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Solvent Extraction of Silver(I) using *N,N*-Diethylacetamido Substituted *p-t*-Octylcalix[4]arene in Nitrate Media

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Solvent extraction of silver ions using *tetrakis*(*N*,*N*-diethylaminocarbonylmethoxy)-*p*-*t*-octylcalix[4]arene (EATOC) in chloroform from nitrate medium is presented. The influences on the extraction conditions affecting the behaviour of extraction depending upon the factors such as concentrations of acids, extractants and silver ions as well as extraction time were investigated. Various stripping reagents for back extraction to recover the loaded silver ions by forward extraction process were applied. The extraction mechanism of silver ions using EATOC was established on the ^{1}H NMR chemical shift of the extractant as well as the slope assessments of extraction conditions both before and after loading the silver ions.

Keywords: Calix[4]arene, Silver, Metal extraction, Slope analysis.

INTRODUCTION

The amount demanded of precious metals, including gold, silver and the six platinum group metals (PGMs) has increased a lot in industry, furthermore, their demand for higher and even ultra-high purity usually is put emphasis on especially as well. As the supply of precious metals could not match the demand the gap between the demand and supply for natural sources has increased and must be replenished by recycling of spent materials, containing these metals. However, the processes of separation and purification of precious metals are difficult and complicated due to their similar chemical properties and formation of many chemical species [1-3]. To overcome these problems and replace the traditional routes, intensive research and development to meet new challenges has been done. And then, more effective technique for their recovery from ores and spent materials have been prompted.

Solvent extraction, also called the liquid-liquid extraction, is a process which allows separation of two ore more components, *e.g.* metal ions making use of their unequal solubilities in two immiscible liquid phases [4]. The solvent extraction is a suitable method for the removal of precious metals from leaner sources, because it offers several advantages like highly selectivity and purity [5,6]. Besides, more efficient recovery of metals is possible using multi-stage extraction. Moreover, solvent extraction has several advantages for precious metals such as high selectivity, easy scale-up, mass disposal, versatility, simple operation and high efficiency, which is a highly preferred method and several factors influencing this process have been reported [7,8].

Numerous attempts have been reported on the extraction of precious metals using various macrocyclic compounds such as crown ether, calixarene and kryptand, among which the functional group-substituted calixarene derivatives have been used as attractive hosts for solvent extraction because they contribute as selective and efficient extractants [9-12]. From the literature, it was found that calixarenes are phenolic cyclic oligomers and are well-known as very attractive and interesting host compounds, because they possess plural phenol groups for easy modification and provide three-dimensionally cyclic structure [13-18].

The diethylamide-substituted calix[4]arene derivatives were used as selective extractants of precious metals from the acidic solutions [17] and the extraction behaviour of silver and gold in highly acidic chloride media as well as silver and platinum in dilute nitric acid solution were investigated [19]. The solvent extraction kinetics with diethylamide calix[4]arene derivative was reported using a modified Lewis cell system

[20] and elucidated using slope analyses by the influences of extracts and extractants in nitric acid media [21].

However, few works have been reported on the parameters and mechanisms relevant to the extraction and separation of silver from acidic solutions with diethylamide-substituted calix[4]arene. This study reports the detailed investigations of silver extraction using *tetrakis*(*N*,*N*-diethylaminocarbonylmethoxy)-*p*-*t*-octylcalix[4]arene (EATOC) (Fig. 1) in the acidic solutions, as well as the stripping of silver and extraction mechanism from the slope analyses and ^{1}H NMR spectra before and after silver loading to the media.

