Comparison of interfacial behavior and silver extraction kinetics with various types calix[4]arene derivatives at heterogeneous liquid-liquid interfaces

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ABSTRACT

Various *p-tert*-octylcalix[4]arene derivatives as hydrophobic extractants have been prepared to investigate Ag(I) extraction efficiency in a batch-wise process in nitric acid media. The influence of the functional groups of the hydrophobic extractants on the interfacial behavior and Ag(I) extraction efficiency in nitric acid media has been investigated using the drop-volume method. Fitting of the interfacial tension isotherms to the Gibbs and Szyszkowski equations has provided parameters characterizing the interfacial activity of the extractants, in particular the Gibbs free energy of adsorption at the interface, the interface excess on saturation (Γ_∞) and the average area per the adsorbed extractant molecule (A_{min}). The amido-type *p-tert*-octylcalix[4]arene derivatives have strong interfacial activity and fast extraction rates. The interface excess at saturation (Γ_∞) increased with the type of functional groups in the following order: methyl ketonic < phenyl ketonic < dibenzyl amido < diethyl amido < quinolyl < pyridyl. The relationship between the interfacial activity and the dependence of the Ag(I) extraction efficiency on the different functional groups is discussed. The interfacial behavior of the extractants affected both the solvent extraction equilibrium and the kinetics and the overall results are consistent with a mass transfer mechanism at the heterogeneous liquid-liquid interfaces.

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1. Introduction

Solvent extraction is one of the most versatile and selective methods of separation technology and continues to find new ranges of application [1–8]. The liquid-liquid interface involved is of fundamental importance because the transport of substrates must occur through it [9] and the significance of the properties of the liquid-liquid interface in relation to the solvent extraction equilibrium and kinetics has become increasingly evident in recent years [10–15]. In the case of metal ion extraction by hydrophobic extractants, adsorption of the extractant molecules at the interface and their subsequent reaction there with metal ions are processes of primary importance. Knowledge of all interfacial phenomena which occur in heterogeneous liquid-liquid metal ion extraction systems is very helpful for selecting and designing useful extractants and for optimizing the separation process. Interfacial adsorption of hydrophobic extractants, such as the calix[4]arene

derivatives presently studied, results in a decrease in interfacial tension [13,15–17] and this interfacial activity is a property which has been subjected to increasing attention [18,19]. It's understanding is not only helpful in relation to the mechanism of the interfacial reaction but also for its relevance to important physical phenomena such as wetting, foaming and miscibility. Interfacial tension studies can provide useful information about the extractant concentration at the interface, expressed as the number of extractant molecules per unit interfacial area and measurement of interfacial tension isotherms has therefore become a routine procedure complementing conventional extraction studies and facilitating optimization of the extraction system [15]. In metal extraction processes, the metal ion forms complex with the extractant at the interface and the formed complex is transferred from the interface to the bulk organic phase(chloroform). The rate of the overall process is therefore dependent upon the interfacial activity of the hydrophobic extractant itself and the metal complex and their diffusive it in the extraction systems [20–26]. These factors are essential to elucidate the kinetics and mechanism of the solvent extraction [25–29]. Because of the easy structural variations influencing their properties as extractants, macrocyclic compounds

such as calixarene derivatives are attractive [30,31]. In our earlier work with such species, discrimination among various metal ions has been observed depending on the cavity size. For example, in comparison to amido-type p-tert-octylcalix[4]arene derivative with those of calix[6]arene and the corresponding monomeric, the cyclic tetramer was the most effective in extractive separation of silver and gold ions [32]. In recent work, ketonic-type p-tert-octylcalix[4]arene derivatives exhibit high selectivity for extraction of precious metals [33], even though the ketonic compound was not expected, on the basis of the HSAB principle, to be suitable for Ag(I) uptake because of the hard nature of the ketonic oxygen atom [34].

In the present work, we have summarized and compared systematically the interfacial behavior of various types p-tert-octylcalix[4]arene derivatives in nitric acid media to evaluate the effect of the interfacial activity of the extractants on the kinetics of Ag(I) extraction in heterogeneous liquid-liquid extraction systems. We report: (1) The interfacial activity of three types p-tert-octylcalix[4]arene derivatives at liquid-liquid interfaces. (2) The relationship between Ag(I) extraction efficiency and the interfacial activity for the extractants in extraction systems. (3) Evidence for a mass transfer mechanism at the heterogeneous liquid-liquid interfaces. Thus, this study provides useful knowledge concerning liquid-liquid extraction systems for selecting and designing more effective extractants and for optimizing separation processes.

2. Experimental

2.1. Materials

Chemical structures of the p-tert-octylcalix[4]arene derivatives used and their trivial names are shown in Fig. 1.

