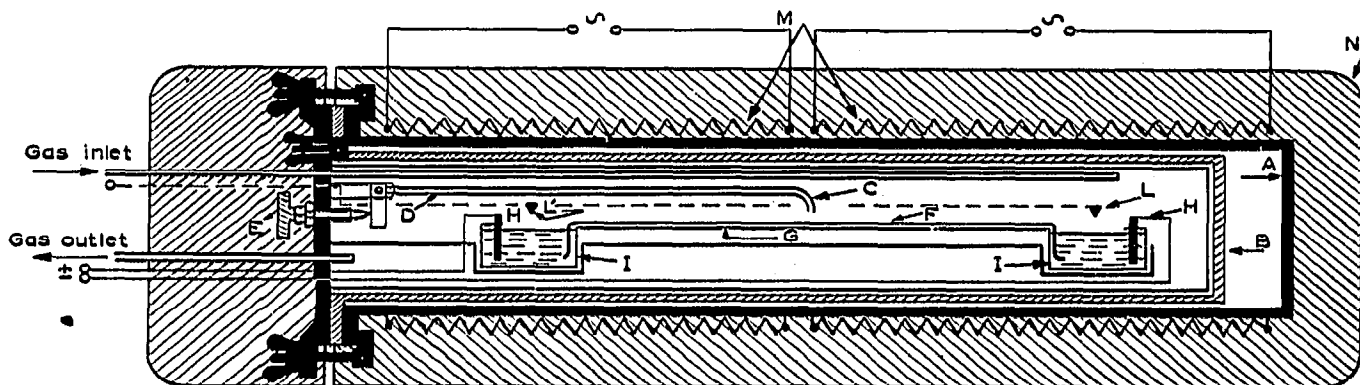


Fig. 1. Cross-sectional view of the apparatus: A = furnace; B = electrophoretic chamber; C = capillary; D = tube supporting the capillary; E = screw to rise or lower tube D; F = glass fiber paper; G = pyrex glass plate; H, H' = graphite electrodes; I, I' = pyrex vessels; L, L' = thermocouples; M = Ni-Cr heating wire; N = insulating jacket.

dry-box in order to prepare the experiment. The furnace is electrically heated by two electric resistances controlled by two thermocouples.

The chromatographic experiments were performed in an assembly similar to that described in ref. 1 (Fig. 3).

### *Techniques for electrophoretic and chromatographic experiments in anhydrous conditions*

In order to perform chromatographic and electrophoretic experiments under perfectly anhydrous conditions, all the preliminary operations must be done in a dry-box.

The dehydrated salts, prepared as described above, are dissolved in the anhydrous eutectic contained in the apparatus shown in Fig. 2. Anhydrous hydrogen chloride is

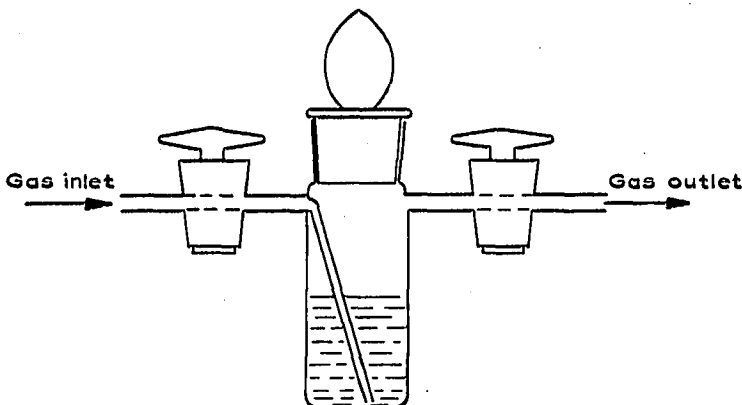


Fig. 2. Apparatus used to dissolve chlorides of metal ions in molten LiCl-KCl eutectic.

