

CHROM. 7466

Note

High-voltage paper electrophoresis of Hg(II), Cd(II), Pb(II) and Cu(II) in aqueous solution of EDTA and glycolic acid

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(First received February 18th, 1974; revised manuscript received March 15th, 1974)

The electrophoretic mobilities of divalent mercury, cadmium, lead and copper ions in various inorganic and organic acids have been investigated by many workers¹⁻⁶ by both low- and high-voltage electrophoresis: in many instances ethylenediamine-tetraacetic acid (EDTA) was used as an electrolyte.

In this paper the results of an electrophoretic investigation of the behaviour of mercury, cadmium, lead and copper ions as a function of EDTA and glycolic acid concentrations are given. The electrophoretic mobility curves obtained showed the formation of metal complexes at certain electrolyte concentrations. Separation of the ions was achieved on the basis of different ionic mobilities under defined experimental conditions.

EXPERIMENTAL

EDTA disodium salt (Titriplex III, E. Merck, Darmstadt, G.F.R.) solution in the concentration range $1 \cdot 10^{-6}$ – $1 \cdot 10^{-2}$ M at pH 7 and unbuffered glycolic acid solution of concentration $1 \cdot 10^{-3}$ – $3 \cdot 10^{-1}$ M (Koch-Light, Colnbrook, Great Britain) were used as electrolytes. A Beckman Zeromatic pH meter was utilized for measurements of the pH of the solution.

Aliquots of 0.001 ml of mercury(II), cadmium(II), lead(II) and copper(II) chloride or nitrate solutions (ion concentration *ca.* $2 \text{ mg} \cdot \text{ml}^{-1}$) were placed centrally on Whatman 3MM papers ($100 \times 2 \text{ cm}$): mercury(II) nitrate was employed throughout. Papers washed free from chloride ions gave the same results as unwashed papers. High-voltage paper electrophoresis was performed by using a Virus-type chamber with an agar-agar bridge, platinum electrodes and a Cryomate Laude 30D as the cooling system at a temperature of $0 \pm 0.2^\circ \text{C}$, a $60 \text{ V} \cdot \text{cm}^{-1}$ potential gradient and strip stream up to 6 mA for 45 min. For identification of ions a solution of dithizone in acetone was used⁷.

RESULTS AND DISCUSSION

The mobilities of the ion zones separated by electrophoresis ($U_z \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$) were calculated by use of the expression $U_z = d_E \cdot L_j / t \cdot V$ (refs. 7-9), where d_E is the ion distance (in centimetres) travelled under the influence of the electric field, corrected

for electro-osmosis, L the length of the paper strip in centimetres, t the time in seconds and V the applied voltage.

The correction for electro-osmosis is obtained by using the expression $d_E = D - D_{H_2O_2}$, where D is the ion electrophoretic mobility observed and $D_{H_2O_2}$ is the mobility of hydrogen peroxide determined under the same experimental conditions as used for the moving ions. The identification of hydrogen peroxide was performed by using 5% potassium iodide solution. Conventionally, the mobility of the ion towards the cathode was taken as positive and the mobility towards the anode as negative.

Table I gives U_Z values for the EDTA disodium salt solutions. Each value represents the average of 3-8 independent determinations. Fig. 1 shows U_Z as a function of the logarithm of the complexing acid concentration.

TABLE I

ELECTROPHORETIC MOBILITY OF Hg^{2+} , Cd^{2+} , Pb^{2+} AND Cu^{2+} IN EDTA

Electric field 60 V/cm; time 45 min; temperature 0 ± 0.2 .

Na_2 -EDTA concentration (M)	U_Z ($cm^2 \cdot V^{-1} \cdot sec^{-1}$) $\times 10^{-3}$			
	Hg^{2+}	Cd^{2+}	Pb^{2+}	Cu^{2+}
$1 \cdot 10^{-6}$	-0.013	0.655	-0.013	-0.034
$1 \cdot 10^{-5}$	-0.118	0.630	-0.068	-0.061
$3 \cdot 10^{-5}$	-0.600	0.385	-0.155	-0.067
$5 \cdot 10^{-5}$	-1.200	0.919	-0.108	0.064
$8 \cdot 10^{-5}$	-1.208	0.983	-1.091	1.135
$1 \cdot 10^{-4}$	1.116	0.973	-1.020	0.988
$5 \cdot 10^{-4}$	1.315	1.233	1.277	1.280
$1 \cdot 10^{-3}$	1.553	1.257	1.378	1.413
$1 \cdot 10^{-2}$	1.595	1.311	1.383	1.456

By the analysis of the shape of the electrophoretic curves obtained, it is possible to determine the electric charge and the type of ion complexes formed. It is evident from Fig. 1 that the mobilities of mercury(II), lead(II) and copper(II) ions are about zero and the cadmium(II) ion moves towards the cathode at low EDTA disodium

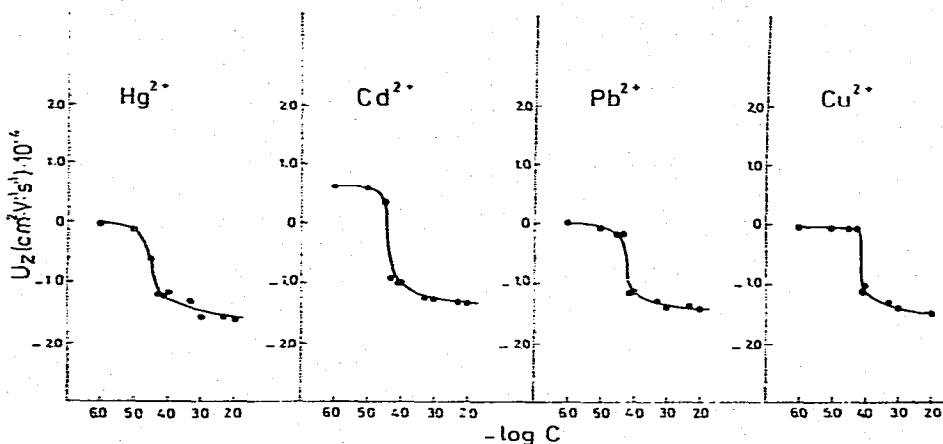


Fig. 1. Electrophoretic mobility of Hg^{2+} , Cd^{2+} , Pb^{2+} and Cu^{2+} versus log (EDTA concentration).

