INVESTIGATION OF COMPLEXATION MECHANISMS IN SOME CATION SOLUTIONS

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ABSTRACT
Metal cations represent a considerable part among surface water and land pollutants. Industrial and agronomic effluents, containing in the most cases mercury, cadmium, lead and other cations, until now have been treated by mechanical, physicochemical and biological methods. Biological treatments are the most effective and economically suitable method. Anyway, even biological treatment could not remove all organic and anorganic pollutants. Latest researches deal with removing pollutants from land using bioextraction, based on biosynthetic processes in plants, including toxic metals (phytoremedation). Bioextraction processes where metal cations are transported from land in plant, especially cations of heavy metals, are dependent on balances that are establishing in aqueous solutions, depending on pH and present coexisting components. Present investigations of bioextraction treatment included monitoring of efficiency in removing heavy metals with addition of various organic components.
This paper deals with investigation of Cd(II), Pb(II) and Fe(III) interactions in aqueous solutions with addition of crown ethers, cationic and anionic tenzides. Specially there is considered impact of tenzides, as surface active components, present in waste waters. Mechanism of complexation and balance state restoration are investigated depending on solution pH and metal cationic and organic additive concentration. Used methods were extraction, tenziometry, spectrometry and polarography.
Key words: complexation, cations, crown ether, surfactants

1. INTRODUCTION
Every chemical equilibrium state, in homogenous and heterogenous system, can be described by the equilibrium constant K. This is a most useful quantity and can be used to describe chemical processes, such as acid-base equilibria, complex formation and redox reactions.

In homogenous equilibrium system, several chemical reactions compete simultaneously with each other and we must learn to classify them. In an aqueous solution the solute is often ionized and we refer to it as being electrolyte solution. However, the solute ions are not "bare" ions, but exist as the products of specific interactions, which according to their physical nature may be classified as ion-ion, ion-dipol, or covalent interactions. Another distinction is based on the chemical nature of the interactions, and we classify them as ion association, hydration (or solvation), and complexation.

Heterogenous equlibrium states and the kinetic aspects associated with them are of great importance in environmental chemistry, and natural chemical cycles are based on multiphase system. The principles underlying the understanding of heterogeneous equlibrium states were formulated by Josiah Willard Gibbs (1839-1903) in 1876. A thermodynamic equilibrium exists between different phases when thermal, mechanical, and chemical equilibrium states are established. This statement is summarized in the expression:

$$dG = VdP - S\,dT + \Sigma\,\mu_i\,dn_i \tag{1}$$

Here, the volume V, entropy S, and mole number n_i of component i are extensive variables, whereas the temperature T, pressure P and chemical potential μ_i are intensive variables.

The distribution ratio (D) of some compound between the two phases is often used to enrich or separate a chemical species or a group of species from each other or from the matrix. Metal ions easily form complexes in aqueous solution, when an appropriate ligand is available. Because of their electrical charge, metal ions, usually do not extract well into an organic phase. The situation may be quite different with neutral complexes. An example is the extraction of metal cations from aqueous chloride solutions with tributyl phosphate (TBP) and trioctyl phosphin okside (TOPO).

In this paper, complexation between Cd (II), Pb (II), Fe (III) and ligands: crown ether [18]-crown-6 and its dibenzo- and dicyclo- supstituents, nonionic surfactant polyoxyethylen-octyl-phenyl ether (Triton X-100), cationic surfactant tetradecyltrimethylammonium bromide (TTAB) and dithizone, were studied. The influence of crown ethers structure on selectivity of cation extraction from water solutions is important because crown ethers are involved in the selective membrane processes. Cd (II) and Pb (II) solubilization in micelles of surfactants is also important as a possible procedure of heavy metal ions separation from the environment. Complexation and the establishment of equilibrium state are investigated, depending on the concentration and pH, using methods of extraction, tensiometry, spectrometry and polarography [1, 2].

