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Photocontrolled Selective Isolation of UO_2^{2+} from Aqueous Solution onto a Quartz Plate Covered with a Novel Langmuir–Blodgett Film

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ABSTRACT

A new application of Langmuir–Blodgett (LB) film for the selective isolation of UO_2^{2+} from aqueous solution is reported. UO_2^{2+}can be isolated onto a quartz plate coated with a novel LB film which possesses the potential to form a complex with transition metal cations. The isolation process can be switched on by photoillumination and is distinguished by optical absorption spectroscopy. Isolated UO_2^{2+} can partly be released into acid solution, and the film can be used repeatedly for this extraction. This ion-exchange capability is sufficiently selective for UO_2^{2+} because of its strong affinity to the functional group in the LB film. Using the results traced by optical measurements, the lower limit of ion concentration for extraction was estimated to be 5×10^{-5} M.

Key Words. Uranium collection; Uranyl cation; Photoillumination; Langmuir–Blodgett (LB) film; Cation exchange

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INTRODUCTION

Extraction of UO_2^{2+} from aqueous solution is one of the most important processes in nuclear engineering (1). This process can be applied to the re-collection of uranium from nuclear fuel waste, the collection of uranium from seawater, and other treatments which are valuable for optimum use of uranium resources on our planet. The number of pretreatments required for characterization and quantitative analysis of uranium also depends on its extractability from samples to be examined.

The most popular techniques are based on the partition of uranium compounds into two liquid phases (1). The mechanism of partition across a liquid–liquid interface is essentially realized by the difference in its solubility into the two liquid phases, and thus the efficiency of the recovery depends on the equilibrium constant of the partition across the interface. Therefore this method can be applied only to uranium solutions with sufficiently high concentrations.

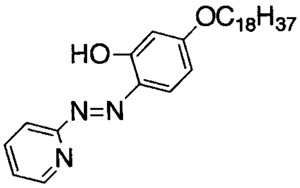
For solutions with low uranium concentrations, other types of extraction, including liquid–solid partitioning, seem to be more effective. Several of these methods have been reported and applied for practical use (2–4). These methods are based on the use of an adsorbent containing some chemicals which can form complexes with uranium compounds.

Recent progress in studies of Langmuir–Blodgett (LB) film provide opportunities to develop various kinds of new functional materials (5). Molecular orientation and packing can be highly controlled when LB films are formed from neat compounds. Two of the present authors (M.L., K.U.) and their coworkers presented a novel example of an LB film in which various metal cations dissolved in the liquid phase can be combined by photoillumination (6–8). The film possesses the potential to achieve selective isolation of particular metal cation with strong affinity in complex formation. Moreover, the combination process can be controlled by photoillumination, and this property is realized only in LB systems. The combined cations can be easily released into an acid solution, similar to the case of ion-exchange resins.

In the present paper we report an extensive study of previous papers (6–8) on the uranyl cation which has an extremely strong affinity to the film. The progression of the extraction of UO_2^{2+} was faster than in the case of Cu^{2+}. The results of this study clearly prove that the LB membrane can be applied to the extraction of UO_2^{2+} and indicate a practical procedure by which UO_2^{2+} can be isolated from a solution with 5×10^{-4} M UO_2^{2+}.

EXPERIMENTAL

The compound employed in this study, PARC18 [5-octadecyloxy-2-(2-pyridylazo)phenol], has the structure



This compound was obtained through the alkylation of 4-(2-pyridylazo)resorcinol, monosodium salt hydrate, purchased from Aldrich, Inc. The detailed description of the synthesis is reported in a separate paper (8). A 40-layer Y-type LB film was fabricated by successive deposition on a quartz plate at 30 mN/m at 20°C with nearly a unity transfer ratio (downstroke, $4\ \mathrm{mm\cdot min^{-1}}$; upstroke, $2\ \mathrm{mm\cdot min^{-1}}$), and was used in the present experiments. The total amount of PARC18 molecules was about 5×10^{-5} moles on each quartz plate.

The aqueous solution of uranyl nitrate was prepared by diluting a stock solution (100 mM in 3 N HNO_3) which was obtained from metal uranium provided by Nuclear Fuel Industries, Ltd. The LB plate was put into a 1-cm cell containing aqueous solutions of metal ions, and complex formation progressed with photoillumination using an ultrahigh-pressure mercury lamp (USHIO UI-501C, 500 W) with a 330-nm band-pass filter (HOYA U330). The cell was located about 10 cm in front of the output of the collimating lamp house for some period, then was analyzed using a Shimadzu UV-2100 spectrophotometer to monitor the change in the optical absorption spectrum. A releasing process using a nitric acid solution was also performed in the 1-cm cell.

