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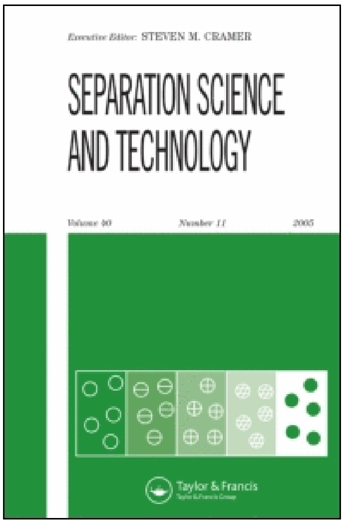

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TECHNICAL NOTE

Poly(Ethylene) Glycol as a Selective Biphasic Transfer Agent for the Extraction of Chromium(VI) from Aqueous Salt Solutions

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ABSTRACT

Poly(ethylene) glycol (PEG) has been used as a medium for the phase transfer recovery of chromium from aqueous salt solutions. Bubbling ammonia through an aqueous solution with the Cr(VI) in the upper PEG layer results in transfer of Cr(VI) to the lower layer. Similarly, passing carbon dioxide through the system in aqueous ammonia with Cr(VI) in the lower layer results in its transfer to the upper phase. Addition of ferrous sulfate leads to reduction of Cr(VI) to Cr(III) and essentially quantitative transfer of the chromium from the PEG to the salt layer. A combination of electrolysis and the Fe(II),(III) redox couple can be used to reduce Cr(VI) to Cr(III) because after oxidation of the added Fe(II) to Fe(III) by Cr(VI), the Fe(III) can be electrolytically reduced back to Fe(II). The Fe(II) needs to be present in only catalytic quantities.

Key Words. Poly(ethylene) glycol; Chromium; Phase transfer; Fe(II),(III); Electrolysis

INTRODUCTION

The synthesis of complexants and hosts for specific metals is an important goal for metals that are toxic and commercially valuable. For such metals it is important that they be removed from contaminated soils and waters and recovered in pure form. For cations the metal can be directly bound to a ligating group on the host. Whereas numerous molecules act as hosts and complexants for cations, fewer hosts are available for anions (1–4). From an environmental viewpoint, it would be useful to have selective hosts available for the

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oxyanions of chromium(VI). This represents a strategic variation from designing cationic hosts since these anions will likely have no direct interaction between the metal center and the host. These anions are important both because of their high toxicity (5–10) and their presence in soils and waters (11). Chromium (VI) is a carcinogen in humans and animals, and it is mutagenic and genotoxic. Chromium(VI) requires intracellular reduction for activation, and this in vivo reduction can produce several reactive intermediates such as Cr(V) and Cr(IV) that can target and damage DNA (10). By contrast, water-soluble Cr(III) compounds are not considered to be carcinogenic, possibly because they do not cross plasma membranes (12, 13).

Several approaches have been used for the environmental removal of Cr(VI). Among the methods presently available are extractions with carbonate or phosphate buffers, or sonication with hydroxide solution. Another direct method uses a mixture of Na_2CO_3 and NaOH at 90–95°C (14). An alternative approach involves reduction of Cr(VI) in the presence of oxide surfaces, using α-hydroxyl carboxylic acids such as mandelic acid (15), or with oxalic acid or substituted phenols (16). Another approach couples the microbial reduction of Cr(VI) with the anaerobic degradation of benzoate (17).

One approach to designing extractants for Cr(VI) is to use salt formation with alkylammonium ions (18, 19). Another is ion exchange (20–22). Recently, however, a number of chemically modified calixarenes have been synthesized that can be used as anion hosts (23), and we have used calix[4]arenes with amine or amide functionalities on their lower rim as extractants for anionic Cr(VI) (24–26). Although a calix[4]arene diamine transfers Cr(VI) from aqueous acid into chloroform and back into the aqueous layer in the presence of base (24), the system has limited usefulness because of the toxicity of chloroform and the susceptibility of the amine to oxidation. The use of calix[4]arenes with butylamine functionalities allows for phase transfer of Cr(VI) into isooctane rather than chloroform; however, amine oxidation still occurs (27). Despite this research, a quantitative extraction method for the total removal of Cr(VI) from soils and waters is still needed (17).

