Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Alp, Hakan , Ocak, Miraç , Özdemir, Mustafa and Ocak, Ümmühan(2006) 'Evaluation of a (E,E)-Dioxime Containing Two 15-Membered Dioxatrithiamacrocycles and its Mononuclear Ni(II) Complex as Ag Extractants', Separation Science and Technology, 41: 13, 3039 — 3046

To link to this Article: DOI: 10.1080/01496390600854610

URL: http://dx.doi.org/10.1080/01496390600854610

Separation Science and Technology, 41: 3039–3046, 2006

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390600854610

Evaluation of a (E,E)-Dioxime Containing Two 15-Membered Dioxatrithiamacrocycles and its Mononuclear Ni(II) Complex as Ag^+ Extractants

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Abstract: A macrocyclic vic-dioxime (**1**) and its mononuclear Ni(II) complex (**2**) were studied as extractant. The aqueous solutions of Ag^+, Mn^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, and Zn^{2+} picrates were used for extraction experiments. The solutions of the ligands in two different organic solvents were used as organic phases. The metal picrate extractions were carried out at 25 ± 0.1°C by using UV-visible spectrometry. The most effective transport was observed for Ag^+ picrate among the tested metal picrates. The effect of pH on the extraction of Ag^+ picrate was evaluated with the ligands. The ratio of extracted Ag-complex to chloroform phase was 2:1 (L:M) for (**2**). In other cases the ratios were 1:1 for both (**1**) and (**2**). Molar ratio method was also used to demonstrate the composition. The values of the extraction constants (log K_{ex}) were determined for the extracted Ag-complexes.

Keywords: Alkali metal cation, tetra-crowned ligand, transition metal cation, solvent extraction

Received 15 February 2006, Accepted 16 May 2006

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INTRODUCTION

Host-guest interactions between macrocyclic ligand and metal cation are interesting for analytical processes. Crown ethers have been studied for this purpose for many years. Especially, it is possible to find so many examples of cation complexation with classical crown ethers in literature (1–5). These are generally mono- and bis- crown ethers ligands. There have been fewer investigations on the extractant properties of the molecules consisting of three or four macrocyclic moieties. Bartsch has synthesized some bis[benzo(15-crown-5)]-crowned clefts and some tetra[benzo(18-crown-6)]-crowned clefts and studied their extraction ability for alkali metal cations (6). Lindoy and Meehan have investigated the interaction of some tri-linked N_2S_2-donor macrocyclic ligands and their single ring analogues with Ag^+ (7). However, there are no efficient investigations on extraction properties of tetra-crowned molecules with oxygen and sulfur donor atoms. This study involves the transition of metal picrate extraction from the aqueous solution to the organic phase by (E,E)-dioxime containing two 15-membered dioxatrithiamacrocycles (**1**) and its mononuclear Ni(II) complex containing four dioxatrithiamacrocycles (**2**), which were synthesized in our laboratory (8). Our aim was to investigate the extraction properties of the bulky molecule with four dioxatrithiamacrocycles (**2**) according to model compound (**1**). The extraction experiments were carried out with the aim to reveal the efficiency especially of the compound (**2**) as an extractant. For this goal, the effect of pH and the solvent was investigated in different ligand to metal concentration ratios. We expected that compound (**2**) has extracting efficiency and selectivity to Ag^+ because of its four ion binding centers with proper donor atom types.

EXPERIMENTAL

Reagents and Apparatus

$Pb(NO_3)_2 \cdot H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $AgNO_3$, $Mn(NO_3)_2 \cdot 4H_2O$, $NaNO_3$, HNO_3, CH_3COOH, CH_3COONa, chloroform, dichloromethane, and picric acid were the analytical grade reagents and purchased from Merck. Demineralized water was used in the extraction experiments. The solvents were saturated with each other before use in the order to prevent volume changes of the phases during extraction.

The spectrophotometric measurements were carried out with Unicam UV2 UV-visible spectrophotometer. In solvent extraction experiments a Grant SS 30 type shaker with a thermostat was used. An Orion Research Model 601 Digital Ionalyzer was used for adjusting the pH of metal picrate solutions.

Solvent Extraction

Extraction experiments were performed according to the previously reported procedure (9). Transition metal picrates were prepared by the stepwise addition of 1×10^{-2} M of metal nitrate solution to 1.25×10^{-5} M aqueous picric acid solution and shaking at 25°C for 1 h.

