IS THERE ANY EFFECT OF PRESSURE ON METAL CATION EXTRACTION PROPERTIES OF 7, 13-BIS (2' -THIAZOYL)-1,4,10-TRIOXA- 7,13-DIAZA-CYCLOPENTADECANE?

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Abstract: The effect of pressure on extraction of cations has been investigated in a mechanically stirred pressure chamber. By using the title compound, an effective complexing agent for Ag^+, to extract cations at high pressures, albeit up to 0.15 GPa, we demonstrated an absence of a pressure effect. It was deduced that the efficiency of stirring, sample volume and area of the liquid membrane are more crucial for effective extraction. We believe this is the first time such a specific study has been reported.

Introduction

The host-guest chemistry of crown ethers has been well summarized in several reviews.[1-6] Accounts of recent investigations vary from basic crown ethers and azacrown ethers[7-10] to more diverse crown ethers that incorporate heteroatoms of sulphur,[11-24] or selenium,[25] where Ag^+ was the predominantly complexed metal ion. High pressure S_NAr reactions have proved useful routes for the synthesis of mono- and diazacrown crown ethers bearing directly linked aromatic heterocycles.[11-14] The well-recognized bacteriostatic properties of Ag^+ still occur when the ion is incorporated into a chitosan-crown ether macromolecule.[26] The incorporation of additional ligands such as quinolin-8-methyl side arms exemplify the potential for extension of the chelating ability of species like diaza-18-crown-6.[27] The enantiomeric discrimination afforded by Yb^{3+} chelated with (+)-(18-crown-6)-2,3,11,12-tetracarboxylic acid is likely to serve as a useful aid in organic chemistry.[28] The continued development of crown ethers as sensors for ions and also as molecular scaffolds for materials and biological models has recently been reviewed.[29] Earlier accounts by our group have recounted high pressure S_NAr reactions for the preparation of mono- and diazacrown ethers linked directly to aromatic heterocycles and their selective binding and transport properties for Ag^+.[11-14] In connection with high pressure mediated functionalization of aza-crown ethers, much interest has been generated in high pressure methodology, since it has been demonstrated that high pressure is not only useful in effecting cycloadditions, but also in several kinds of ionic reactions.[30] However, only a few applications of high pressure in supramolecular chemistry have been performed hitherto. One of the typical examples is the incorporation of noble gas atoms into the cavity of buckminster fullerene C_{60} that takes place at 0.25 GPa and 600 °C.[31] Since we have envisaged performing heterogeneous reactions at high pressure, we have developed a high pressure apparatus with a mechanical stirring unit that, however, can generate a maximum pressure up to 0.3 GPa (Fig. 1). Although it is more desirable to construct a high pressure instrument with magnetic stirring unit, it was much more difficult to design such an apparatus because a high pressure instrument is usually made with stainless steel. The serious drawback of the present instrument is the bearing system which limits its repetitive use to pressures less than 0.15 GPa. To the best of our knowledge, there is no report that describes the effect of pressure on the extraction properties of some host compounds for metal cations. Conceptually, as shown in Fig. 2, a pressure effect on this process would be expected since the formation of host-guest would lead to volume contraction, thus being expected to assist extraction unless solvating or desolvating the hosts and/or guests is under consideration. Therefore we have attempted this present experiment and used the title compound as host and Ag^+ as guest cation.

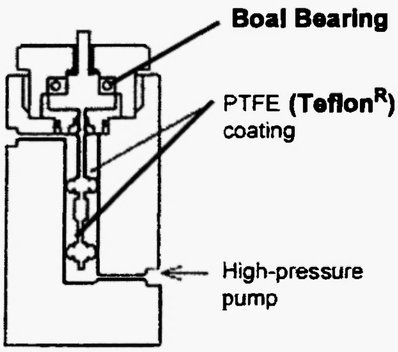


Figure-1: High pressure apparatus with mechanical stirring

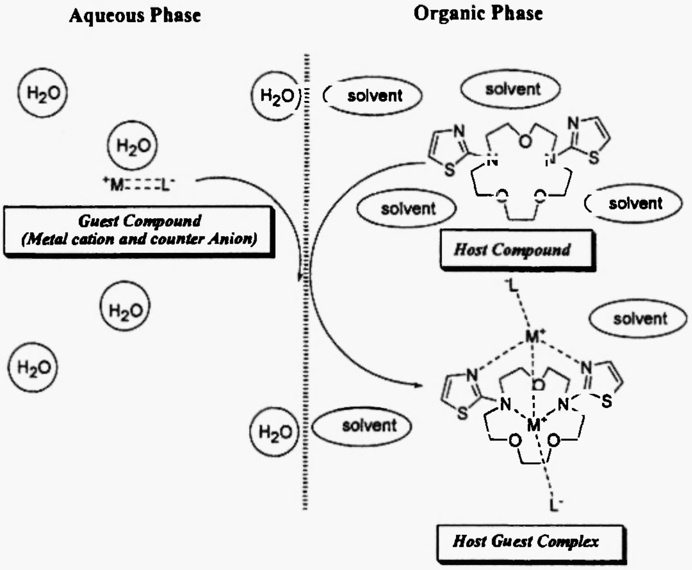
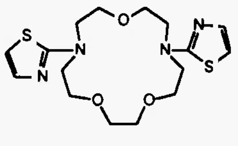


