ORIGINAL ARTICLE

Comparative metal ion extraction of Ag(I), Cu(II), Ni(II), Zn(II), Mn(II), Cd(II) and Co(II) cations using dibenzo 18C6 as a carrier

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Abstract   The competitive metal ion extraction of Ag(I), Cu(II), Ni(II), Zn(II), Mn(II), Cd(II) and Co(II) cations were examined and compared each with other. The experiments were buffered (acetic acid/sodium acetate and formic acid/sodiumformate) at pH 4–6. The extraction of Cu(II) and Ag(I) and Co(II) with Dibenzo 18 crown 6 (DB18C6) ligand is possible, but the extraction efficiency for Ag(I) is much better than Cu(II) and Co(II) ion. The concentrations in the all experiments for the cations and ligand were 0.01 M and 1.0×10^{-3} M respectively. Organic phase employed chloroform, dichloromethane and 1,2dichloroethane in individual experiments. The effect of picric acid in aqueous phase to the efficiency of extraction was investigated. The effect of extraction time, rate of shaking, concentration of ligand and presence of picric acid were investigated and optimized.

1. Introduction

The liquid–liquid extraction (LLE) is a popular technique which partitioning the sample between two immiscible phases.

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Peer review under responsibility of Faculty of Engineering, Alexandria University.

The industrial importance of metal ion separation has made the study of metal ion extraction behavior an area of increasing research interest [1]. A motivation for these studies has been the potential for obtaining new metal ion separation processes for use in a range of industrial and analytical applications [2]. In two-phase system, slow kinetics together with thermodynamic stabilities that are either too low to permit uptake of a metal into the organic phase, or too high to allow its loss to the organic phase, will inhibit extraction efficiency and also influence selectivity. In similar manner, an increase in lipophilicity of the ionophore may increase the efficiency of uptake of a metal salt from an aqueous phase to organic phase [3–5]. Metal ion extraction depends up on number of parameters. Some of these include ligand structure, pH of solutions, solvent, temperature and time of extraction [6].

Scheme 1

In this study we investigated the extraction of Ag(I), Co(II), Ni(II), Zn(II), Cu(II), Cd(II) and Mn(II) metal cations with chloroform, dichloromethane and 1,2dichloroethane as organic phase, using dibenzo 18 crown 6 (DB18C6) as carrier (Scheme 1).

2.2. Experimental

2.1. Materials and solutions

All reagents were of analytical grade and used without further purification (Merck). All aqueous solutions were prepared with double distilled deionized water. The standard stock solution of Ag(I), Co(II), Ni(II), Zn(II), Cu(II), Cd(II) and Mn(II) was prepared by dissolving nitrate salts of them. A 1 mM stock solution of DB18C6 was prepared in chloroform, dichloromethane and 1,2dichloroethane separately.

2.2. Instrumental

Concentrations of cations were obtained using a Philips PU9100 atomic absorption spectrometer (AAS). All of the pH measurements were carried out by Metrohm-691 pH Meter. The extraction samples were shaken on an IKA-WERKE shaker.

2.3. Procedure

The competitive metal ion extraction from an aqueous phase into an organic phase including chloroform, dichloromethane and 1,2dichloroethane in different experiments was employed. The aqueous phase was buffered (acetic acid/sodium acetate) at pH 4.0, 4.5, 5.0, 5.5 and 6.0. The metal ion present were

as their nitrate salts at concentration of 0.01 M. The metal ion concentrations were determined after each extraction experiment, using AAS. Each experiment was performed in triplicate runs and the reported value is the average of them.

The optimal value for pH in a selected organic phase was used to optimize time of extraction. Alternatively, the obtained values were used in the optimizations of shaking rate and then ligand concentration and finally, all these values were used to optimize the concentration of added picric acid on the extraction experiments.

3. Results and discussion

3.1. Effect of pH and organic solvent on extraction efficiency

The competitive metal ion extraction to obtain optimum conditions with the effects of pH and organic solvents were investigated. To obtain the selected solvent as organic phase chloroform, 1,2dichloroethane and dichloromethane were used in the extraction experiments. As shown in Table 1 using dichloromethane has good extraction efficiency for silver ion against chloroform and dichloroethane.

The comparison of extraction efficiency of metal cations shows similarity in the order of extraction efficiency in all of the pH of aqueous phase and all of the solvents. But the best extraction was obtained in pH 4 of aqueous phase and dichloromethane as organic phase. Fig. 1 shows the solvent effect on the extraction efficiency of silver ion from a mixture of Ag(I), Cu(II), Ni(II), Zn(II), Mn(II), Cd(II) and Co(II) cations to organic phase.

The order of extraction efficiency for silver ion using different solvents is as: dichloromethane > chloroform > 1,2dichloroethane. This result is according to the physicochemical properties of the solvents such as polarity [7,8], viscosity and dielectric constant. This result may be attributed to the lower viscosity of dichloromethane ($\eta = 0.449$) than chloroform ($\eta = 0.580$) and 1,2dichloroethane ($\eta = 0.887$) which leads to increase the extraction efficiency in dichloromethane [9].

The NO_3^- anion is highly polarizable and interacts to a fair extent by dispersion forces with dichloromethane molecules, which are more polarizable than chloroform and then 1,2dichloroethane molecules. Also acceptor number of 1,2dichloroethane (AN = 16.7) is lower than chloroform (AN = 23.1) and then dichloromethane (AN = 20.4), this reason increase in free energy of solvation of Ag-anion with cationic species in this solvent which can relate the ion

Table 1 The effect of pH and organic solvent on the competitive extraction of cations. Conditions: initial concentration of [Ag(I), Cu(II), Ni(II), Zn(II), Mn(II), Cd(II) and Co(II)] 10 mM, shaking, rate: 300 rpm and extraction time 24 h (1, dichloromethane. 2; 1,2dichloromethane. 3; chloroform as a organic phase).

%Extraction

Ag(I)			Cu(II)			Co(II)			Mn(II)			Ni(II)			Cd(II)			Zn(II)			pH
1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	
35.2 ± 0.2	21.2 ± 0.2	28.2 ± 0.1	0	0	0	5.1 ± 0.2	11.3 ± 0.6	8.3 ± 0.1	0	0	0	0	0	0	0	0	0	0	0	0	4
7.6 ± 0.7	15.3 ± 0.2	14.1 ± 0.3	0	0	0	5.3 ± 0.2	11.1 ± 0.1	7.4 ± 0.6	0	0	0	0	0	0	0	0	0	0	0	0	4.5
9.2 ± 0.1	7.1 ± 0.2	8.2 ± 0.1	0	0	0	6.1 ± 0.1	10.4 ± 0.1	8.1 ± 0.1	0	0	0	0	0	0	0	0	0	0	0	0	5
11.4 ± 0.3	14.5 ± 0.3	9.3 ± 0.1	3.2 ± 0.3	10.2 ± 0.3	5.4 ± 0.4	6.6 ± 0.7	11.1 ± 0.6	10.4 ± 0.5	0	0	0	0	0	0	0	0	0	0	0	0	5.5
26.6 ± 0.7	20.3 ± 0.6	22.2 ± 0.7	8.3 ± 0.1	10.5 ± 0.9	13.6 ± 0.9	7.1 ± 0.2	13.3 ± 0.2	9.1 ± 0.2	0	0	0	0	0	0	0	0	0	0	0	0	6