2. EXPERIMENTAL

2.1. Reagents

Crown ethers: [18]-crown-6 (18C6), Dicyclohexano[18]-crown-6 (DC18C6), Dibenzo[18]-crown-6 (DB18C6), (Fluka). *Surfactants*: polyoxyethylen-octyl-phenyl ether (Triton X-100), tetradecyltrimethylammonium bromide (TTAB) (Sigma). *Phosphates*: Tributyl phosphate, $(CH_3(CH_2)_3O)_3PO$ (TBP), Trioctylphosphine oxide, $(CH_3(CH_2)_7)_3PO$, (TOPO) (Fluka). *Organic solvents*: Benzene, (C_6H_6), Acethonitrile (CH_3CN), (Fluka), Chloroform $(CHCl_3)$, (J.T. Baker), CCl_4, (Panreac). *Basic chemicals*: Dithizone $(C_6H_5NHNHCSN{=}NC_6H_5)$ (Analar), Acids: picric, $C_6H_3N_3O_7$ (HPic) (Fluka), nitric, (HNO_3), perchlor, $(HClO_4)$ (Kemika), Salts: $Pb(NO_3)_2$, $Cd(NO_3)_2$ x 4 H_2O, $CdCl_2$ x 2,5 H_2O, $Cu(NO_3)_2$ x 3 H_2O, ZnO, $HOOCC_6H_4COOK$ (Fluka), NH_4VO_3, (Riedal-de Haen), $FeCl_3$ x 6 H_2O (Kemika). *Standard solutions*: Pb^{+2} (1,00 g/L and 0,05-1,00 mg /L); Cd^{+2} (1,00 g/L); Cu^{+2} (1,00 g/L); Zn^{+2} (1,00 g /L); *Other chemicals*: HCl, Kemika; NaOH, Aldrich, NH_4OH, Merck; conc. H_2SO_4, Merck.

2.2 Instruments

- UV/Vis spectrophotometer, Cecil 2021, with 1 cm path lenght
- pH-meter, Radiometer Copenhagen TTT2, with Quatro 220 K, electrode system
- Conductometer, GLP 31 Crison Instruments
- Potentiostat/Galvanostat, PAR 263 A Princeton Applied Research; Electrochemical Cell, Princeton Applied research (EG&G) model 303 A, with mercury drop electrode(HMDE) with computer system M250/270 Research Electrochemistry Software, 4.3;
- Digital tensiometer, K10 ST, Krüss.

3. RESULTS AND DISSCUSION

3.1. Extraction

Selective Pb(II), Cd(II), Cu(II) and Zn(II) extraction in water/benzene system with crown ethers (18C6, DC18C6 and DB18C6) and organic-phosphate compounds (TBP and TOPO) were studied [3] (figure 2). Also, Fe(III) extraction in water/CCl_4 system have been studied [4] (figure 3).

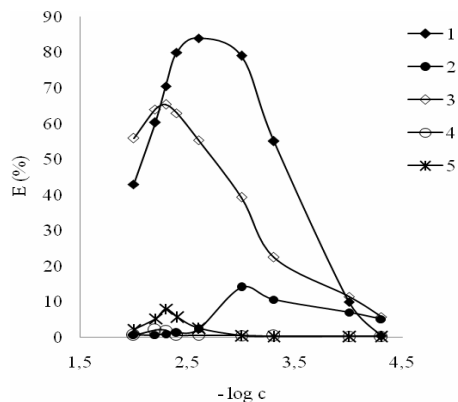*Figure 2. Effect of Pb(II) extraction as a function of ligand concentration (c $_{Pb(II)}$: 5x10^{-4}molL^{-1} (1); 1x10^{-4}molL^{-1}(2); 1x10^{-3}molL^{-1}(3); 2,5 x 10^{-2}molL^{-1} (4 i 5), ligands: 1-18C6; 2-DB18C6; 3- DC18C6; 4-TBP; 5-TOPO*
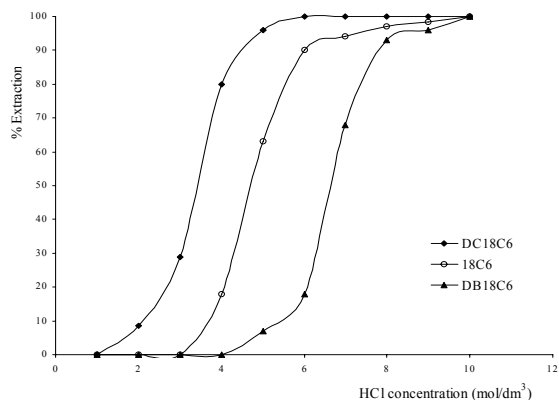
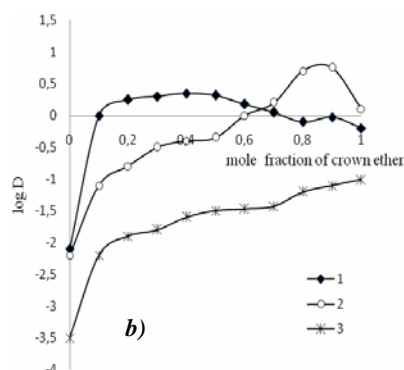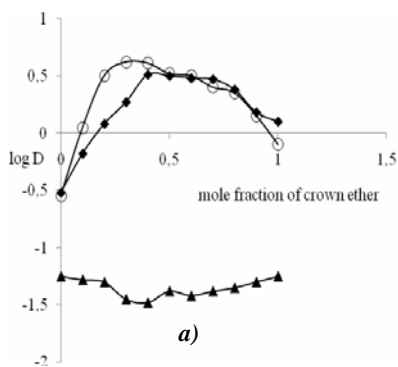*Figure 3. Fe(III) extraction with crown ethers in water/CCl$_4$ system*