RESULTS AND DISCUSSION

The Role of LB Films in the Present Work

Use of the present LB film (PARC18) provided the new ability of photocontrol of the extraction of uranyl cations. Here we review our previous results in which the basic concepts and results of the present study are included. Details have already been presented in separate papers (6–8).

We applied two compounds, PARC18 and TARC18 (5-(octadecyloxy)-2-(2-thiazolylazo)phenol), to metal ion extraction in previous work. The free molecules of these compounds can thermally react with transition metal cations in solution to form complexes. However, once they form an LB film in which all the molecules are aligned and stacked in a compact space, the rate of complex formation is considerably reduced and its ability for complex formation is almost lost. We immersed the film solutions containing various transition metal cations; almost no reactions were seen after a few hours in the dark. This is understandable since the configuration of each molecule is restricted, as in molecular crystals, and there is no room for *cis-trans* transformation between molecules in the stacked environment of LB films.

However, upon photoillumination, the LB films start to react with transition metal cations, which can be monitored by absorption spectroscopy or the color change of the film. The inclusion of transition metals was confirmed by ESR spectroscopy and ICP analysis of materials displaced from the LB films (7). Without any metal ions, *cis-trans* transformation should occur during photoillumination but the complex form cannot be generated and no *trans* form is stable in the LB film. The metal cations were revealed to be well aligned in the films, as monitored by ESR and x-ray diffraction (7). Up to now we have confirmed that various metal or metal-containing cations can be applied to this process by both or either TARC18 and PARC18. (The metals are Ag^{+}, Hg^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, VO^{2+}, Cd^{2+}, Pb^{2+}, Fe^{3+}, and Eu^{3+}.) Use of these films for photorecording was also suggested (8).

Once the metal cations are extracted from the films, they can be released upon contact with various acid solutions, and the films can be used repeatedly for the extraction process. We also performed extraction in a mixed-cation solution (Cu^{2+}, Ni^{2+}, Zn^{2+}) (7), the results of which indicate that the cation with the highest affinity is selectively extracted.

PARC18, compared with TARC18, is superior in extracting transition metals with a very large ion radius. TARC18 could not be used for uranyl cation extraction, as described in the following section. Although several characterization methods, such as ICP, ESR, and x-ray diffraction, could not be used for uranyl systems because of our present legal regulation of the treatment of nuclear fuels, the present reaction process can be discussed in parallel to those of previous work for other transition-metal-containing cations.

Extraction and Stripping Process

All the conversion processes of the LB film plate presented in this paper are summarized in Fig. 1. Since the structural conversion process was discussed in a previous paper (8), we merely provide a new scheme for UO_2^{2+} without further discussion. The various stages are visually distinguished by the surface color of the film (yellow, purple, and orange), and therefore we called each structure Y, P, and O, respectively. The most probable structural changes are also indicated. Y in *cis* form is converted to a *trans* form P that forms a stable complex with a uranyl cation. Although this conversion pro-

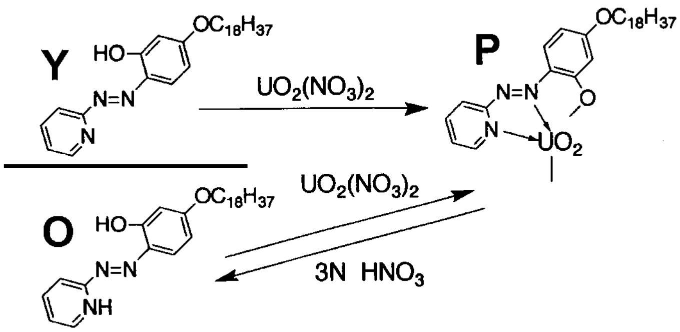


FIG. 1 A schematic diagram representing the structural conversions involved in the isolation of UO_2^{2+} onto the LB film of PARC18.

cess is not reversible, interconversion between P and O is reversible. O is assumed to be a protonated (acid) form of P since treatment with acidic solutions is effective in the stripping process from P to O. All these conversion processes were monitored by the change in the optical absorption spectrum as described below.