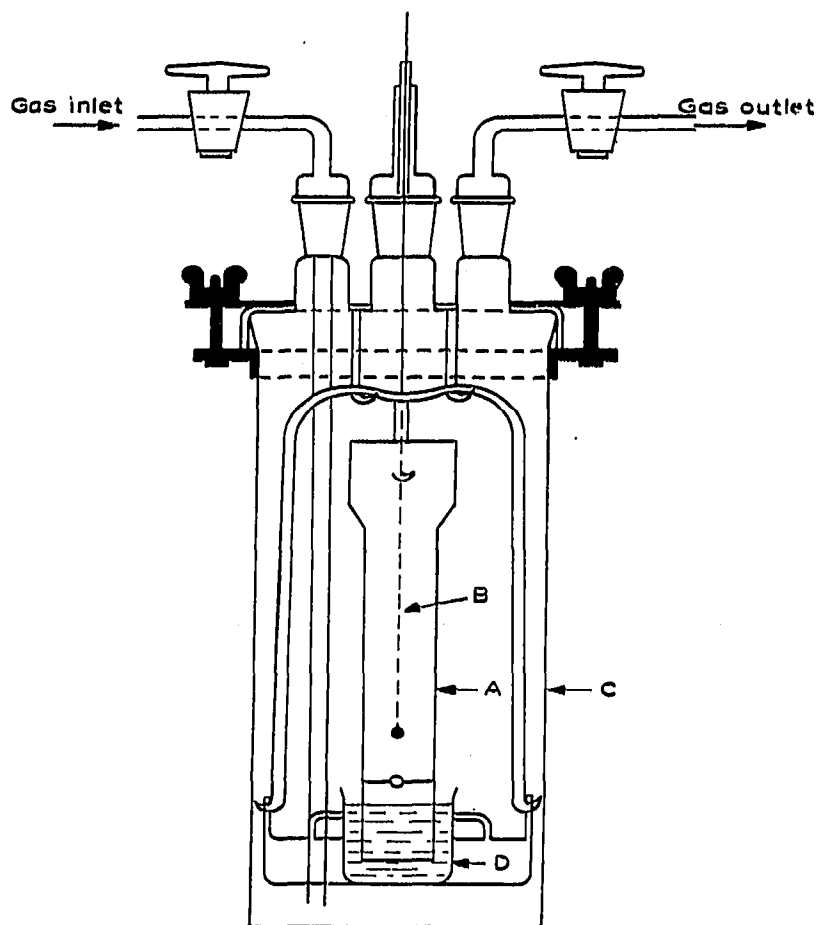


Fig. 3. Apparatus for chromatographic experiments. A = glass fiber paper; B = thermocouple; C = pyrex cylinder; D = pyrex vessel.

passed for approximately  $\frac{1}{2}$  h, followed by anhydrous nitrogen for about 10 min. In the chromatographic experiments the ion to be examined is placed, by means of a glass capillary, directly on the fiber glass paper in the dry-box. To perform electrophoresis under anhydrous conditions, the capillary C (Fig. 1) is filled with the melt containing the ion being examined. The strip of glass fiber paper is placed on the support G, and the vessels I-I' are filled with the dehydrated eutectic. The electrophoretic chamber is then removed from the dry-box and placed in the furnace. At this stage, only one section of the furnace was heated, in order to melt only the eutectic contained in one vessel. The glass fiber strip is then chromatographically impregnated by the fused chlorides. After about 2 h, the other section of the furnace is heated in order to melt the eutectic contained in the second vessel. In this way, the junction of the two chromatographic fronts is no longer located at the center of the strip, but is displaced towards one of the vessels. It is thus possible to avoid any concentration of the impurities of the paper at the center of the strip where the spot is placed.

The current between the two vessels is then switched on and allowed to become constant, and is then turned off. The tube D is then lowered by means of an external device E, so that the end of the capillary C lies directly on the glass fiber strip. In order to make sure that most of the salt flows from the capillary to the strip, this operation is repeated several times. An electric field (3.3 V/cm) is then again applied for 1-3 h

according to the electrophoretic mobility of the ions being examined. During the whole experiment, a slow stream of anhydrous nitrogen is passed through the electrophoretic chamber.

### RESULTS AND DISCUSSION

#### (a) *Chromatography of metal ions*

The chromatographic experiments, under air and using the hydrated LiCl-KCl eutectic, showed that while some metallic ions travel freely with the front of the fused eutectic, others remain at the point of application (see Table I, column a).

To determine whether these ions stayed at the point of application as a result of a reaction with the support or because they were precipitated as oxides, the possible sources of  $O^{2-}$  ions in the melt were eliminated. The main cause was found to be the appreciable solubility of water in the fused eutectic even at temperatures of  $450^{\circ}$  to  $500^{\circ}$ <sup>4</sup>. The eutectic should therefore be carefully dehydrated in order to avoid the hydrolysis reactions in this temperature range.

The  $O^{2-}$  ion could also be present in the melt as a result of the oxidation of the  $Cl^{-}$  ion by the oxygen present in the chromatographic chamber, according to the reaction:



The equilibrium constant for this reaction is not known. Its numerical value should be very small as the potential of the  $Cl_2/Cl^{-}$  system, referred to the Pt/Pt<sup>2+</sup> electrode, is 0.322 V<sup>7</sup>, while that for the  $O_2/O^{2-}$  system, according to DELARUE<sup>8,9</sup>, is in the range 0 to 0.06 V.

The small concentration of  $O^{2-}$  ions from reaction (1), when air is used as filling gas, can be high enough to precipitate those ions forming highly insoluble oxides. Moreover, the presence of oxygen in the filling gas, may cause the oxidation of some ions such as Fe(II) or U(IV), modifying their chromatographic and electrophoretic behaviour. Therefore, in experiments with ions forming highly insoluble oxides in LiCl-KCl melts and ions that could be oxidized, it is necessary to use pure nitrogen as filling gas for the chromatographic chamber.