The p-tert-octylcalix[4]arene derivatives were classified into three types, all involving functionalization of all four phenolic-O sites. Type (i) contained aliphatic (MKTOC) or aromatic (PKTOC) ketonic substituents, type (ii), aliphatic (EATOC) or aromatic (BATOC) substituents, and type (iii) pyridyl (PyTOC) or quinolyl (QuTOC) substituents. These extractants were prepared from 5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene-25,26,27,28-tetrol (TOC) [38]. Ketonic- [33,34], and amido-types [34] derivatives were prepared in a similar manner to that described previously. All reagents were of analytical grade and were employed without further purification. Silver nitrate was used for the extraction experiments.

2.2. Forward extraction procedure and measurement

Organic solutions were prepared by dissolving each p-tert-octylcalix[4]arene derivative in analytical grade chloroform to the desired concentrations. Aqueous solutions were prepared by dissolving metal salts in aqueous nitric acid at various concentrations. Equal volumes ($3\,cm^3$) of both phases were mixed and shaken vigorously at 303 K for the time necessary to attain equilibrium. After phase separation, metal concentrations in the aqueous solutions before and after equilibration were measured by ICP-AES (Shimadzu, ICPS-8100). The percentage extraction of metal ion (%E) was calculated using Eq. (1):

$$\%E = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

where, C_i and C_e represent in initial and equilibrium metal concentrations in the aqueous phase (M), respectively.

Measurement of interfacial tension by the drop volume method
Drop volume measurement [39] as a modified drop weight measurement was carried out by slowly adding 10 drops of the chloroform phase 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 ($25\,cm^3$) of the desired concentration was added to the reservoir. To maintain a constant nitric acid solution temperature, the apparatus was placed in a thermostatted water bath. The interfacial tension γ was determined from Eq. (2):

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

where V, Δr, g, r, and f are volume of drop (m^3), the density difference between the aqueous and organic phases ($kg\,m^{-3}$), gravitational acceleration ($m\,s^{-2}$), the glass edge radius (m), and the correction factor, respectively [39].

3. Results and discussion

3.1. Ag(I) extraction efficiency

The time dependency of silver extraction was investigated with all six p-tert-octylcalix[4]arene derivatives, the results being shown in Fig. 2. The silver extraction efficiency for MKTOC especially and PKTOC were much slower than those for the other extractants, and for MKTOC changing the acid concentration from 0.1 to 1.0 M caused a rather minor effect. For MKTOC, it took at least 72 h to reach the extraction equilibrium at both acid concentrations, while for PKTOC more than 96 h was required to reach equilibrium for 0.1 M nitric acid but only 4 h for 1.0 M nitric acid (Fig. 2(B)). Even, extraction with PKTOC was still slow compared to extraction with the amido- and aza-aromatic derivatives for 1.0 M HNO₃. The silver extraction efficiency for BATOC and EATOC were little affected by the change in acid concentration but extraction by EATOC was perceptibly slower, although ultimately giving a higher degree of extraction. This is perhaps indicative of less favourable interface adsorption of EATOC, with its aliphatic amido substituents, than that of BATOC with aromatic ones.

3.2. Interfacial tension study

The effects of the extractant concentration on the interfacial tension of six p-tert-octylcalix[4]arene derivatives at the chloroform/nitric acid interface in different nitric acid concentration were depicted in Fig. 3. The interfacial tensions for four derivatives were decreased with increasing extractant concentration at both nitric acid concentrations. The interfacial tensions at 1.0 M nitric acid for all derivatives were lower than those at 0.1 M nitric acid. It indicated that the extractants at 1.0 M nitric acid were more interfacially-active than those at 0.1 M nitric acid. That is, the interfacial tension of the extractants at 1.0 M nitric acid was reduced rapidly than that at 0.1 M nitric acid. However, the values of the interfacial tension were significantly dependent on the structure and the nature of the extractant. The interfacial tension of EATOC was much lower than those of both ketonic-type derivatives. It indicated that EATOC was more interfacially-active than the ketonic-type extractants at both nitric acid concentrations.

The interfacial activity of BATOC and EATOC would be reduced rapidly because of their highly polar nature. Significant difference in the interfacial tension values between 0.1 M and 1.0 M nitric acid was not observed for MKTOC. It meant that MKTOC was not interfacially-active in nitric acid media. It would cause slow extraction efficiency of MKTOC. The interfacial tension at 1.0 M nitric acid was similar to that at 0.1 M nitric acid at the extractant concentration from 10^{-8} to 10^{-3} M, while it was very low at the extractant concentration higher than 5 mM compared with that in 0.1 M nitric acid. It indicated that PKTOC in 1.0 M nitric acid was more interfacially-active than that in 0.1 M HNO₃. Although the suddenly falling point of the interfacial tension was not completely correspondent with the extractant concentration of the present