Figure-2: Schematic concept of metal cation binding process by 1 through liquid membrane

Result and Discussion

In the previous work, it was demonstrated that the thiazole-armed diaza crown ethers such as the diaza-15-crown-5 1 and the diaza-18-crown-6 2 specifically coordinated Ag^+ ion by the cooperative binding of two kinds of nitrogen atoms, whereas they rarely accommodated alkali and alkaline earth metal cations of similar ion sizes.[11] Remarkably, they form quite different types of binuclear complexes with Ag^+.[12] Thus, the thiazole moiety has proved to be a most effective binder for Ag^+ ion. Indeed, this property has been employed in the design of a molecular ballbearing.[32]



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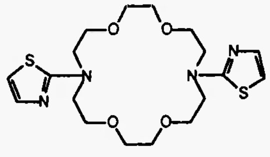

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Therefore, we chose the diaza-15-crown-5 1 as a model compound for investigation of a pressure effect on host-guest complex formation under mechanical stirring of 50 rpm at 0.15 GPa. Among the metal cations Na^+, K^+, Ag^+ and Pb^{2+}, the crown 1 selectively extracted Ag^+ as shown in Fig. 3. The cation extraction trend was almost exactly parallel to that at 0.1 MPa under magnetic stirring at 50 rpm,[11,14] although the cation extraction was less efficient. On the basis of a simple consideration of the entropy factor as described above, it was anticipated that extraction of Ag^+ by 1 would be promoted by applied pressure. However, it was ineffective.

There are the necessary multiple interactions to form host-guest complex.[1-4] Specifically, the solvent often plays an important role in these processes by solvating or desolvating the hosts and/or guests. Indeed, most of the reaction volumes, determined for the complexation of the alkali metal cations from the measurement of the partial volumes of such crown ethers as 15-crown-6, 18-crown-6, dibenzo-18-crown-6, dicyclohexyl-18-crown-6 and the corresponding complexes have proved to be positive and ranged from $+4 \sim +28\ cm^3 \cdot mol^{-1}$, except in the case of dimethylsulfoxide. The results are in agreements with the assumption that the decrease in volume due to the host-guest association is overcome by the the increase in volume by the desolvation of hosts and guests during complex formation.[33]

Initially, we thought our results were also in agreement with the same assumption. To help clarify this aspect, we envisaged a control experiment in which the same extraction experiment was performed under mechanical stirring at 0.1 MPa. However, the Ag^+ ion extraction properties did not vary with applied pressure as shown in Fig. 4.

In conclusion, no pressure effect was observed at 0. 15 GPa. Instead, the mode of stirring (mechanical or magnetic, e.g. efficiency of stirring), sample volume, and also probably area of liquid membrane seem to be more crucial for the extraction process.

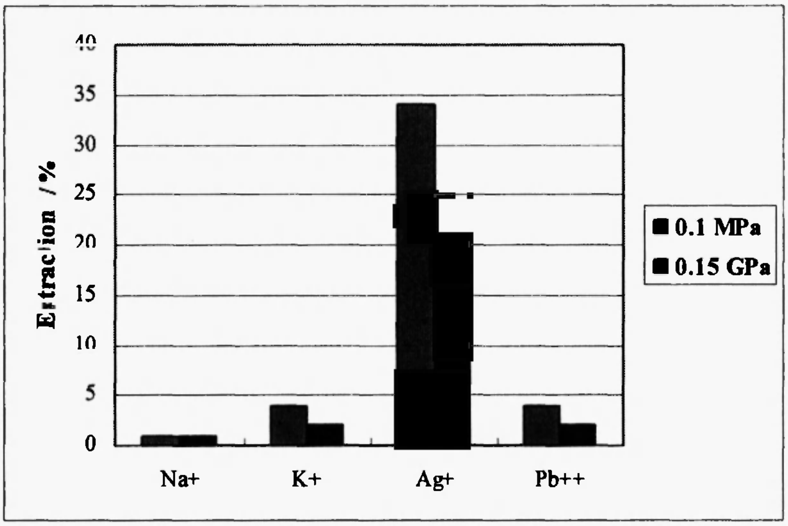

Figure 3. Cation extraction properties of 1 at normal and high pressure (0.15 GPa)

