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PAPER ELECTROPHORESIS AND CHROMATOGRAPHY OF URANIUM(VI)
IN CHLORIDE-ORGANIC SOLVENT MEDIA

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SUMMARY

The electromigration of uranium(VI) using paper as carrier and its chromatographic behaviour in hydrochloric acid (0.5–5 *M*) and metal chloride solutions containing varying amounts of ethanol or acetone is reported. The influence of the concentration of the ligands, as well as that of the organic solvents on the complex formation, and the significance of the solvation state of the uranyl species, as well as the influence of the potential gradient applied, are discussed.

INTRODUCTION

The first report on electromigration in uranyl chloride solutions was given by DITTRICH¹, who found that uranium(VI) moved to the cathode. BACHELET *et al.*² observed cationic motion of uranium(VI) in mixtures of HCl and NaCl of high concentration applying potential gradients of 5–50 V/cm. Cationic migration was observed in 0.1 *M* solutions of HCl, KCl and NH₄Cl by MUKERJEE³ and in 0.1 *M* HCl by MOJUMDAR⁴.

This paper describes an investigation on the electromigration of uranium(VI) in hydrochloric acid and metal chloride solutions containing ethanol or acetone, dependent on the ligand concentration and on the content of the organic solvent of the solution, as well as on the voltage applied. The purpose of these electrophoresis studies was to obtain information about the complex formation in chloride solutions containing organic solvents. The investigation on the paper chromatographic behaviour of uranium(VI) in these systems should complete the studies.

EXPERIMENTAL

Whatman No. 3 paper and Schleicher & Schüll 2043b Mgl were used as carriers. Solutions of uranium(VI) were prepared from UO₂(NO₃)₂·6H₂O (Riedel de Haën A.G., Seelze b. Hannover) by repeated evaporation with conc. HCl. The chloride concentration of these solutions containing uranium (5 mg/ml) was, in each case, as high as that of the electrolyte system studied.

The technique of electrophoresis and chromatography used has been reported in a previous paper⁵. The electropherograms and chromatograms were dried at 130°. As the details of the determination of the mean migration distance and of the possibilities of quantitative interpretation of the data, as well as the widest range of voltage that can be applied have already been discussed⁵, no further description will be given here.

Each system was investigated in the widest range of voltage possible.

RESULTS AND DISCUSSION

Solutions containing ethanol

If the distance of migration, d , is plotted against the period of electrophoresis, t , the resulting straight line indicates that the composition of the solution is constant during the electrophoresis. This is the case during the first 20 min in chloride systems containing ethanol. After longer periods, the evaporation of ethanol results in changes of the complex formation, and hence in a flexure in the curve; whereas in aqueous solutions the composition of the system is constant during a period of 60 min.

The slope of the $d-t$ curves represents the macroscopical velocity of migration, $v_t = \delta d / \delta t = z e_0 \xi / 6 \pi \eta r_i^*$. Assuming that only one kind of migration species is present in the solution, the velocity should increase in a solution of constant composition in the same relation as the applied voltage (that is 1:1). This is not the case in all systems, e.g. in 2.5 M HCl-80 vol. % ethanol (Fig. 1). According to the comprehensive explanations previously given⁵, the existence of several differently charged migrating species should be considered in these systems, though cations and neutral species predominate in the solution.