Figure 2 shows a series of absorption spectra which indicate the progression of the extraction process of UO_2^{2+} from its solution of 5×10^{-4} M $UO_2(NO_3)_2$ in 1.5×10^{-2} M (0.015 N) HNO_3. No change was observed in an experiment

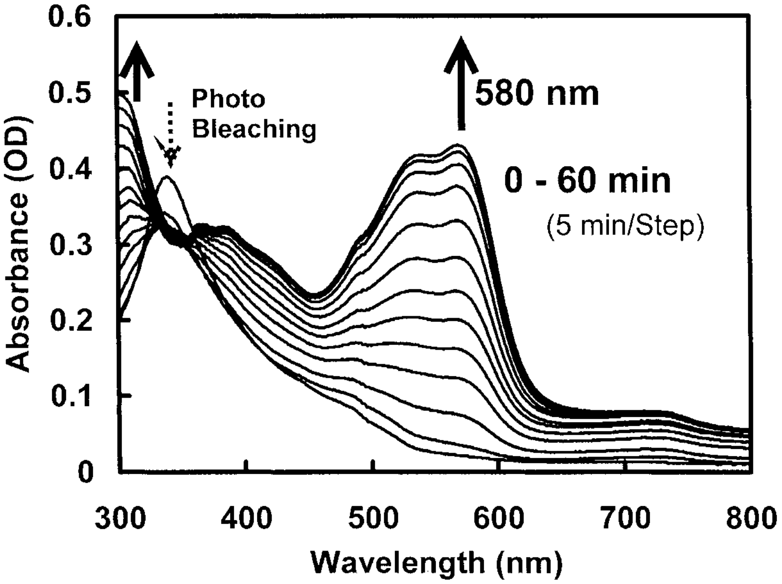


FIG. 2 Change of the absorption spectrum of the LB film of PARC18 during the extraction process of UO_2^{2+} from a solution of 5×10^{-4} M $UO_2(NO_3)_2$ in 1.5×10^{-2} M (0.015 N) HNO_3.

without photoillumination. The initial absorption spectrum is attributed to species Y. Upon photoillumination, the absorption spectrum changed gradually and a new absorption maximum appeared at around 580 nm. The isosbestic point was unclear but seemed to be located at around 380 nm. Since this spectral change should be due to *cis-trans* transformation, as described in previous papers (6–8), the progression of the extraction process is distinguished from the absorption spectra. The resultant spectrum should be attributed to the complex form of P shown in Fig. 1.

The spectral change stopped after 30 minutes of photoillumination, where the extraction process seemed to be almost saturated. The increase of absorption at 580 nm versus illumination time is plotted in Fig. 3; the results for the case of 5×10^{-4} M $CuCl_2$ in 1.5×10^{-2} M (0.015 N) HNO_3 are also displayed for comparison. The increase was saturated after 30 minutes of photoillumination for both systems. However, the optical density at the saturation point of Cu^{2+} is about half of that for UO_2^{2+}. Since this absorption is assigned to the diazo group, the extinction coefficient seems to be almost independent of the kind of metal cation. Therefore, it is concluded that the affinity of UO_2^{2+} is stronger than that of Cu^{2+} which possessed the strongest affinity as observed in the previous study. As indicated previously, the cation with the strongest affinity is isolated from the mixed solution. Because of present legal regulations, the experiment using mixed solution could not be carried out. However, since the affinity of Cu^{2+} is the strongest among the cations examined, this LB film should possess a capability to accumulate UO_2^{2+} on it.

