

ELECTROPHORESIS OF LANTHANIDES, Sc, Th, U AND Zr IN GLYCOLIC ACID

R. A. GUEDES DE CARVALHO

Centro de Estudos de Química Nuclear, Faculdade de Engenharia, Porto (Portugal)

(Received September 22nd, 1964)

Hydrocarboxylic acids in general, and particularly lactic acid, have been extensively used as eluants in lanthanide separations using cationic exchangers¹⁻³. Several papers on formation constants of glycolate, lactate and α -hydroxybutyrate complexes of lanthanides have appeared recently⁴⁻⁶. KONRAD-JAKOVAC AND PUČAR⁷⁻⁹ describe a paper electrochromatographic technique to separate lanthanides using lactic acid as eluant.

CHOPPIN *et al.*^{6,10} have proved that anionic complexes of the type ML_4^- (L = glycolate, lactate, α -hydroxybutyrate) are formed in solutions with high concentrations of ligand. Based on this fact the present paper describes the influence of pH and glycolate ion concentration of the electrolyte in the separation of lanthanides. Further work will deal with a similar study with lactic and α -hydroxybutyric acids.

EXPERIMENTAL

The technique used has been described elsewhere¹¹. Solutions of 0.1 M lanthanide perchlorate were used. Alcoholic solutions 0.005 % of 8-hydroxyquinoline and 0.1 % of xlenol orange were employed as reagents for detection.

In the preliminary experiments only La, Gd and Yb were used as representatives of light, medium and heavy lanthanides.

RESULTS

To determine the most suitable voltage for use, experiments were carried out at 2, 6, 9 and 12 V·cm⁻¹. As had already been observed in a former paper¹¹, the mobility (expressed as cm²·V⁻¹·h⁻¹) is dependent on the voltage used.

Fig. 1 shows the electrophoregram obtained with 9 V·cm⁻¹, which was the value selected for all experiments. Neutral spots of Gd and Yb (same mobility as hydroquinone) are observed. The composition possible of the species present is indicated for gadolinium in the figure. The separation of these species increases as applied voltage increases.

In a second series of experiments the influence of electrolyte concentration was determined. The results are shown in Fig. 2 and the following conclusions can be drawn:

- (a) The spots are always cationic whatever the electrolyte concentration.
- (b) The spots are more elongated with low concentrations of electrolyte.

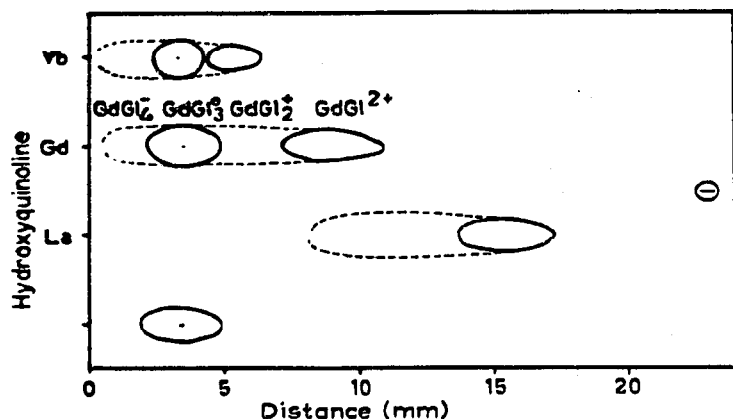


Fig. 1. Electrophoregram obtained under the following conditions: Electrolyte: glycolic acid (1%) neutralized with NaOH to pH 5; voltage: $9 \text{ V}\cdot\text{cm}^{-1}$; time: 3 h.

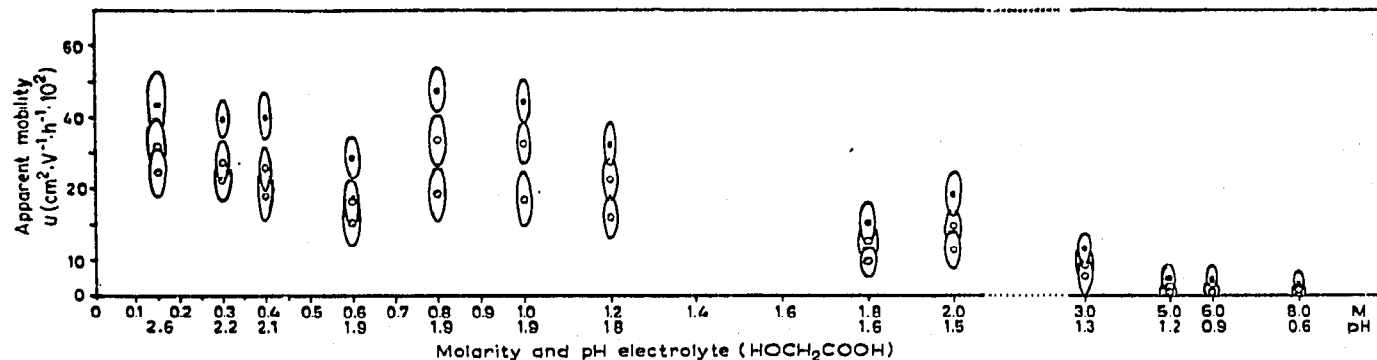


Fig. 2. Variation of mobility of La, Gd and Yb with electrolyte molarity (glycolic acid). Cationic spots: ● = La; ○ = Gd; ○ = Yb. Voltage: $9 \text{ V}\cdot\text{cm}^{-1}$; time: 3 h.

