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Original Research

Evaluation of Organic Ligands as Copper Complexing Agents Using the Isotachophoresis Method

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Abstract

The motion of ions in an electric field for solutions containing Cu^{2+} ions in the presence of 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), N-trismethylenephosphonic acid (NTMP) and N-(phosphonomethyl)imino-diacetic acid (PMIDA) was investigated using a capillary electrophoresis analyzer. Satisfactory agreement between the cation isotachophoretic determination results and the results calculated from the protonation constants of the relevant ligand species and the stability constants of copper complexes was obtained. The research results can be useful for the electrokinetic method of removing copper from soil.

Keywords: capillary isotachophoresis, phosphonic acids, copper, contaminated soil

Introduction

Soil can be cleaned directly on the contaminated site (*in situ*) or the surface soil can be transported to a treatment site (*ex situ*). Soil cleaning can be physical, chemical, biological and electrochemical. Physical methods include solvent extraction, ventilation and the chemical methods for example redox processes. The biological methods include bioremediation, biostimulation, bioaugmentation, biofiltration and composting. Thermal methods, in which soils subjected to high temperature are very efficiently cleaned of most pollutants (but not metals), are popular. Their disadvantage is that soil after such a treatment remains dead for many years and toxic products of organic compound combustion escape into the air. None of the above methods is universal, i.e. suitable for the removal of all kinds of contamination. Cleaning is usually done by several methods simultaneously.

Heavy metal soil contaminations are extremely toxic and do not undergo biodegradation. On the European Commission's list of substances most dangerous to the environment [1] one can find (among others): Cu, Ni, Cr, Pb, As, Sb, Ti, Sn, Co, Ag, Hg and Cd. There are many sources of metal soil pollution. Metals may be introduced into soil with artificial and natural fertilizers and pesticides. They are emitted in combined heat and power plant ashes and in ore treatment and smelting processes. A source of considerable metal contaminations, including the most toxic ones from galvanizing plants, is the chemical industry. Metals get into soil in scrapyards, rubbish dumps and scrap processing plants.

The main sources of copper contamination are: the copper mining and processing industry, electronics wastes, scrapyards, corrosion of copper and copper alloy products and pesticides. In a cultivated land down to a depth of 0.3 m the soil copper content should not exceed 36 mg/kg.

One of the experimental methods of removing heavy metals from soil is the electrokinetic method exploiting an electric field in which directed transport of ions occurs. The method's effectiveness depends mainly on transmuting the metal into such an ionic form which will show mobility in a soil solution when an electric field is applied. The two principal mechanisms of pollution transport in

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soil, electromigration and electroosmosis, are exploited here [2]. The former dominates when there are ions dissolved in water and the soil's zeta potential is negligible. The latter dominates when uncharged or poorly dissociated pollutants (e.g. hydrophobic compounds [3], phenols, etc.) are removed from soil with a significant zeta potential [4].

In order to increase the efficiency of removal of heavy metals immobilized in soil, weak acids and complexing or chelating compounds causing desorption of the metals and formation of water-soluble and charged complex compounds (chelates) are used [5-8]. When complexing agents are added to soil, heavy metals (e.g. Cu, Fe, Cd, Hg) are fixed in the form of appropriate anions [7, 9] and transported in the electric field towards the anode. From here they can be removed using conventional physicochemical methods while water in soil pores is transported exclusively towards the cathode and does not dilute the complexed metals being removed [7]. The so-called electrodialytic soil remediation (the electrokinetic method and electrodialysis combined) makes it possible to remove many heavy metals (including copper) from soil to a level significantly below the one allowable by the standards [10].

The knowledge of the charge and concentration of the particular forms of anion copper complexes formed with different ligands allows one to evaluate their suitability for the electrokinetic removal of this metal from soil.

Experimental Procedures

Our paper presents possibilities of using isotachophoresis for quick evaluation of selected ligands with regard to their suitability for the electrokinetic remediation of copper-contaminated soil. The motion of ions in an electric field was studied using a capillary electrophoresis analyzer. On the basis of the results the degree of complexing Cu^{2+} ions by selected phosphonic acids can be determined. Difficulties which may arise when isotachophoresis is used as an investigative technique are discussed.