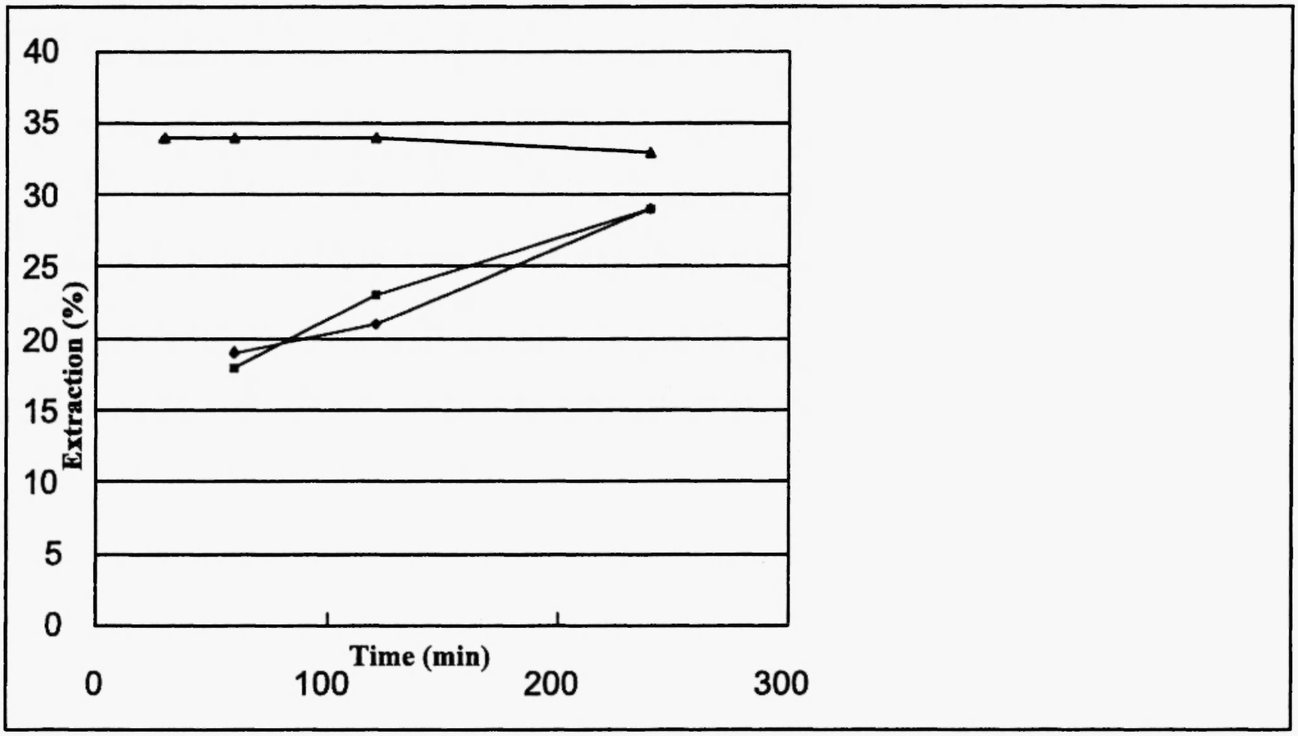

Figure 4. Control experiments of Ag^+ extraction properties under mechanical stirring and conventional method[11,14]; ◆: 0.15 GPa under mechanical stirring in high pressure vessel, ■: 0.1 MPa under mechanical stirring in high pressure vessel, ▲: 0.1 MPa under conventional method .

Experimental

The high pressure apparatus was designed by us and was constructed by Hikari Koatsu Kiki Co., Ltd, Hiroshima, 733-0012, Japan. 7,13-Bis(2'-thiazoyl)-1,4,10-trioxa-7,13-dizacyclopenta-decane 1 was prepared by the reported method.[11]

General procedure for estimating extraction properties for metal cations

A dichloromethane solution of 1 (0.01 M, 20 mL) was added to an aqueous solution of metal perchlorates (0.01 M, 20 mL).

Immediately after the mixture had been stirred mechanically (50 rpm) at 0.15 GPa (or 0.1 MPa) for 120 min (or appropriate time), the aqueous phase was separated. The concentrations of metal cations were deduced from concentrations of co-extracted perchlorate anions which were determined by a perchlorate ion-selective electrode (Orion EA940 Autochemistry System). This estimation procedure had already been established before by measuring concentrations of metal cations by atomic absorption or flame spectroscopy (Shimadzu AA-630-12 Atomic Absorption/Flame Emission Spectrometer). Furthermore, calibration was made with an Orion EA940 System by using 10^{-2} M, 10^{-3} M, and 10^{-4} M standard solutions of each metal perchrolate. It is a standard procedure already used by this group. [11,14]

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