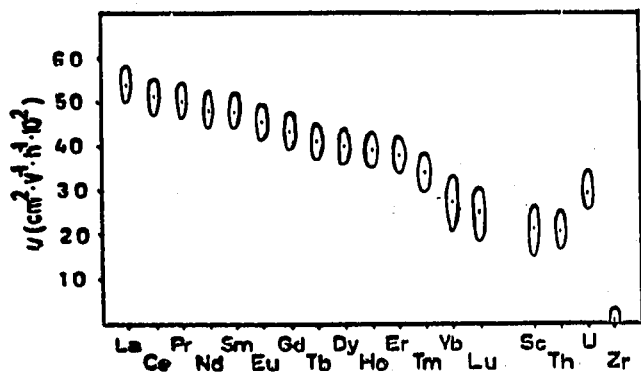


Fig. 3. Mobilities in 1 M glycolic acid. Voltage: $9 \text{ V}\cdot\text{cm}^{-1}$; time: 3 h.

(c) The separation factor of the three spots has a maximum between 0.8 and 1.0 *M* glycolic acid.

(d) Up to a concentration of 2.0 *M* the separation of La from Yb is always possible and complete. Between 0.8 and 1.0 the separation of the three elements is also complete.

The mobilities of all the lanthanides, and also of Sc, Zr, Th and U, were determined using 1.0 *M* glycolic acid as electrolyte. Fig. 3 shows the results obtained and thus the possibility of separations.

The influence of the concentration of electrolyte with a fixed pH was studied in the experiments represented in Fig. 4, where glycolic acid solutions varying from 0.5 to 4.0 % and neutralized to pH 5.0 were used as electrolytes.

Experiments represented in Fig. 5 were made using 1.0 *M* glycolic acid, partially neutralized with NaOH, in order to determine the minimum concentration of glycolate ion necessary to change the charge of La.

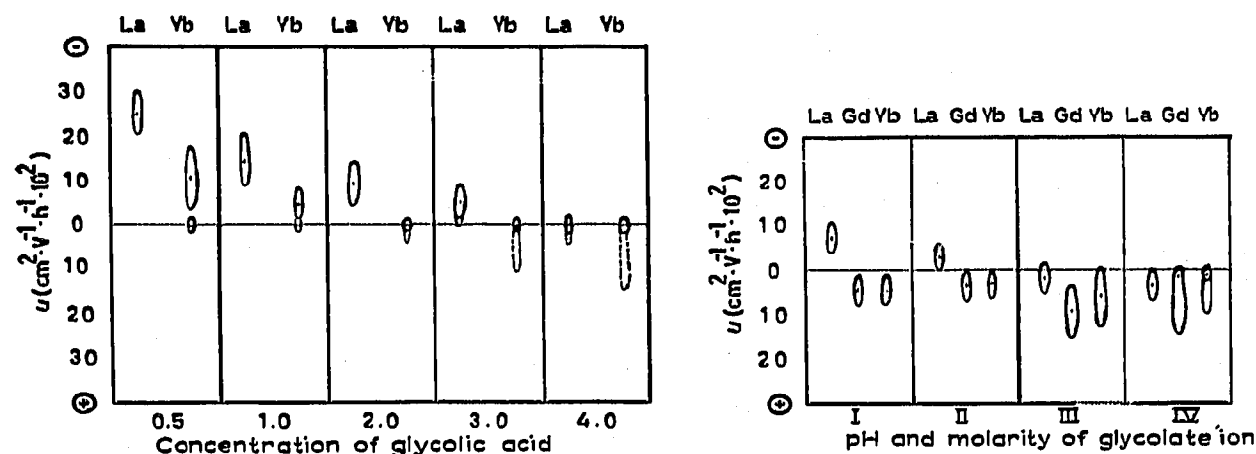


Fig. 4. Variation of mobility of La and Yb with concentration of glycolic acid partially neutralized to pH 5.

Fig. 5. Variation of mobility with concentration of glycolate ion. (I) 0.10 *M*, pH 2.55; (II) 0.18 *M*, pH 2.90; (III) 0.26 *M*, pH 3.20; (IV) 0.33 *M*, pH 3.40.

DISCUSSION

The experimental results indicated in Fig. 1 are in accordance with the stability constants of the glycolates, which increase with the atomic number of the lanthanides⁶ and so greater concentrations of neutral and anionic species will exist in heavier lanthanides.

Lanthanum is cationic when $[\text{HOCH}_2\text{COO}^-] \ll 0.2$ *M* and anionic at higher concentrations. Gadolinium and lutetium are anionic when $[\text{HOCH}_2\text{COO}^-] \geq 0.1$ *M*.

Several experiments were performed to determine the possibility of separation by a gradient of glycolate ion concentration in the electrolyte. But the irregularity of the neutralization front, the lengthening of anionic species (presumably due to the simultaneous presence of neutral and anionic species) and the formation of insoluble glycolates of heavier lanthanides (Yb and Lu) when glycolate concentrations increase, did not permit satisfactory separations.

Except when the signs of the electrical charges of the ionic species are different, the conditions of Fig. 3 (1.0 *M* glycolic acid without neutralization) are to be preferred when separating lanthanides by electrophoresis.

SUMMARY

The influence of the concentration of glycolic acid and glycolate ion in the electrophoresis of lanthanides is studied. The best conditions for lanthanide separation are with 1.0 *M* glycolic acid without neutralization. The sign of the predominant ionic species depends on the concentration of glycolate ion. Above 0.3 *M* glycolate all the lanthanides are anionic.

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J. Chromatog., 18 (1965) 381-384