Isotachophoresis – one of the capillary electrophoresis techniques [11, 12] – is a method of separating the components of a solution, which exploits the differences in the mobility of the particular ions in an electric field. It is also used for analytical purposes: qualitative and quantitative analyses of solutions. It allows one to draw conclusions concerning the mobility of specific cations and anions.

In the isotachophoresis method a sample of the tested solution is introduced into a capillary column to the interface between the leading electrolyte (LE) and the terminating electrolyte (TE). In order to analyze anions LE must contain an anion whose mobility is higher than that of the anions present in the tested solution, while TE contains an anion with the lowest mobility. Only the anions whose mobility is within the range in-between the LE and TE anion mobilities are analyzed. The same applies to the analysis of cations. This means that the choice of a system of LE-TE electrolyte solutions is of crucial importance.

A characteristic feature of isotachophoresis is that all the ions are separated into closely contiguous zones which in an electric field migrate with the same velocity to a given electrode. The lengths of the zones and ion concentrations in the zones stabilize so that the following equation is satisfied:

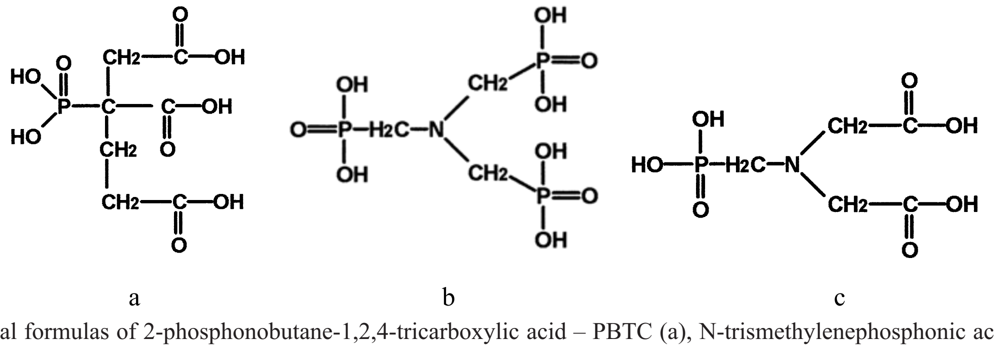
$$v = v_i = u_i \cdot E_i$$

where: v – the velocity of an ion in the electric field; u_i– the mobility of an ion; E_i – the electric field intensity in zone.

An EA 100 capillary electrophoresis analyzer manufactured by *Villa Labeco* (Slovakia) was used in the investigations. Its main part is a separating unit consisting of 2 capillaries differing in their diameter. The analyzer is equipped with conductivity and UV detectors. The conductivity of the solutions is measured by electrodes set in the capillary walls. The UV detector measures light adsorption at a wavelength of 254 and 289 nm.

2-phosphonobutane-1,2,4-tricarboxylic acid ($C_7H_{11}O_9P$ – PBTC), N-trismethylenephos-phonic acid ($C_3H_{12}O_9NP_3$ – NTMP) and N-(phosphonomethyl)iminodiacetic acid ($C_5H_{10}O_7NP$ – PMIDA) (Fig. 1) were selected as the agents complexing copper ions. All the above compounds were commercial laboratory-grade reagents used without further purification: NTMP – purity 98.0% and PMIDA – purity 97.0% (Fluka) and PBTC – as 50.0% water solution (Bayer [19]). All other reagents were of analytical grade and were used as supplied.

The isotachophoretic investigations were conducted at pH=6. The system of electrolytes was selected on the basis of literature reports [11-13] and in-house research [14-16]. It was decided to carry out the cation analysis in the following system:



a b c

Fig. 1. Structural formulas of 2-phosphonobutane-1,2,4-tricarboxylic acid – PBTC (a), N-trismethylenephosphonic acid – NTMP (b) and N-(phosphonomethyl)iminodiacetic acid – PMIDA (c).

Table 1. Protonation constants and stability constants of complexes with Cu^{2+} ions for investigated acids.