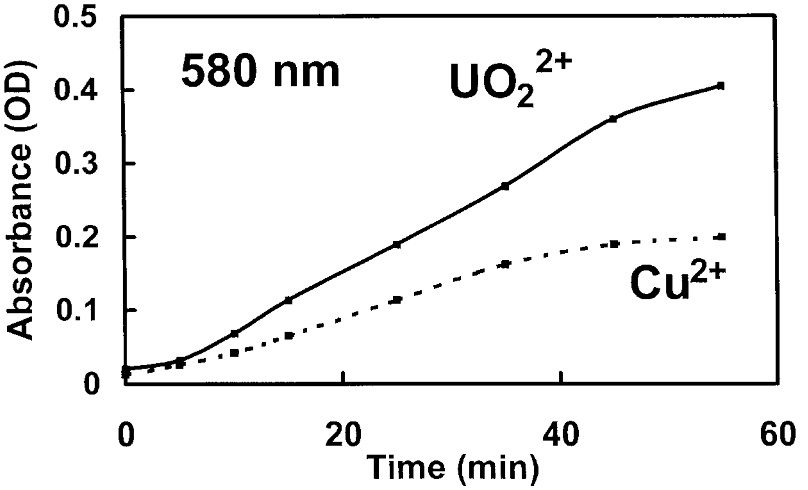


FIG. 3 The time profile of the absorption at 580 nm of the LB film of PARC18 on the extraction of UO_2^{2+} from a solution of 5×10^{-4} M $UO_2(NO_3)_2$ in 1.5×10^{-2} M (0.015 N) HNO_3, and that of Cu^{2+} from a solution of 5×10^{-4} M $CuCl_2$ in 1.5×10^{-2} M (0.015 N) HNO_3.

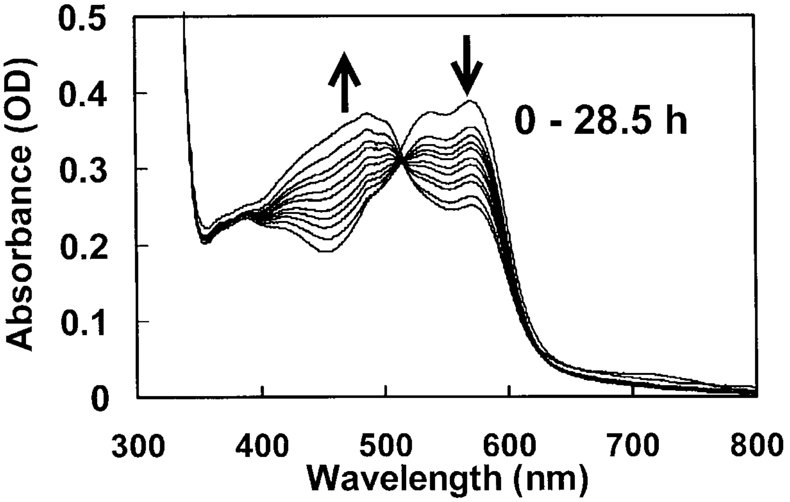


FIG. 4 The spectral change of the LB film of PARC18 on stripping UO_2^{2+} into 3 N HNO_3 solution in the dark.

We transferred the LB plate saturated with UO_2^{2+} into 3 N HNO_3 solution and monitored the change in the optical absorption spectrum, the results of which are shown in Fig. 4. The sample was left in the dark for several hours. The absorption at 580 nm decreased and the cation seemed to be completely released into the acidic solution after 10 hours. However, the resultant absorption spectrum is different from that in the initial stage of Fig. 2. This absorption was previously assigned to the protonated structure O of the *trans* form of Y. The results indicate that the first extraction process is irreversible. The time profile on this releasing process is shown in Fig. 5. The releasing time profile seems to be an exponential curve, but only 50% of the UO_2^{2+} is released after 1 day. More concentrated HNO_3 could not be used because it seemed to gradually destroy the LB film. However, almost no reduction of the absorption peak at 580 nm was observed when a 1 N HNO_3 solution was used.

Next, we performed the reextraction of UO_2^{2+} using the same LB plate after the previous releasing process. Photoillumination of the LB plate was done in the same way as in the experiment shown in Fig. 2. The results in Fig. 6 indicate that the UO_2^{2+} was again extracted onto the LB plate. The spectral change saturated after 30 minutes of photoillumination, and the final spectrum was the same as that in the initial stage in Fig. 4. This process is completely reversible, and the LB plate can be repeatedly used for the extraction of uranyl cations. The time profile of the spectral change is also indicated in Fig. 5.

It is clearly shown in this paper that the LB film of PARC18 has the capability of photocontrolled isolation of UO_2^{2+}. As discussed in previous studies,