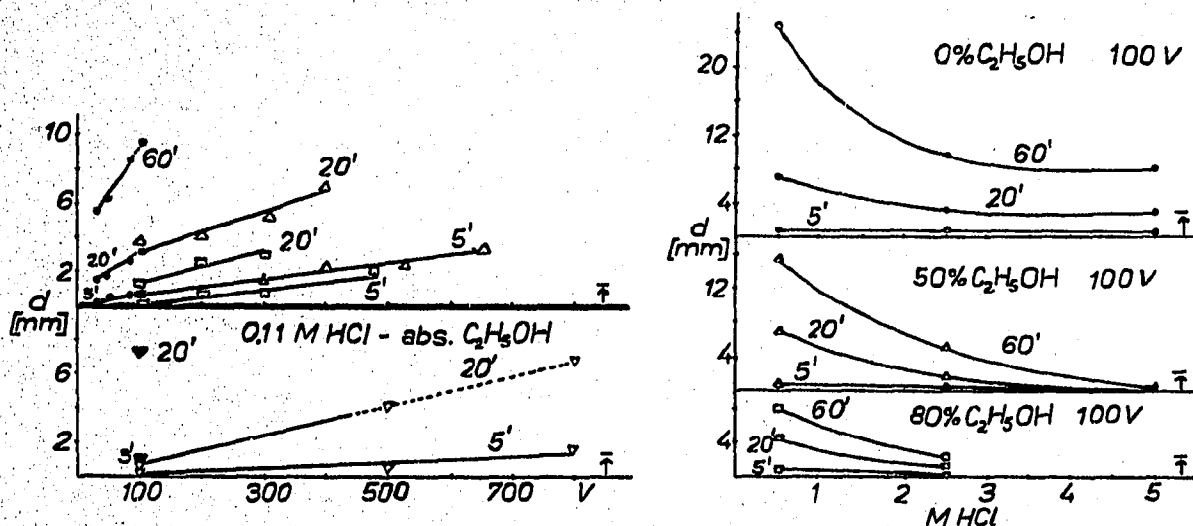


Fig. 1. Migration distance of uranium with changing potential at different acid and ethanol concentrations and after various periods of electrophoresis. 100 V voltage corresponds to a potential gradient of about 5 V/cm, 300 V to 15 V/cm, 500 V to 25 V/cm and 800 V to 40 V/cm. —●—, 2.5 M HCl; —△—, 0.5 M HCl-80 vol. % ethanol; —□—, 2.5 M HCl-80 vol. % ethanol; —▽—, 0.11 M HCl-absolute ethanol. For comparison values in 0.5 M HCl are presented, —▼—.

Fig. 2. Migration distance with changing acid concentrations at different ethanol concentrations at a constant potential (100 V) after various periods of electrophoresis. —○—, 0% ethanol; —△—, 50 vol. % ethanol; —□—, 80 vol. % ethanol; —●—, extrapolated values.

* r_i corresponding to ionic charge; ξ = field strength; η = viscosity; r_i = ionic radius.

The migration distance and velocity depend on the position of the equilibrium of complex formation and on the ratio of the rate of complex formation and migration velocity of the ions involved.

In hydrochloric acid solutions containing ethanol, uranium is predominantly present as cationic and neutral species in the concentration range studied. No information about the nature of the cations (UO_2^{2+} to UO_2Cl^+) present can be obtained from these data, since quantitative interpretation of the results is not possible.