10 mL of organic ligand solution (1.25×10^{-4} M) and 10 mL of aqueous solution containing metal picrate (1.25×10^{-5} M) were placed in a stoppered flask, and shaken for 3 h at $25 \pm 0.1°C$. The resulting mixtures were allowed to stand for at least 2 h at that temperature in order to complete the phase separation. For investigation of the effect of pH on E%, which is the percentage of the extracting efficiency, the aqueous solution was buffered to pH 2.1, 2.6 and 3.3 (0.01 M $NaNO_3/HNO_3$) and pH 4.0, 4.3, and 5.0 (0.01M CH_3COONa/CH_3COOH). In these experiments, 1.25×10^{-5} M metal picrate and 1.25×10^{-5} M ligand solution were used. The concentration of the picrate ion remaining in the aqueous phase was then determined spectrophotometrically at 355 nm. Blank experiments showed that no picrate extraction occurred in the absence of the ligand. The extractability was determined by measuring the absorbance of picrate ion in the aqueous solutions. The extractability was calculated from equation (1).

$$E(\%) = [(A_0 - A)/A_0] \times 100 \tag{1}$$

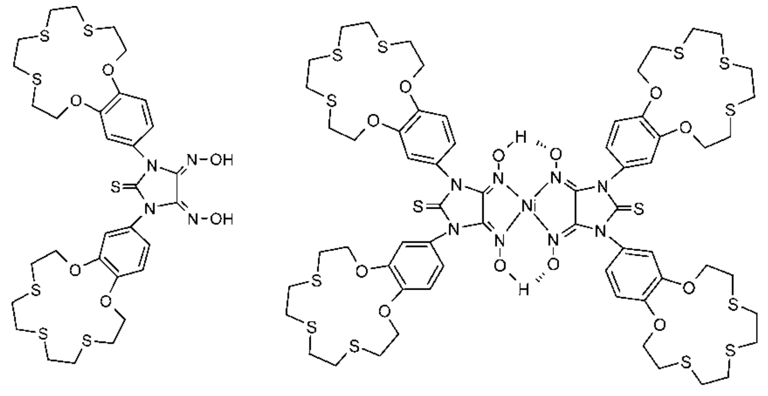
where A_0 is the absorbance in the absence of ligand. A denotes the absorbance in the aqueous phase after the extraction.

The dependence of the distribution ratio D of the cation between the aqueous phase and the organic phase upon the ligand concentration was examined. The concentration range of the ligand was between 2.5×10^{-6} and 1.25×10^{-4} M.

RESULTS AND DISCUSSION

The structure of the ligands **(1)** and **(2)** used in this study were shown in Fig. 1. Extraction data was obtained by using chloroform and dichloromethane solutions of the ligands, which transfer metal picrates from the aqueous solution. The equilibrium concentration of picrate in aqueous solution was than determined spectrophotometrically.

Table 1 shows the extractability of Ag^+, Pb^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}, Cd^{2+}, and Zn^{2+} picrates from the aqueous phase into the chloroform phase by compound **(1)** and compound **(2)**. When chloroform was used as an organic solvent, compound **(1)** extracted Ag^+ ion 78.3% but all the other metal ions were extracted less than 17.9%. It is clear that both compound **(1)** and compound **(2)** showed a high extraction for Ag^+ ion compared to the other metal ions. However, the Ag^+ extractability result for **(1)** is higher than that



(1) **(2)**

Figure 1. Structure of ligands.

for (**2**). It is interesting that the percentage of the extraction of all the metal ions with compound (**2**) is lower than that of compound (**1**) except for Cu^{2+} when chloroform was used as organic solvent. Similar results were also obtained for dichloromethane. Whereas it was expected that compound (**2**) could transport Ag^{+} twice more than that of compound (**1**). This result shows that the smaller structure shows higher extraction. Bulky molecules form bulkier ion associations (metal-ligand-picrate). Therefore, they cannot

Table 1. The extractability of aqueous metal picrates for compound (**1**) and (**2**) into chloroform phase[a]

Metal ion	Extractability (%) (**1**)	Extractability (%) (**2**)
Ag^{+}	78.3 ± 0.5	58.6 ± 0.7
Pb^{2+}	17.9 ± 0.7	2.9 ± 0.9
Cd^{2+}	16.0 ± 1.2	2.6 ± 0.4
Zn^{2+}	7.3 ± 1.1	1.9 ± 0.3
Cu^{2+}	10.9 ± 0.9	17.6 ± 0.6
Ni^{2+}	4.6 ± 1.1	4.5 ± 0.4
Mn^{2+}	15.7 ± 1.0	12.9 ± 0.5

[a] Temperature: 25.0 ± 0.1°C; aqueous phase (10 mL); $[pic^{-}] = 1.25 \times 10^{-5}$ M, organic phase (10 mL); $[L] = 1.25 \times 10^{-4}$ M; pH: 4.6. The values and standart deviations calculated from three independent extraction experiments.

easily be transported to the organic phase. Similar results are seen for tri-linked N_2S_2-donor macrocycles in literature (7).