PBTC [19]		NTMP [17]		PMIDA [18]	
Equilibrium Quotient	Log K	Equilibrium Quotient	Log K	Equilibrium Quotient	Log K
$HL^{4-}/H^{+}\cdot L^{5-}$	10.8	$HL^{5-}/H^{+}\cdot L^{6-}$	12.1	$HL^{3-}/H^{+}\cdot L^{4-}$	10.29
$H_2L^{3-}/H^{+}\cdot HL^{4-}$	6.8	$H_2L^{4-}/H^{+}\cdot HL^{5-}$	7.30	$H_2L^{2-}/H^{+}\cdot HL^{3-}$	5.57
$H_3L^{2-}/H^{+}\cdot H_2L^{3-}$	4.9	$H_3L^{3-}/H^{+}\cdot H_2L^{4-}$	5.86	$H_3L^{-}/H^{+}\cdot HL^{2-}$	2.44
$H_4L^{-}/H^{+}\cdot H_3L^{2-}$	4.0	$H_4L^{2-}/H^{+}\cdot H_3L^{3-}$	4.64	$H_4L/H^{+}\cdot HL^{-}$	1.2
$H_5L/H^{+}\cdot H_4L^{-}$	1.8	$H_5L^{-}/H^{+}\cdot H_4L^{2-}$	1.5		
		$H_6L/H^{+}\cdot H_5L^{-}$	0.3		
$CuL^{3-}/Cu^{2+}\cdot L^{5-}$	7.6*	$CuL^{4-}/Cu^{2+}\cdot L^{6-}$	17.4	$CuL^{2-}/Cu^{2+}\cdot L^{4-}$	13.1*
$CuHL^{2-}/CuL^{3-}\cdot H^{+}$	4.5*	$CuHL^{3-}/CuL^{4-}\cdot H^{+}$	6.4	$CuHL^{-}/CuL^{2-}\cdot H^{+}$	6.2*
		$CuH_2L^{2-}/CuHL^{3-}\cdot H^{+}$	4.7		
		$CuH_3L^{-}/CuH_2L^{2-}\cdot H^{+}$	3.5		

* – Complex stability constants determined by the authors through potentiometric pH measurements (0.1 M KCl, 25ºC).

- LE: NaOH – $1.0\cdot10^{-2}$ mol/dm^3, 2-(N-morpholino)ethane sulphonic acid (MES), pH=5.7; methyl-2-hydroxyethyl cellulose (MHEC) – 0.1 %,
- TE: creatinine – $1.0\cdot10^{-2}$ mol/dm^3, HCl (0.01 mol/dm^3 - being added until pH=6.0 has been obtained).

Table 1 shows protonation constants and stability constants of the complexes with Cu^{2+} ions for three tested acids.

Results and Discussion

Information about the degree of complexing of copper ions can be obtained from a cation analysis using the analytical curve for Cu^{2+} ions. Isotachopherogram from analytical column detector for twice distilled water (analysis 'boundary') shows that no intermediate steps between the initial level (the leading ion) and the highest level (corresponding to the cation which migrates the slowest in the terminating electrolyte) are noticed. Thus the adopted system of electrolytes does not contain ions which would hinder correct interpretation of results, provided that its components do not react with the analyzed substance.

The isotachopherograms obtained from the analysis of cations in the standard solutions of $Cu(NO_3)_2$ show one distinct intermediate step at relative height h ≈ 12%, which corresponds to Cu^{2+} ions (Fig. 2a). In the tested concentration range the length of this step varies in direct proportion to the concentration of copper ions (correlation coefficient r=0.9998).

An analysis of solutions containing Cu^{2+} and PBTC allows one to determine the degree of complexing of copper ions. In the case of solutions in which the initial concentrations of Cu^{2+} and PBTC were 0.5, 1.0, 1.5 and 2.0 mmol/dm^3, an isotachophoretic analysis of the data obtained from the analytical column detector showed that the successive concentrations of copper ions were: 0.425, 0.839; 1.141 and 1.496 mmol/dm^3 (Fig. 2b). This means that less than 25% of Cu^{2+} was complexed by PBTC. By performing calculations based on the Cu(II)–PBTC complex stability constants shown in Table 1 one can demonstrate that at pH=6 in such conditions about 80% of the Cu^{2+} ions occur in a noncomplex form in the solution and about 20% in the form of Cu–PBTC^{3-}.