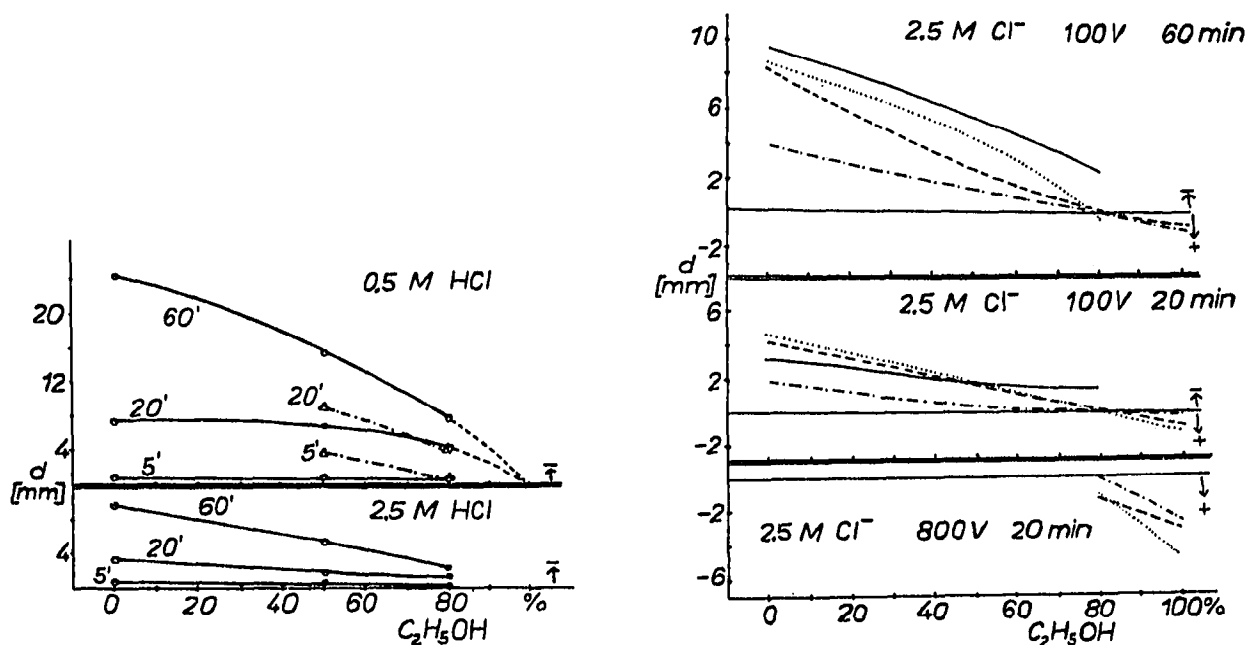


Fig. 3. Migration distance with changing ethanol concentrations at different acid concentrations and at different potentials after various periods of electrophoresis. —○—, 100 V; -·-△-·-, 200 V.

Fig. 4. Migration distance with changing ethanol concentrations at a constant ligand concentration (2.5 M Cl^-) at different potentials after various periods of electrophoresis. —, HCl; - - - -, LiCl; ·····, MgCl_2 ; -·-·-, AlCl_3 .

Increasing acid concentration (Fig. 2) as well as increasing content of ethanol (Fig. 3) increase the formation of higher complexes. The higher the amount of the neutral species, the smaller the cationic migration. In 5 M HCl–60 vol. % ethanol solutions no migration occurs at all at 100 V. Although only overall cationic migration can be observed in the systems studied, in solutions with a high amount of ethanol, the existence of anionic species seems to be possible, as has been mentioned above.

Addition of ethanol increases the complex formation as the dielectric constant of the mixture decreases, and hence the ionic interaction increases. The cationic species are not only stabilized by a solvate shell in aqueous solutions but also in ethanol to some extent, since in solutions containing dry HCl dissolved in absolute ethanol cationic migration was observed (Fig. 1).

The complex formation is increased in the salt solutions studied (Figs. 4 and 5). In systems containing a chloride concentration of 2.5 M and 80 vol. % ethanol or 5 M $[\text{Cl}^-]$ and 60 vol. % ethanol, the amount of the anionic species (UO_2Cl_3^-) is noticeable. In solutions in which the salt has been dissolved in pure ethanol, the amount of the anions is great, since anionic migration occurred. Usually the cationic

migration increases in the following order: $\text{AlCl}_3 < \text{LiCl} < \text{MgCl}_2 < \text{HCl}$. The explanation of these data is rather difficult since the situation in solutions of the same Cl^- concentration is complicated by the influence of the varying pH value, viscosity, dielectric constants and activity coefficients. (The electrode compartments contained 50 ml of salt and 10 ml of acid solution.) The pH of the salt solutions is lower than that of the acid systems, and hence hydrolysis and polymerization yielding higher uranium aggregates might be possible. There is a possibility that in acid solutions the anions UO_2Cl_3^- and the hydronium ions form ion pairs, that is neutral units, whereas the ionic association in salt solutions, especially if higher charged cations are involved, is less probable.