An alternative to the traditional liquid/liquid extraction based on the partitioning between a water immiscible organic solution and an aqueous phase is the use of a system comprising a polymer and an inorganic salt that separate into two immiscible aqueous layers. One such system uses poly(ethylene) glycol and ammonium sulfate. In this biphasic system the upper phase is referred to as the PEG-rich phase and the lower as the salt-rich phase (28).

EXPERIMENTAL

PEG-2000 was purchased from Aldrich Chemical Co. and used as received. All metal salts were purchased from Fisher and used as received. High purity water was produced by passing distilled water through a Milli-Q deionizing system. A Perkin-Elmer Plasma 400 Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) equipped with a pneumatic crossflow nebulizer was used for all chromium determinations. For chromium analyses a wavelength of 205.552 nm was used along with analogous conditions to those previously used (29). No interferences from other elements were present at this wavelength.

Biphasic extractions were performed by mixing PEG-2000 (2.0 g) and $(NH_4)_2SO_4$ (2.0 g), and adding $Na_2CrO_4{\cdot}2H_2O$ (10^{-3} M in either 1% HNO_3 or 1 M NH_4OH) to bring the total volume to 6.0 mL. For ICP-AES measurements the more viscous PEG-200 rich upper layer was diluted with water to the same viscosity as the lower salt phase to eliminate sample flow rate discrepancies between the two, and the factor of dilution was taken into account when determining the chromium content of the upper layer.

The proton switch experiments were carried out using a modified chromatography column fitted with a gas permeable frit on the bottom through which ammonia and carbon dioxide could be introduced. A biphasic system as described above was prepared, placed in the column, and allowed to settle into separate layers. Gaseous ammonia or carbon dioxide (from the sublimation of dry ice) was bubbled upward through the solution vigorously, affording complete mixing of the phases. After 5 minutes the gas flow was stopped and the phases were allowed to separate again.

The electrochemical studies were performed using a custom-built cell which held the biphasic system with a Pt electrode situated in the upper layer and a second identical electrode in the lower layer. Volume ratios were 1:1 in both the column and the cell.

RESULTS AND DISCUSSION

In this note we report that poly(ethylene) glycol (PEG) can be used as a medium for the phase transfer recovery of chromium from aqueous salt solutions. This polymer was chosen because it is inexpensive, nontoxic (30), relatively stable to oxidation, water soluble, and has useful biphasic properties (31–38). Furthermore, PEG has a sequence of ether oxygen functionalities available for hydrogen bonding with the oxo groups of the Cr(VI) anions, or for coordinating to the alkali metal cations in the salts Na_2CrO_4 or $K_2Cr_2O_7$. As such, PEG can be considered as an open-chain form of a crown ether, compounds that are well known for their complexation properties with Group I metal ions (3). The chromium can be recovered from the PEG layer by a proton switch, or by reduction to the Cr(III) state, when it transfers back to the aqueous salt phase.

Phase Distribution

The distribution of Cr(VI) into the upper PEG and the lower salt layers, as determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), is shown in Table 1. These data show that the majority of the Cr(VI) is in the PEG layer under conditions where it has a pH of 7 and the aqueous salt layer has a pH of 6. By contrast, under these solution conditions the species Na(I), Co(II), Zn(II), Mn(II), Al(III), Pb(II), Nd(III), Eu(III), Gd(III), Th(IV), and U(VI) are dissolved almost entirely in the lower salt layer, thereby allowing for this biphasic system to be used for the phase separation of Cr(VI) from these metals. Preparing the solutions in aqueous ammonia results in both layers having a pH of 8 and the Cr(VI) partitioning to the lower layer.