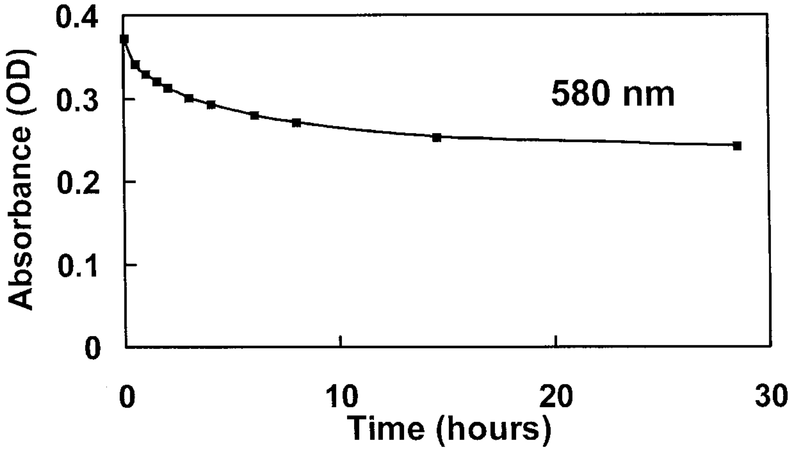


FIG. 5 The time profile of the absorption change at 580 nm on the stripping indicated in Fig. 4.

the free compound of PARC18 can react with various metal cations to form the complex P through a thermal reaction, losing the capability of photoswitching. The activation energy for the *cis-trans* conversion of free molecules can be supplied thermally at room temperature. Since the process of combination of the LB film of PARC18 with metal cations is extremely slow and is accelerated by photoillumination, we speculate that the photoswitching originates from the space formation which can involve a whole metal cation. A large structural conversion and/or local annealing from the

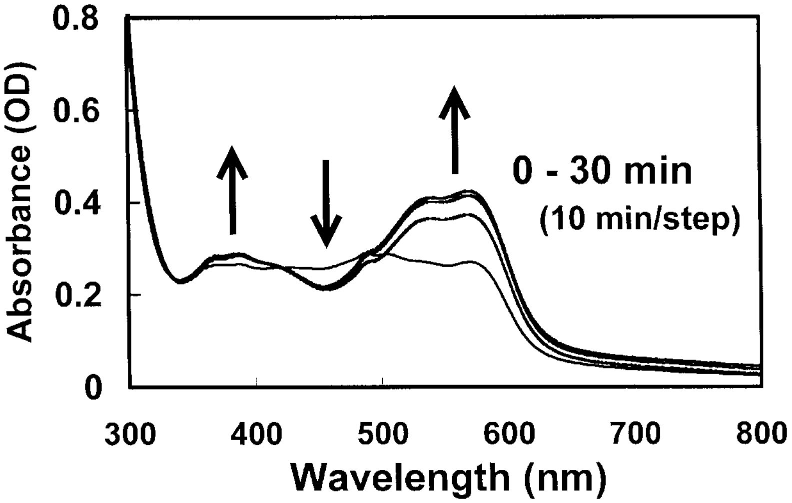


FIG. 6 The absorption spectral change of the LB film of PARC18 on reextraction of UO_2^{2+} from a solution of 5 × 10^{-4} M $UO_2(NO_3)_2$ in 1.5 × 10^{-2} M (0.015 N) HNO_3.

heat produced by nonradiative relaxation may loosen the local structure around the diazo group. The other compound, TARC18, which was used in a previous study, was also examined; no UO_2^{2+} extraction was observed. We also confirmed that the present compound (PARC18) is superior to TARC18 in its potential to extract a large metal cation like Eu^{3+}, probably because the intermolecular space in the LB film is larger for PARC18 than for TARC18. Since UO_2^{2+} is extremely large, only PARC18 possesses the capability to extract this cation. We also confirmed, by an x-ray diffraction experiment, that the alignment of each molecule in the LB films showed a sharp contrast between PARC18 and TARC18.

Using the present LB film of PARC18, several useful applications can be proposed. For example, extraction and isolation of UO_2^{2+} onto a plate can be used in a qualitative analysis to check for the existence of UO_2^{2+} in solution. Once the ions are isolated on the plate, they can be utilized in another characterization such as ICP. Although we only distinguished the extraction process based on the optical spectra and the lower limit of the ion concentration appeared to be about 5×10^{-5} M, the sensitivity should be improved by using other sensitive characterization methods. Photoswitching capability is also useful since a real-time monitoring system of the uranyl cation can be devised using these LB films. The capability of successive use of the interconversion between P and O species is also convenient for constructing an effective system for the recovery of uranyl cations.

In conclusion, the LB film of PARC18 can be applied to the recovery of uranyl cations, and this capability can be switched on by photoillumination. Since the affinity of this cation to the film appears to be stronger than that of any metal or metal-containing cation surveyed so far, the LB film also possesses the capability to isolate uranyl cations from mixed solutions of various cations.

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