Solutions containing acetone

The composition of aqueous acid solutions containing acetone is constant during the first 12–13 min of electrophoresis. In these systems the capillary effect is also more significant.

Increasing acid and acetone concentrations increase the complex formation.

The voltage dependence of the migration⁵ indicates that in 2.5 and 5 M solutions of considerable acetone concentration differently charged species, cations and anions, are present. The inversion of the migration direction with increasing voltage in 2.5 M HCl–60 vol. % acetone solutions, for instance, is due to the high amount of the anionic complexes (UO_2Cl_3^-) in these solutions (Fig. 7). In solutions of 60 vol. % acetone, cations and neutral species predominate in about 0.5–1 M HCl, whereas in 4–5 M HCl predominantly anions are present (Fig. 6). As expected, the inversion of the migration direction occurs in solutions of an acid concentration (Fig. 6) or of an acetone content (Fig. 7) which are lower, the higher the voltage applied. Anionic migration can be clearly observed in all systems containing no or only small amounts of "free" water (e.g. 5 M HCl–60 vol. % acetone, 2.5 M HCl–80 vol. % acetone). (It should be mentioned that in such media condensation reactions take place altering the viscosity,

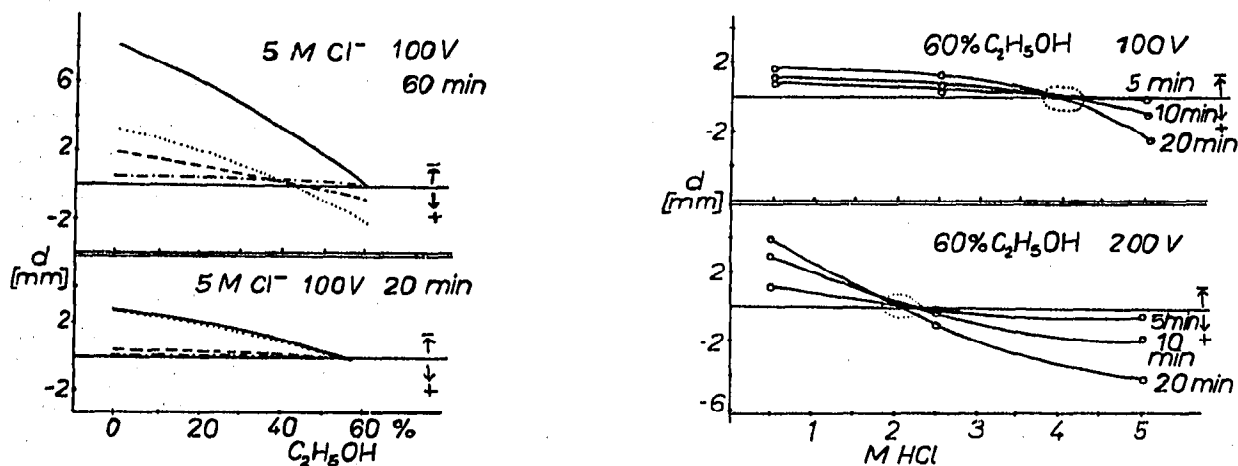


Fig. 5. Migration distance with changing ethanol concentrations at constant ligand concentration (5 M Cl^-) and at a constant potential (100 V) after various periods of electrophoresis. —, HCl; ----, LiCl; ·····, MgCl_2 ; -·-·-, AlCl_3 .