Proton Switch

A proton switch for transferring a metal ion between phases is an attractive strategy (21), especially if it can be achieved without generating salts that will need to be removed subsequently. We have therefore investigated whether we can accomplish this for chromium with a biphasic PEG system. Bubbling ammonia through an aqueous solution with the Cr(VI) in the upper PEG layer results in transfer of Cr(VI) to the lower layer. Similarly, passing carbon dioxide through the system in aqueous ammonia with Cr(VI) in the lower layer results in its transfer to the upper phase. The sequential addition of ammonia and carbon dioxide results in a switching of Cr(VI) between the two layers.

TABLE 1
Distribution of Chromium between the Upper PEG and Lower Aqueous Salt Layers

Conditions	$[\mathrm{Cr}]_{\mathrm{upper}}/[\mathrm{Cr}]_{\mathrm{lower}}$	$\mathrm{pH}_{\mathrm{upper}}$	$\mathrm{pH}_{\mathrm{lower}}$
5 minutes (min)	12.25	7	6
20 hours (h)	2.89	7	6
5 min/Fe(II)	0.10	7	6
20 h/Fe(II)	0.11	7	6
5 min/HNO_3	10.85	4	4
20 h/HNO_3	4.58	4	4
5 min/HNO_3/Fe(II)	0.07	4	4
20 h/HNO_3/Fe(II)	0.05	4	4
5 min/NH_3	0.22	8	8
20 h/NH_3	0.20	8	8
5 min/NH_3/Fe(II)	<0.01	8	8
20 h/NH_3/Fe(II)	<0.01	8	8

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These compounds are favored over others in the design of a chemical switch because their sequential use does not lead to salt formation since ammonium carbonate readily dissociates to gaseous carbon dioxide and ammonia, which can be readily removed from solution.

Redox Switch

Poly(ethylene) glycol offers a potential route to extract Cr(VI) selectively from salt solutions and recover it in its Cr(III) form. An alternative switch uses the reduction of Cr(VI) that is primarily in the upper PEG layer to Cr(III), where it is a blue solution in the lower salt solution. The cell has the anode in the upper layer. Similarly, the addition of ferrous sulfate results in reduction of Cr(VI) to Cr(III), and essentially quantitative transfer of Cr(III) from the PEG to the salt layer. A combination of electrolysis and the Fe(II),(III) redox couple can also be used to reduce Cr(VI), since after oxidation of the added Fe(II) to Fe(III) by Cr(VI), the Fe(III) can then be electrolytically reduced back to Fe(II) in a continuous process with Fe(II) being present in only catalytic quantities (Scheme 1). The precise form of the chromium under these conditions is presently unknown. The chromium-containing solution is blue, which is suggestive of the presence of a Cr(II) form. However, Cr(II) solutions are strongly reducing, and we have observed no color loss upon the addition of aqueous hydrogen peroxide. Clearly Cr(II) is not a viable option, although oxy- or hydroxy-bridged Cr(III) clusters are possibilities. The availability of these switches to reduce the chromium rapidly to its trivalent form is important because long-term exposure of PEG to Cr(VI) results in degradative oxidation of the polymer. This problem will need to be remedied before any scale-up of such a process can be considered.

$$\mathrm{Cr(VI)} + 3\mathrm{Fe(II)} - \mathrm{Cr(III)} + 3\mathrm{Fe(III)}$$

$$3\mathrm{Fe(III)} + 3e^{-} \rightarrow 3\mathrm{Fe(II)}$$

SCHEME 1

CONCLUSION

Poly(ethylene) glycol can be used for the phase separation of chromium(VI) from aqueous salt solutions. Ammonia causes transfer of the Cr(VI) in the upper PEG layer to the lower aqueous layer. Carbon dioxide causes the reverse. Ferrous sulfate causes reduction of Cr(VI) to Cr(III), and transfer of the chromium from the PEG to the salt layer. A combination of electrolysis and the Fe(II),(III) redox couple can be used to reduce Cr(VI) to Cr(III) because after oxidation of the Fe(II) to Fe(III) by Cr(VI), it can be electrolytically reduced back to Fe(II).

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