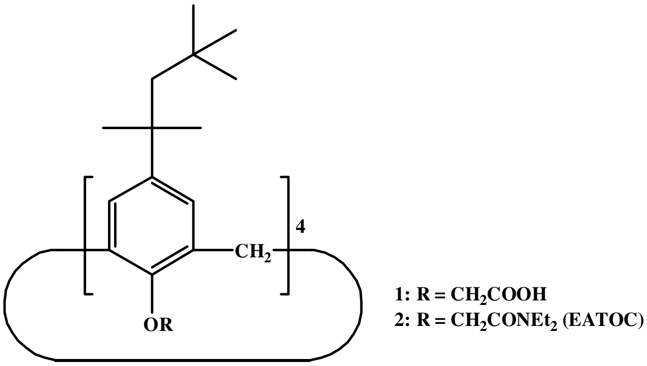

Fig. 1. Chemical structure of diethylamide calix[4]arene derivative

EXPERIMENTAL

All chemicals were purchased from Aldrich and used without further purification. *tetrakis*(*N*,*N*-Diethylaminocarbonylmethoxy)-*p*-*t*-octylcalix[4]arene (EATOC) was synthesized according to reported procedure and characterized by ^{1}H NMR [17]. ^{1}H NMR spectra were recorded on Jeol JNM-GX 300. Silver concentrations after phase separation were measured by using ICP-AES (Shimadzu, ICPS-8100) instrument.

Extraction and analysis: Each 3 mL of EATOC (3.3 mM in chloroform) and $AgNO_3$ (0.1 mM in 0.1 M HNO_3) was mixed in a vial (10 mL) and extracted at 303 K. The amount of silver extracted into organic phase was determined based on the mass balance by measuring silver concentration in aqueous phase. In backward extraction, several stripping agents (ammonia, thiourea and ammonium thiocyanate) of different concentrations (0.1 M and 1 M in water) were applied after forward extraction. The stripping solution (3 mL) was added to each extracted organic phase and re-extracted at 303 K for 72 h, respectively, before measuring the silver concentration in the extractant.

The distribution ratio (D) and the extraction ratio (% E) of silver(I) as well as the stripping ratio (% S) were calculated by the following equations, where subscript "ini", "e", "a" and "o" denote the initial state, equilibrium state, aqueous phase and organic phase, respectively; $V_{(o)}$ and $V_{(a)}$ are the volume of aqueous and organic phases [22].

$$D = \frac{[M]_{(ini)} - [M]_{(e)}}{[M]_{(e)}} \times \frac{V_{(a)}}{V_{(o)}} \tag{1}$$

$$E\ (\%) = \frac{[M]_{(ini)} - [M]_{(e)}}{[M]_{(e)}} \times 100 \tag{2}$$

$$S\ (\%) = \frac{[M]_{(a)}}{[M]_{(o)}} \times \frac{V_{(a)}}{V_{(o)}} \tag{3}$$

The drop volume measurement as a modified drop weight measurement was carried out by slowly adding 10 drops of chloroform medium that contained the extractant into the acidic aqueous phase to obtain the average volume per drop. The extractant in chloroform of a desired concentration was placed in a glass pipette. Nitric acid solution (25 mL) of the desired concentration was added to the reservoir. To maintain a constant nitric acid solution temperature, the apparatus was placed in the thermostatic water bath [23].

Interfacial tension (γ) was determined from eqn. 4:

$$V\Delta\rho g = 2\pi r\gamma f\left(\frac{r}{V^{1/3}}\right) \tag{4}$$

where V, $\Delta\rho$, g, r, f are volume of drop (m^3), density difference between the aqueous and organic phases (kg m^{-3}), gravitational (m s^{-2}), glass edge radius (m) and correction factor, respectively.

RESULTS AND DISCUSSION

Extraction of silver(I): The amounts of silver(I) extracted depending on extraction times using EATOC in 0.1 M and 1 M nitrate medium were measured, respectively (Fig. 2). The extraction rate of silver(I) was not fast in both concentrations and extraction equilibrium reached approximately 90% within 20 h, which may be due to the low interfacial activity and binding activity of neutral EATOC.