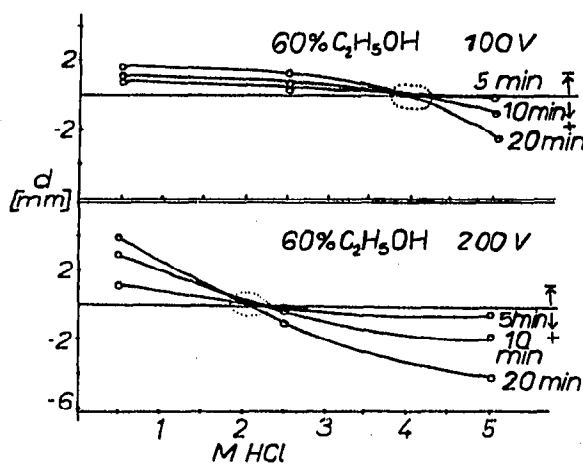


Fig. 6. Migration distance with changing acid concentrations at a constant acetone concentration (60 vol. %) at different potentials after various periods of electrophoresis.

the composition and hence the dielectric constants of the solutions and the tendency to complex formation.) In these solutions only one kind of migrating species, that is anions, exists.

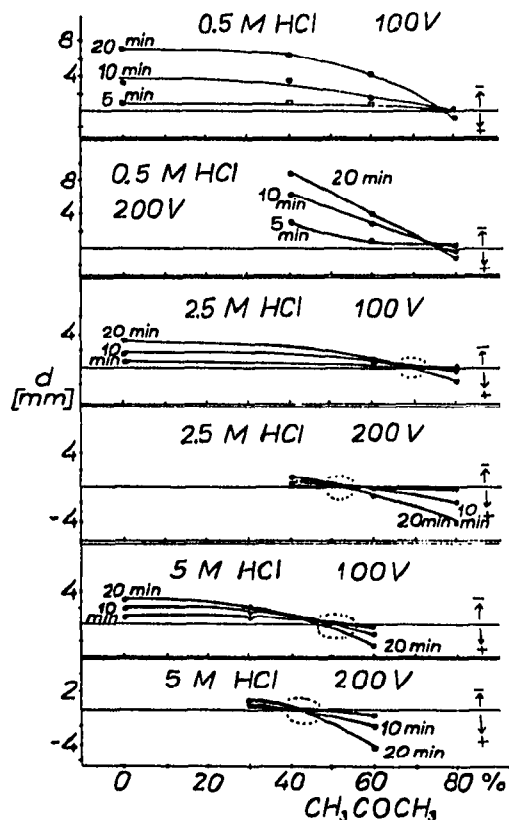


Fig. 7. Migration distance with changing acetone concentrations at different acid concentrations and at different potentials after various periods of electrophoresis.

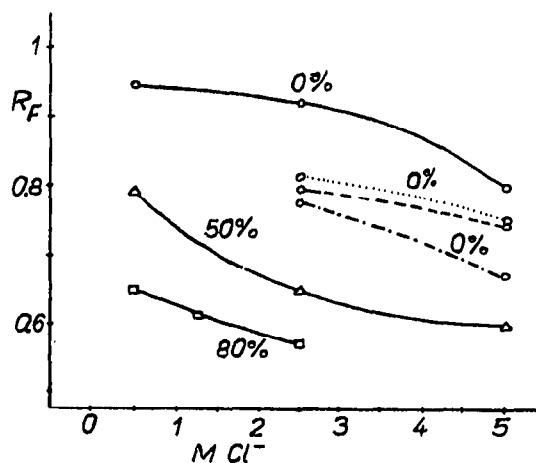


Fig. 8. R_F values with changing ligand concentrations at various ethanol concentrations. —, HCl; ---, LiCl; ·····, $MgCl_2$; -·-·-, $AlCl_3$.

Concerning the complex formation and hence the migration in the systems containing ethanol or acetone, the discrepancy observed may be due to the different solvation tendency of the solvents studied. Ethanol, but probably not acetone, is able to stabilize the uranyl cations by a solvate shell. This would explain the increased complex formation in acetone solutions.