*Figure 4. Pb(II) extraction with: **a)** crown ether + TOPO mixture and **b)** crown ether + TBP mixture in water/benzene system (crown ethers: 1-18C6; 2-DB18C6; 3-DC18C6, c$_{Pb(II)}$: 1x10^{-2} molL^{-1}, pH=2)*

Extraction effects are better when using ligand mixtures than single ligands. In investigated systems [5], synergetic effect decrease by order: 18C6 > DB 18C6 > DC18C6, and table 1 shows mole fraction of crown ether R$_2$18C6 for maximal synergetic effects. Values of Pb(II)-crown ether extraction constants were experimentaly determined (table 2).

Table 1. Maximal synergetic effects in Pb(II) extraction in water/benzene system

mole fraction of crown ether R$_2$18C6	LIGAND MIXTURE	
	crown ether + TBP	crown ether + TOPO
R = -H (18C6)	0,9	0,8
R= C$_6$H$_5$- (DB18C6)	0,1	0,4
R=C$_6$H$_{11}$- (DC18C6)	0,1	-

Table 2. Extraction constants of Pb(II)-crown ether in water/benzene system at 25°C

R$_2$18C6	R = H- (18C6)	R = C$_6$H$_5$- (DB18C6)	R=C$_6$H$_{11}$-(DC18C6)
log K$_{ex}$	3,52	1,71	0,018

3.2. Solubilization

Dithizone complexes of Cd(II) and Pb(II) ions are extractible in CCl$_4$, depending on pH values. Extraction with 100% effectivity is at pH=13 for Cd(II) and at pH=8 for Pb(II) ions [6]. By introducing of tenzides in water solution, it is possible to solubilizing those complexes. Critical micellar concentrations for tensides were determined by tensiometric method [7,8]. (figure 5). Absorption spectra of dithizone complexes in micellar solutions are shown at figure 6.
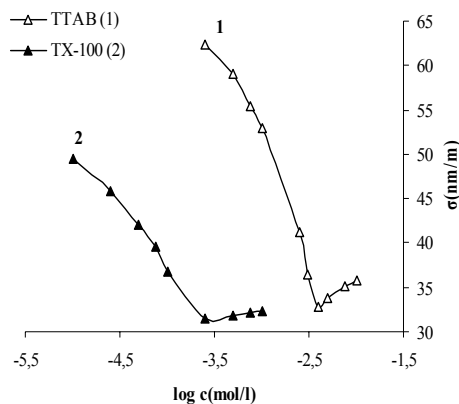

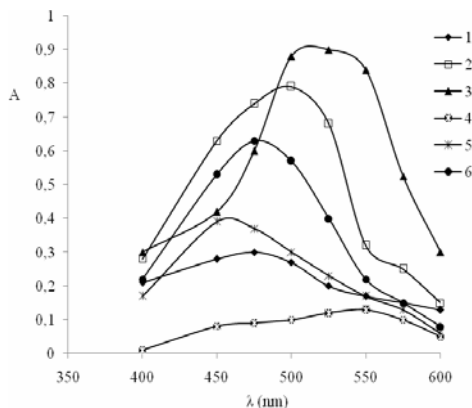Figure 5. Surface tension as a function of tenside concentration

Figure 6. Absortion spectra of Cd(II)and Pb(II) dithizonates (c$_{Cd(II)}$ = 20 mg/L; c$_{Pb(II)}$=30 mg/L) in: 1,4-CCl$_4$, 2,5-Triton X-100, 3,6-TTAB

Complex anion, M^{+2}-dithizone, in alkaline medium posses strong anionic properties and shows electrostatic interactions toward positive charged groups in cationic micelle. In presence of nonionic tenzide micelles, its possible that chelate effect of oxyethylene groups with Cd(II) cations took place, while dithizone formed hydrogen bonds.

4. CONCLUSIONS

- Stability and extractibility of Pb(II)-crown ether complexes depends on supstituents, and decrease by order: 18C6 > DB18C6 > DC18C6
- Stability and extractibility of Fe(III)-crown ether complexes depends on supstituents, and increase by order: 18C6 < DB18C6 < DC18C6
- Extraction of Pb(II) ions with ligand mixtures crown ether + phosphate shows synergism
- Cd(II) dithizonates solubilization in cationic and nonionic micellar solutions took place by electrostatic micelle-dithizonate interactions
- Contribute of cationic tenzide in alkaline medium is greater than nonionic

5. REFERENCES
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