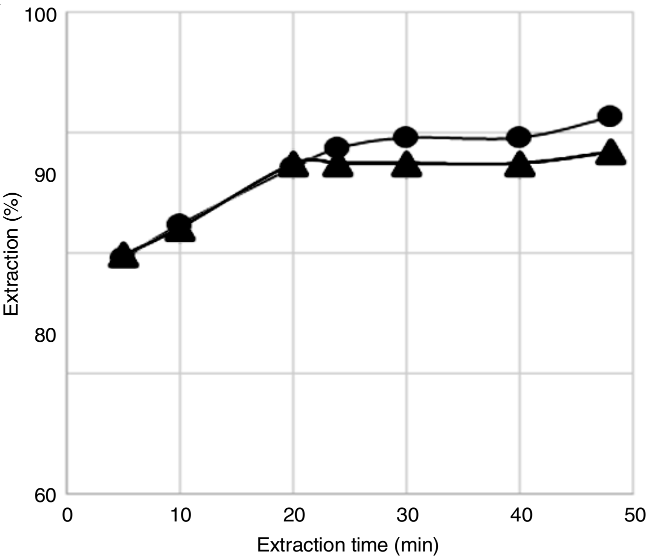

Fig. 2. Extraction ratio of silver(I) depending on extraction times; $[Ag^+]_{ini}$ = 0.1 mM, [EATOC] = 3.3 mM, ● 0.1 M HNO_3, ▲ 1.0 M HNO_3

Interfacial tension study: As the EATOC concentration in nitrate media increases, the interfacial tension (γ) gradually decreases (Fig. 3), which shows the same tendency as reported works [23]. The interfacial tension (γ) of the EATOC solution in 0.1 M nitric acid is slightly higher than that in 1 M solution. It gradually increases as the EATOC concentration decreases to less than 10^{-2} M in the former case and 10^{-3} M in the latter case. This indicates that the extractant is more readily adsorbed

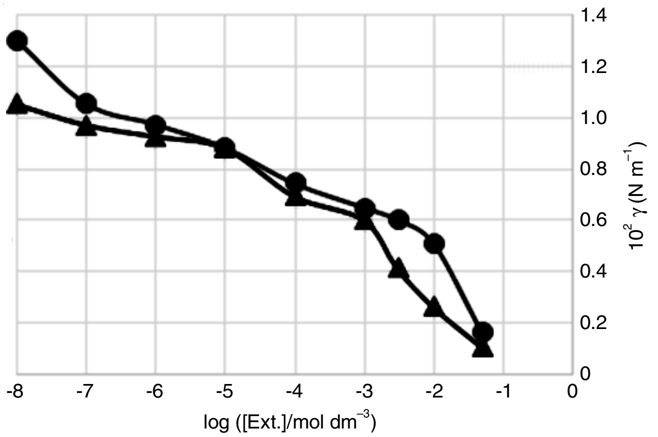

Fig. 3. Interfacial tension depending on EATOC concentration on nitric acid-chloroform interface; [Ext.] = Concentration of EATOC, $[Ag^+]_{ini}$ = 0.1 mM, [EATOC] = 3.3 mM, ● 0.1 M HNO_3, ▲ 1.0 M HNO_3

to the interface when in contact with the latter solution compared to the former. Namely, the extraction rate of silver(I) in 1 M nitric acid is slightly faster than in 0.1 M.

Slope analyses: Silver extraction using EATOC in nitrate medium was quantitatively investigated by the stoichiometry of distribution ratio depending on various conditions. The distribution ratio dependent on the concentration of EATOC shows a straight line with 1.0 (Fig. 4), indicating that the carbonyl oxygen atoms of EATOC are coordinated to silver(I) to form a 1:1 stoichiometric complex each other.