Paper chromatographic behaviour

Data on paper chromatographic behaviour are presented in Figs. 8–II. Increasing ligand concentrations as well as increasing concentrations of organic solvents decrease the R_F values in all systems in which, on the one hand, overall cationic migration or no movement and, on the other hand, an increase in the distribution on anion exchange resins⁶ can be observed. This decrease in mobility is due to the increased formation of neutral complexes. The R_F values increase in systems in which overall anionic migration and a decrease in the distribution occur. This increase in the mobility can be explained by an increase in the amount of the ionic species in the solution.

In any case, the higher the amount of the ionic species in solution—regardless of whether cations or anions are involved—the higher the R_F value. The ions seem to prefer the mobile phase. A minimum of the curve indicates that formation of neutral complexes and subsequently that of anions take place.

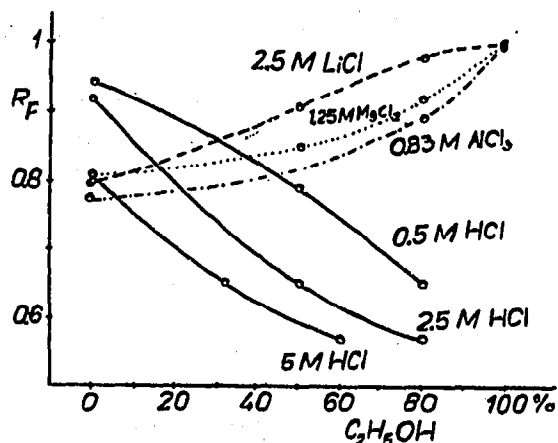


Fig. 9. R_F values with changing ethanol concentrations at various ligand concentrations. —, HCl; - - - - , LiCl; ······, $MgCl_2$; - · - · - ·, $AlCl_3$.

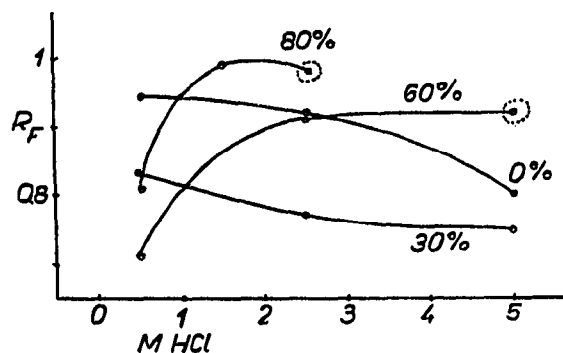


Fig. 10. R_F values with changing acid concentrations at various acetone concentrations. ⊙, systems which do not contain any "free" water.

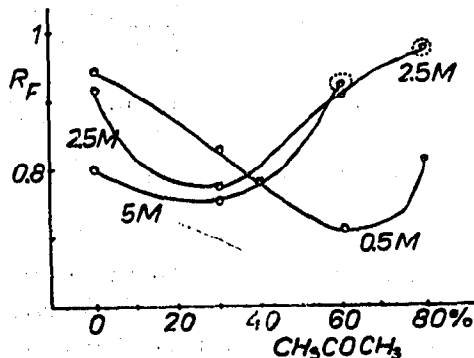


Fig. 11. R_F values with changing acetone concentrations at various acid concentrations. ⊙, systems which do not contain any "free" water.

All data obtained from acid solutions containing ethanol or acetone agree with the results on anion exchange of SCHNEIDER⁶. There is a fairly good agreement between the data obtained from aqueous acid solutions and the results of JØRGENSEN and MARCUS. According to JØRGENSEN⁷ in 1 M HCl $[UO_2Cl(H_2O)_n]^+$ is present and according to MARCUS⁸ in 0.5–4 M HCl UO_2Cl^+ and in 4–6 M HCl UO_2Cl_2 exists. It should be emphasized that the distance as well as the direction of migration depends greatly on the voltage applied; and therefore, for instance, cationic motion can occur at 100 V even in a solution in which the neutral species predominate!

The chromatographic data agree with the results reported in the literature^{9, 10}.

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