A third cause of precipitation of very slightly soluble oxides could be the glass fiber paper. Glass can contain an appreciable quantity of water which dissolves in the melt<sup>6</sup>. Therefore, the strips were dehydrated at  $480^{\circ}$  and stored in a dry-box. Furthermore alkali oxides contained in the glass could dissolve in the fused eutectic giving rise to  $O^{2-}$  ions. A powdered quartz support could possibly give better results than the one used in these experiments.

Drastic conditions would be required, *i.e.* a stream of anhydrous hydrogen chloride, in order to achieve the complete elimination of  $O^{2-}$  ions. Chromatographic experiments in anhydrous hydrogen chloride atmosphere were unsuccessful, as in this case the glass fiber strip is no longer wetted by the fused eutectic. Therefore, the wettability of the glass fiber paper by the LiCl-KCl eutectic, might be related to the presence of traces of water or  $O^{2-}$  ions. As it is not possible to operate under such drastic conditions, a different acceptor of  $O^{2-}$  ions of medium strength ( $S_2O_7^{2-}$ ) was used in some further experiments.

The results obtained by chromatography under various conditions are reported in Table I. In column (a) the results obtained in experiments performed without special

TABLE I  
 CHROMATOGRAPHIC BEHAVIOUR OF INORGANIC IONS IN MOLTEN LiCl-KCl EUTECTIC AT 450° UNDER VARIOUS CONDITIONS

Ions	(a) Non-dehydrated eutectic	(b) Anhydrous eutectic, anhydrous air	(c) Anhydrous eutectic, anhydrous nitrogen (99.998%)	(d) Anhydrous eutectic with 10% $\text{Na}_2\text{S}_2\text{O}_8$ , anhydrous nitrogen (99.998%)
Na(I)	Front	Front	Front	Front
Rb(I)	Front	Front	Front	Front
Cs(I)	Front	Front	Front	Front
Ag(I)	Front	Front	Front	Front
Tl(I)	Front	Front	Front	Front
Cd(II)	Front	Front	Front	Front
Pb(II)	Front	Front	Front	Front
Zn(II)	Front	Front	Front	Front
Co(II)	Front	Front	Front	Front
Mn(II)	Application point	Front	Front	Front
Ni(II)	Application point	Front	Front	Front
UO <sub>2</sub> (II)	Application point	Front	Front	Front
Cr(III)	Application point	Application point	Front	Front
Fe(III)	Application point	Application point	Application point	Front
Th(IV)	Application point	Application point	Application point	Front with tail
CrO <sub>4</sub> (II)	Front	Front	Front	Front
CrO <sub>3</sub>	Front	Front	Front	Front

precautions (hydrated eutectic and presence of air) are listed. In columns (b), (c) and (d) the results obtained with dehydrated eutectic, using respectively air (b), nitrogen (99.998 % purity) (c), and  $\text{Na}_2\text{S}_2\text{O}_7$  10 % (d) are reported.

These results show that, once the causes for precipitation of oxides are eliminated, the ions, except Th(IV), move freely with the front of fused eluant. Therefore, as expected, adsorption on glass is negligible, taking into account the high ionic concentration, *i.e.* the strong eluting power of the eutectic LiCl-KCl.

From these experiments, the ions examined can be arranged according to the solubility of the oxides in LiCl-KCl eutectic and these solubilities correspond to those found by DELARUE<sup>9</sup> by dissolving the oxides in the LiCl-KCl eutectic.

(b) *Electrophoresis of inorganic ions*

The electrophoretic behaviour was determined in anhydrous eutectic under anhydrous nitrogen (99.998 % purity) for those ions moving freely in the chromatographic experiments. All the preliminary operations took place in a dry-box as already described. The results reported in Table II show that  $\text{UO}_2$ (II) gives an anionic complex and Cr(III), Ni(II), Tl(I) and Mn(II) behave as cations.

TABLE II  
MOVEMENT OF INORGANIC IONS IN FUSED ANHYDROUS  
LiCl-KCl EUTECTIC AT 450° AND 3.3 V/cm

Ions	Distance (cm) moved in a h
Mn(II)	4 (+)
Ni(II)	4 (+)
Tl(I)	12 (+)
Cr(III)	13 (+)
Fe(III)	0 *
Th(IV)	0 *
$\text{CrO}_4$ (II)	1 (—)
$\text{CrO}_3$	1 (—)
$\text{UO}_2$ (II)	2 (—)

(+) Movement towards cathode; (—) movement towards anode. Values are from center of initial spot to center of zone after moving.

\* Insoluble precipitate formed.