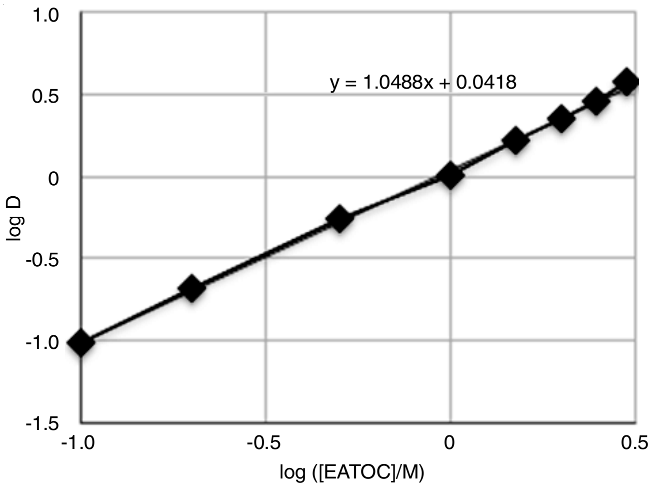

Fig. 4. Effect of the EATOC concentration on the solvent extraction of silver(I) on the nitrate medium; $[Ag^+]_{ini}$ = 0.1 mM, $[HNO_3]$ = 1 M, extraction time = 24 h

The distribution ratio of silver(I) depending on nitrate concentration (Fig. 5) examined a straight line with 0.91. In this extraction, the experiment was suggested 1:1 stoichiometry as well as nitrate as counter ions being included in the extraction process of silver(I). In the pH-dependent distribution ratio of silver(I), the straight line is 0.18 (Fig. 6) indicates that proton is not engaged in the extraction process.

Silver extraction reaction with extractant: From the results of the slope analysis (Figs. 4-6), the equilibrium equation for silver extraction using EATOC is represented by eqn. 5:

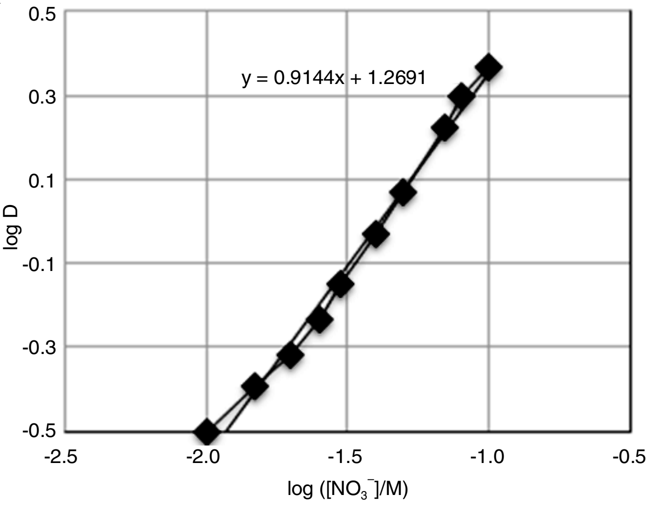

Fig. 5. Effect of nitric acid concentration on the solvent extraction of silver(I) with EATOC; $[Ag^+]_{ini}$ = 0.1 mM, [EATOC] = 3.3 mM, extraction time = 24 h

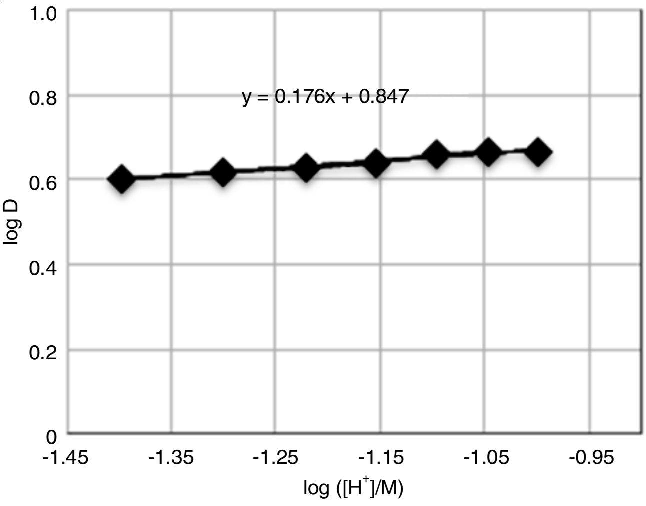

Fig. 6. Effect of pH on the solvent extraction of silver(I) with EATOC; $[Ag^+]_{ini}$ = 0.1 mM, [EATOC] = 3.3 mM, $[NO_3^-]$ = 1.0 M, extraction time = 24 h

$$Ag^+ + EATOC + NO_3^- \overset{K_{ex}}{\rightleftharpoons} [(Ag^+)(EATOC)(NO_3^-)] \quad (5)$$

where K_{ex} denotes the extraction equilibrium constant.