Since the zone with Cu^{2+} ions forms quite quickly, the concentration of the ions can also be determined on the basis of the results obtained from the preseparation column detector. The isotachopherograms for this column detector

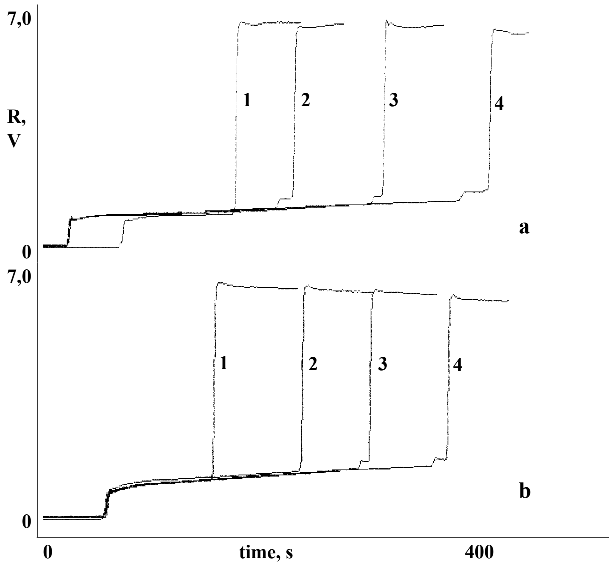


Fig. 2. Isotachopherograms obtained from analytical column detector for cation analysis in:
a – Cu^{2+}-ions containing solutions;
b – solutions containing equimolar concentration (mmole/dm^3) of PBTC and Cu^{2+} - ions. Curve 1 – 0.5; 2 – 1.0; 3 – 1.5; 4 – 2.0.

show a well-defined step for Cu^{2+} ions and the results differ by a maximum of 1.3% from the ones for the analytical column.

The weak complexing of Cu^{2+} ions by PBTC is confirmed by the isotachopherograms for the solutions in which Cu^{2+} and PBTC occurred in different concentrations. In the case of double excess of PBTC (c_{PBTC}= 1.0 mmol/dm^3; $c_{Cu(2+)}$= 0.5 mmol/dm^3) or double excess of Cu^{2+} (c_{PBTC}= 1.0 mmol/dm^3; $c_{Cu(2+)}$= 2.0 mmol/dm^3) the degree of complexing of the Cu^{2+} ions is, respectively, 45.8% and 14.4%.

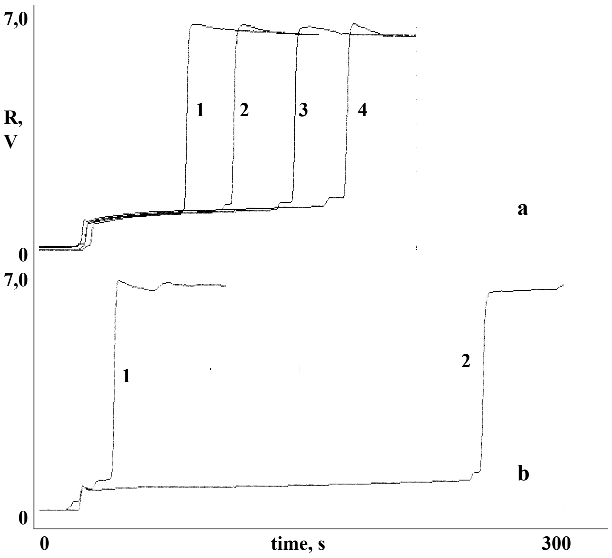


Fig. 3. Isotachopherograms obtained in solutions containing NTMP and Cu^{2+}-ions;
a – equimolar concentration of NTMP and Cu^{2+}-ions (mmole/dm^3): 1 – 0.5; 2 – 1.0; 3 – 1.5; 4 – 2.0;
b – concentrations (mmole/dm^3): 1 – 1.0 NTMP and 0.5 Cu^{2+}; 2 – 1.0 NTMP and 2.0 Cu^{2+}.

NTMP complexes Cu^{2+} ions in a higher degree than PBTC does (Fig. 3). At equimolar concentrations of copper ions and NTMP, the cation isotachopherograms indicate complexing of 68.8, 76.6, 74.0 and 74.0% for the respective concentrations: 0.5, 1.0, 1.5 and 2.0 mmol/dm^3 (Fig. 3a). Through the use of a double excess of NTMP the amount of copper bounded by this complexing agent increased to over 90% and at a double excess of Cu^{2+} ions their complexing amounted to 36.6% (Fig. 3b). Calculations of the degree of complexing of Cu^{2+} ions (based on the Cu–NTMP complex constants shown in Table 1) for pH=6 and an equimolar Cu^{2+}/NTMP ratio indicate that nearly all the copper in the solution should be bound in the form of complexes, with about 30% of the copper in the form of Cu–NTMP^{4-} and about 70% of it in the form of Cu–HNTMP^{3-}. Further research is needed to explain the discrepancies which may be caused by different composition of solutions in isotachophoresis and potentiometry during determination of stability constants.