The general extraction equilibrium is assumed to be given by equation (2).

$$M^{n+}_{aq} + n\ Pic^{-}_{aq} + m\ L_{org} \rightleftarrows [M(Pic)_n\,(L)_m]_{org} \qquad (2)$$

In order to determine the composition of extracted complexes, the effect of changing the ligand concentration over the distribution ratio (D) at constant picrate concentration was investigated. The plot of log $\{D/[Pic^{-}]^{n}\}$ as a function of log [L] should give a straight line with a slope of m and log K_{ex} can be calculated from the intercept by using equation (3).

$$\mathrm{Log}\{D/[Pic^{-}]^{n}\} = \log K_{ex} + m \log [L] \qquad (3)$$

The extraction experiments at different concentrations of the ligands but constant picrate concentration were carried out only for the transport of Ag^{+} to both chloroform and dichloromethane. The results were summarized in Table 2. The log K_{ex} values of compound **(1)** were higher than those of compound **(2)** for both solvents. The composition of the complex of Ag^{+} with compound **(2)** was different in the different solvents. When chloroform was used as an organic solvent, the data in Fig. 2 and equation (3) revealed the 1:1 and 2:1 composition for the Ag-compound **(2)** complex, respectively. For compound **(1)** the composition is 1:1 for both solvents. These results show that the solvent has an important effect upon the complex composition. Chloroform causes the 1:1 composition for the model compound **(1)**. However, the same solvent having low dielectric constant according to dichloromethane is favored for a 2:1 composition for the bulky molecule compound **(2)**. This may be due to the good solvation effect of chloroform for the more lipophilic 2:1 complex. The same composition was obtained for the Ag^{+} complex of some crown ether ligands with N_2S_2 donor atom set when chloroform was used as an organic solvent (10).

Table 2. The relationship between composition and extraction constant for the Ag-compound **(1)** and **(2)** complexes[a]

	Extraction constant		Complex composition	
Ligand	Log K_{ex}[b]	Log K_{ex}[c]	L:M[b]	L:M[c]
(1)	13.53	10.45	1:1	1:1
(2)	12.48	9.42	2:1	1:1

[a] pH: 4.6.

[b] Organic solvent: chloroform.

[c] Organic solvent: dichloromethane.

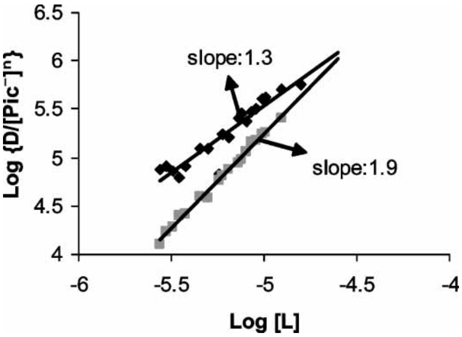


Figure 2. Log$\{D/[Pic^-]^n\}$ versus log[L] for the extraction of Ag-picrate. (◆): Ligand **(1)**, (■): Ligand **(2)**.Organic solvent: chloroform. pH: 4.6.

Geometric optimization of compound **(1)** was also made by using AM1 method (Fig. 3). According to this study, the cavity size of the ligand was calculated as 2.0 Å. This result shows that compound **(1)** cannot form a 1:2 (L:M) composition because of the ionic diameter of Ag^+ (2.52 Å). The existence of a "sandwich" complex is possible because the cavity size of a 15-membered macrocycle does not match the ionic diameter of Ag^+. The extraction experiments show that the two ligands have a certain extraction selectivity to Ag^+. Actually, many factors effect the cation-macrocycle interaction such as size match, shape, and topology, conformational flexibility or rigidity, number, type, and arrangement of donor atoms in the macrocycle. In the present study the main factor is the donor atom type. Especially, it is well known that sulfur atoms in the macrocycles prefer Ag^+ in complexation (11). The reason for this is soft cation-soft donor atom interaction. There are many