In order to study the electrophoretic behaviour of Fe(III) and Th(IV) in molten LiCl-KCl eutectic, some experiments using a stream of anhydrous hydrogen chloride, were carried out. As shown earlier, however, in an anhydrous hydrogen chloride atmosphere, the glass fiber paper cannot be wetted by the eutectic. Therefore, the glass fiber strip was first impregnated in a nitrogen atmosphere, then the dehydration with a stream of anhydrous hydrogen chloride was performed. Under these conditions, diffusion of the ions along the whole strip was observed in a very short time ( $\sim 1$  h) without any applied e.m.f.

Therefore, we were not able to obtain any information about the electrophoretic behaviour of Fe(III) and Th(IV) in molten LiCl-KCl eutectic.

The electrophoretic behaviour of some ions giving soluble oxides has been reported elsewhere<sup>2</sup>. It has to be pointed out that ions precipitating as oxides at the application

point, showed rather high mobilities once the  $O^{2-}$  ion concentration in the melt was lowered (see conditions in Table II).

The  $CrO_4^{2-}$  ion shows a very slight mobility similar to that shown by  $CrO_3$ . This could be due to a decomposition of the  $CrO_4^{2-}$  into  $CrO_3$  and  $O^{2-}$



The chromic anhydride formed, is soluble in the molten eutectic in its molecular state<sup>8</sup>, so that elution to the front in chromatography and no movement in electrophoresis would be expected. This has been confirmed experimentally. The  $CrO_4^{2-}$  ion can only exist in the melt in appreciable concentration in the presence of a relatively high  $O^{2-}$  ion concentration. Therefore, the electrophoretic mobility must be related to the equilibrium constant of reaction (2) and to the  $O^{2-}$  ion concentration. Only when complete elimination of  $O^{2-}$  ions has been achieved, could chromic anhydride be used for the determination of the electroendosmotic effect in fused salts. Owing to the electroendosmotic effect, the data reported in Table II for chromic anhydride are not necessarily conclusive as it is difficult to avoid completely traces of  $O^{2-}$  ions, using glass fiber paper as support.

#### CONCLUSIONS

The results obtained indicate that electrophoresis of inorganic ions in molten LiCl-KCl eutectic is only possible, without special precautions, for ions forming soluble oxides in this melt. For ions forming insoluble oxides a dehydrated eutectic and an atmosphere of an inert anhydrous gas, *viz.* pure nitrogen, is necessary.

Chromatography in fused salts proved to be a very simple method for obtaining information concerning the relative solubility of various oxides. Electrophoresis in fused salts proved to be useful in providing information about the nature of the ions in fused salts. The different electrophoretic mobilities and solubilities of the oxides in a particular eutectic can be used to achieve separation of inorganic ions.

#### ACKNOWLEDGEMENTS

The authors wish to express their thanks to Prof. V. CAGLIOTI and Dr. M. LEDERER for helpful discussions.

#### SUMMARY

The chromatographic and electrophoretic behaviour of different metal ions dissolved in LiCl-KCl eutectic was studied. It was found that:

(a) Traces of water in the eutectic precipitate metal ions forming sparingly soluble oxides in fused alkali chlorides.

(b) The ions examined did not react with the glass fiber paper employed as support.

(c) When the ions to be examined are easily oxidized or give sparingly soluble oxides in molten chlorides the experiments must be performed in an inert gas atmosphere (water and oxygen free).

The chromatographic and electrophoretic behaviour of some inorganic ions is reported and the electroendosmotic effect in fused chlorides, employing glass fiber paper as support, is discussed.

## REFERENCES

- <sup>1</sup> G. ALBERTI AND G. GRASSINI, *J. Chromatog.*, 4 (1960) 425.
- <sup>2</sup> G. ALBERTI, G. GRASSINI AND R. TRUCCO, *J. Electroanal. Chem.*, 3 (1962) 283.
- <sup>3</sup> R. A. BAILEY AND A. STEGER, *J. Chromatog.*, 1 (1963) 122.
- <sup>4</sup> W. J. BURKHARD AND J. D. CORBETT, *J. Am. Chem. Soc.*, 79 (1957) 6361.
- <sup>5</sup> D. M. GRUEN AND R. L. MCBETH, *J. Inorg. Nucl. Chem.*, 9 (1959) 290.
- <sup>6</sup> C. EDELEANU, J. G. GIBSON AND R. LITTLEWOOD, *J. Appl. Chem.*, 12 (1962) 305.
- <sup>7</sup> H. A. LAITINEN AND C. A. LIU, *J. Am. Chem. Soc.*, 80 (1958) 1015.
- <sup>8</sup> G. DELARUE, *J. Electroanal. Chem.*, 1 (1960) 285.
- <sup>9</sup> G. DELARUE, *Bull. Soc. Chim. France*, (1960) 1654.

*J. Chromatog.*, 15 (1964) 420-427