PMIDA was found to be the most effective among the complexing agents used. At an equimolar concentration of Cu^{2+} and PMIDA the complexing of copper ions amounts to nearly 100% as evidenced by the isotachopherograms shown in Fig. 4a, obtained from the analysis of cations in the solution containing only copper ions and in the solution containing Cu^{2+} ions and PMIDA. Calculations made for pH=6, using the Cu(II)–PMIDA stability constants given in Table 1, show that the Cu^{2+} ions have been nearly 100% complexed, with about 40% of the copper in the form of Cu–PMIDA^{2-} and about 60% of it in the form of Cu–HPMIDA^{-}.

A comparison of the isotachopherograms for the solutions containing equimolar concentrations of Cu^{2+} ions and the complexing agent shows that the highest degree of complexing is obtained for PMIDA, lower for NTMP and the lowest for PBTC (Fig. 4b).

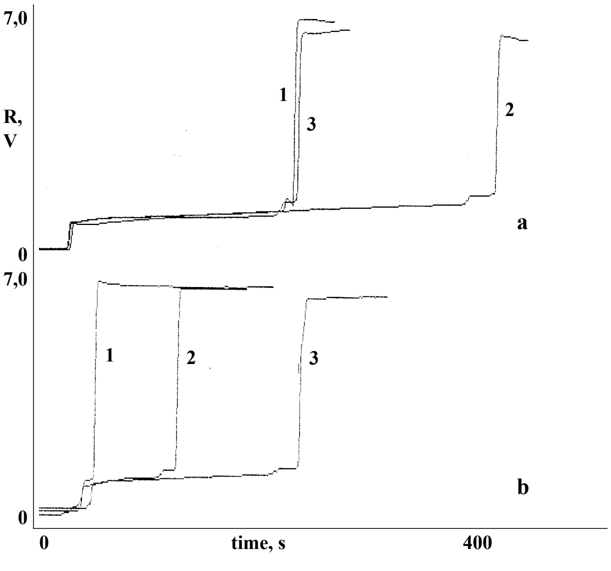


Fig. 4. Isotachopherograms obtained in solutions (mmole/dm^3) containing
a: 1 – 1.0 Cu^{2+}; 2 – 2.0 Cu^{2+}; 3 – 2.0 Cu^{2+} and 1.0 PMIDA,
b: 1 – 1.0 Cu^{2+} and 1.0 PMIDA; 2 – 1.0 Cu^{2+} and 1.0 NTMP; 3 – 1.0 Cu^{2+} and 1.0 PBTC.

Conclusions

Isotachophoresis allows one to quickly determine the degree of binding of copper (and other metal) ions by selected complexing compounds. In addition it is possible to determine the charge of the forming complexes and thereby the direction of their motion in an electric field. Such data are needed for the electrokinetic remediation of soils contaminated with heavy metals.

The most effective complexing agent from among the three phosphonic acids used, i.e. 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), N-trismethylenephosphonic acid (NTMP) and N-(phosphonomethyl)iminodiacetic acid (PMIDA), turned out to be PMIDA. At an equimolar concentration of Cu^{2+} ions and PMIDA in a solution with a pH of about 6, the degree of complexing is almost 100%.

This is corroborated by calculations based on the Cu–PMIDA complex stability data. In the same conditions a complexing degree of about 75% was obtained for NTMP in isotachophoresis, even though if follows from the Cu–NTMP complex stability constants that nearly the whole quantity of Cu^{2+} should be complexed in such conditions. Further research is needed to explain the discrepancies. Since at a solution pH above 8.0 nearly all the copper occurs in the form of $Cu\text{–}NTMP^{4-}$ with a relatively large negative charge, NTMP is a promising agent for copper removal by electrodialytic soil remediation [10]. PBTC was found to be the least effective copper complexing agent.

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