TABLE II

ELECTROPHORETIC MOBILITY OF Hg^{2+} , Cd^{2+} , Pb^{2+} AND Cu^{2+} IN GLYCOLIC ACID
Electric field 60 V/cm; time 45 min; temperature $0 \pm 0.2^\circ$.

Glycolic acid		U_z ($cm^2 \cdot V^{-1} \cdot sec^{-1}$) $\times 10^{-4}$			
Concentration (M)	pH	Hg^{2+}	Cd^{2+}	Pb^{2+}	Cu^{2+}
$1 \cdot 10^{-3}$	3.60	-0.038	-0.916	-0.104	-0.137
$1 \cdot 10^{-2}$	3.00	-0.050	-1.423	-0.967	-0.836
$5 \cdot 10^{-2}$	2.65	-0.133	-1.618	-1.323	-1.033
$1 \cdot 10^{-1}$	2.45	-0.159	-1.710	-1.460	-1.066
$3 \cdot 10^{-1}$	2.20	-0.322	-1.863	-1.530	-0.989

salt concentrations (10^{-6} – 10^{-5} M). Bearing in mind the concentration and the pH of the complexing agent, the results could be explained by the formation of hydrolysis products of the ions investigated. With increasing concentration of the electrolyte, the ions move towards the anode. At EDTA disodium salt concentrations in the range 10^{-4} – 10^{-2} M, a plateau is formed on the curve, indicating the formation of an anionic complex, most probably of the ML^{2-} type (taking EDTA as H_4L) in agreement with published data^{10,11}. It can be seen in Fig. 1 that a mercury(II) complex is formed at an EDTA disodium salt concentration of $5 \cdot 10^{-5}$ M. Absolute values of U_z for the anionic complexes follow the order $Hg > Cu > Pb > Cd$.

From the results obtained it is evident that cadmium(II) can be separated from the mixture of all four ions at EDTA disodium salt concentrations of 10^{-6} – 10^{-5} M. Separations of mercury(II)–cadmium(II), mercury(II)–lead(II) and copper(II)–cadmium(II) are achieved with an EDTA disodium salt concentration of $5 \cdot 10^{-3}$ M for 90 min.

Table II and Fig. 2 show the behaviour of the four ions in glycolic acid. When this hydroxymonocarboxylic acid is applied as an electrolyte, copper(II), lead(II) and cadmium(II) ions show cationic mobility. At glycolic acid concentrations in the range $5 \cdot 10^{-2}$ – $3 \cdot 10^{-1}$ M a plateau is observed on the mobility curve for copper(II), which

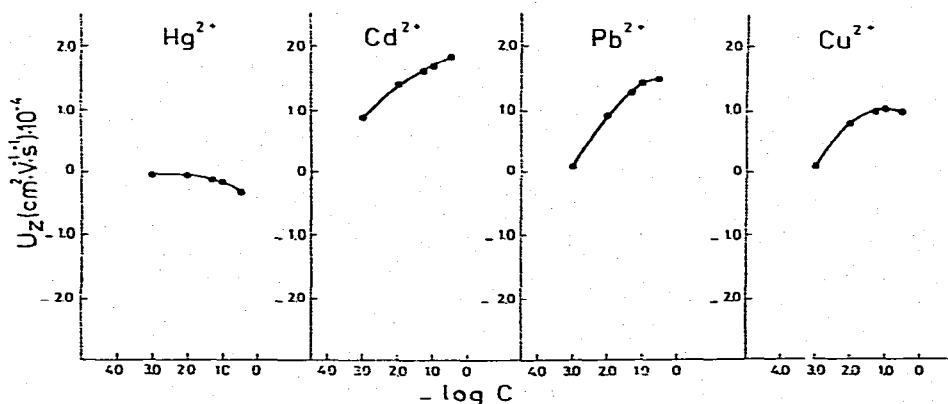


Fig. 2. Electrophoretic mobility of Hg^{2+} , Cd^{2+} , Pb^{2+} and Cu^{2+} versus log (glycolic acid concentration).

indicates the formation of a mononuclear complex of the ML^+ type. Lead(II) and cadmium(II) also show a tendency to form such complexes. Judging from the stability constants given in the literature for cadmium, lead and copper glycolate complexes¹², the stability of monoligand complexes decreases in the order $Cu > Pb > Cd$. On the other hand, the electrophoretic mobility of the mercury(II) ion is about zero at the lower glycolic acid concentrations, which indicates the formation of a neutral complex. With increasing glycolic acid concentration, the mercury(II) ion shows anionic mobility.

The most successful separations of mercury(II), cadmium(II), lead(II) and copper(II) from the mixture of ions was achieved using 0.1 M glycolic acid with an electrophoretic run of 60 min. The electrophoretic mobilities followed the order $Cd > Pb > Cu > Hg$.

ACKNOWLEDGEMENT

The authors are grateful to Mrs B. Pavlovska for valuable assistance with the experiments.

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