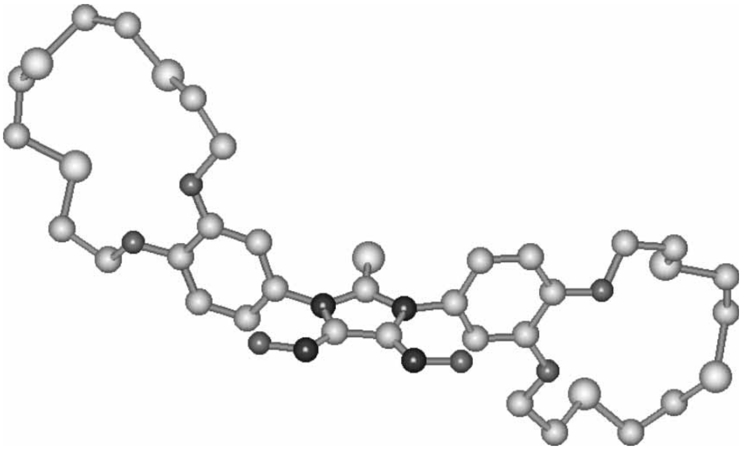


Figure 3. Stable conformation of compound **(1)**.

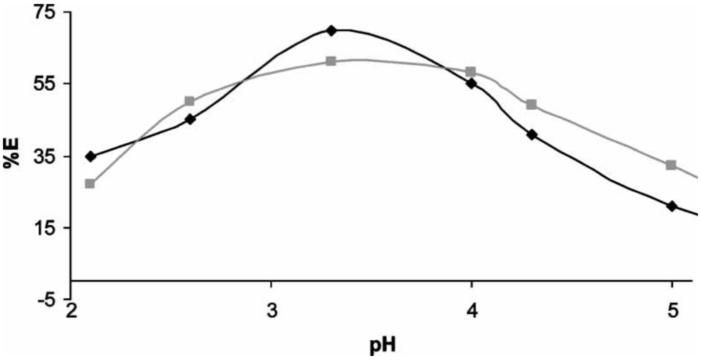


Figure 4. pH dependence for Ag^+ extraction. Aqueous phase; metal picrate: 1.25×10^{-5} M, organic phase: 1.25×10^{-5} M, chloroform. (◆): Ligand (**1**), (■): Ligand (**2**).

examples of effective Ag^+ extraction by the macrocyclic ligands with sulfur donor atoms in literature (12).

In this work we investigated the effect of varying pH upon extraction ability of Ag^+ by using the ligands. The same solvents were used for this purpose. The results are given Fig. 4. and Fig. 5. In Fig. 4, the highest E% value is 70 at pH 3.3 for compound (**1**) in extraction with chloroform. The value of E% related to compound (**2**) is 61% at the same pH. Ag^+ was transported to dichloromethane with a percentage of 54% and 50% by compound (**1**) and compound (**2**) at pH 3.3, respectively. When Figs. 4 and 5 are compared, it can be seen that chloroform is better than dichloromethane as an organic solvent in these extraction experiments.

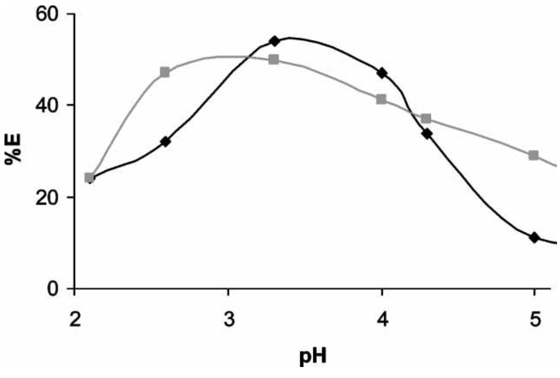


Figure 5. pH dependence for Ag^+ extraction. Aqueous phase; metal picrate: 1.25×10^{-5} M, organic phase: 1.25×10^{-5} M, dichloromethane. (◆): Ligand (**1**), (■): Ligand (**2**).

CONCLUSION

The higher transfer of the Ag^+ ion from the aqueous phase to the chloroform phase was observed with compound **(1)**. It is interesting that compound **(2)** transferred the same ion less effectively than chloroform. The composition of extracted Ag-compound **(2)** complex was 2:1 (L:M) for chloroform.

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