Using eqn. 5, the distribution ratio (D) is represented as

$$D = \frac{[(Ag^+)(EATOC)(NO_3^-)]}{[Ag^+]} \quad (6)$$

Since the distribution ratio is defined as the ratio of silver concentration present in the aqueous and organic phases after extraction, the following equations may be derived.

$$D = K_{ex}[EATOC][NO_3^-] \quad (7)$$

$$\log D = \log K_{ex} + \log[EATOC] + \log[NO_3^-] \quad (8)$$

From this linear equation and experimental data, the equilibrium constant (K_{ex}) for silver extraction using EATOC, was estimated as 3.030×10^2 mol^{-2} dm^6.

^{1}H NMR studies: In the extraction process of silver(I) using EATOC, the ^{1}H NMR spectra were run before and after loading silver(I) to elucidate the interaction between them. The doublet peak assigned to aromatic protons of calixarene was shifted to the lower field (6.75 -> 6.91 ppm) after silver loading (Fig. 7). Carbonyl oxygen atoms, the donors in EATOC, are coordinated to Ag(I) by occupying its coordination sphere, resulting in conformal changes of the moieties in calixarene as well as altered interactions among the protons due to their different distance, which is considered responsible for its chemical shift to the lower field.

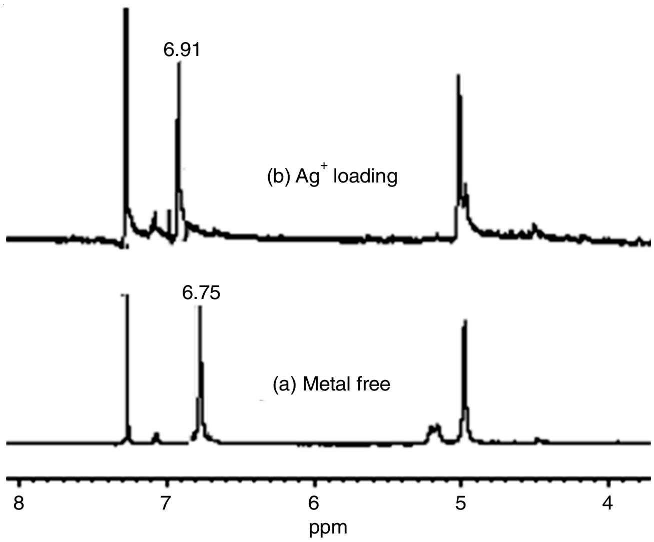

Fig. 7. ^{1}H NMR spectra of EATOC in $CDCl_3$ solvent

Stripping behaviour of Ag(I): Silver loaded in the organic phase by EATOC was re-extracted with various stripping agents and its recovery efficiency is summarized in Table-1, of which the most significant results were achieved by over 70 % in both 0.1 and 1 M thiourea aqueous solution.

TABLE-1
EFFICIENCY OF SILVER(I) BY BACKWARD EXTRACTION WITH VARIOUS STRIPPING AGENTS

Stripping agent	Stripping (%)
0.1 M Thiourea	73
1.0 M Thiourea	74
0.1 M Ammonium thiocyanate	30
1.0 M Ammonium thiocyanate	63
0.1 M Ammonia	39
1.0 M Ammonia	43

Conclusion

Diethylamide derivative of calix[4]arene (EATOC) was used to extract silver(I) from nitrate solution, which was well extracted in its wide concentration range. The extraction rate was not fast, which seems to be attributable to the low adsorption properties on the interface of EATOC. The stoichiometry of silver(I) and EATOC produces a 1:1 complex. Thiourea was the most effective agent for back extraction.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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