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Efficient separation of vanadium from chromium by a novel ionic liquid-based synergistic extraction strategy

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HIGHLIGHTS

- Pure IL [A336][NO_3] plus [RNH_3][NO_3] was used to extract and separate V from Cr.
- It shows a notable synergistic effect for V with improved separation factor $\beta_{V/Cr}$.
- IL is not only extractant but also good solvent for the ion-type extracted species.
- Anion exchange mechanism between NO_3^- and $V_4O_{12}^{4-}$ (or $V_3O_9^{3-}$) was confirmed.
- IL phase can be recycled through stripping the loaded vanadium by 0.5 M $NaNO_3$.

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ABSTRACT

Ionic liquid (IL)-based extraction is a promising and environmentally benign separation technology. To develop sustainable extraction technologies, quaternary ammonium-based IL extraction strategy is attractable. In this work, the separation of vanadium(V) from chromium(VI) by pure tricaprylmethylammonium nitrate ([A336][NO_3]) and organic acidified primary amine N1923 ([RNH_3][NO_3]) was systematically investigated. The optimal proportion of [A336][NO_3] and [RNH_3][NO_3] was studied and results showed that the mixed [A336][NO_3] and [RNH_3][NO_3] exhibited an obvious synergistic-effect for V(V). The extraction of V(V) was strongly dependent on the acidity of the aqueous phase and reaches maximum at pH 2.5–3, while the maximum separation coefficient ($\beta_{V/Cr}$) was located at about pH 9.0. Moreover, $\beta_{V/Cr}$ could be improved through adjusting the molar concentration ratio of V/Cr. The interference of coexisting anions (nitrates, chlorides, sulfate and phosphate) on the extraction of V(V) was examined and the results showed that PO_4^{3-}, NO_3^- and Cl^- had negative effects at various degrees except for SO_4^{2-}. The V(V) extraction behaviors could be properly described by Langmuir and pseudo-second-order rate equations. The maximum extraction capacity for V(V) was estimated as 1.877 mmol/g at 303 K. Increased temperature had little effect on the extraction capacity, but greatly improved the extraction rate. The typical anion exchange mechanism between NO_3^- and $V_4O_{12}^{4-}$ (or $V_3O_9^{3-}$) was proposed for the current extraction system. The IL phase could be renewed through stripping the loaded vanadium by a 0.5 M $NaNO_3$ solution. This work demonstrated that quaternary ammonium IL containing a commercial organic extractant is an efficient and sustainable IL-based extraction strategy for the separation of vanadium from chromium, and as a result, the development of an IL-based extraction process is straightforwardly envisaged.

1. Introduction

Liquid–liquid extraction is the most widely applied technology for metal ion separations due to its advantages including operation in a continuous mode, employment of simple equipment, achievement of high sample throughput and easy scale-up. However, the conventional liquid–liquid extraction process utilizes water-immiscible molecular solvents which are flammable, volatile or toxic. Without doubt, innovative and green extraction processes are highly desired with growing concern about safety issues and environmental impact related with the use of these volatile organic compounds (VOCs).

Ionic liquids (ILs) are a type of organic salts with a melting point below 100 °C. Their negligible vapor pressure and non-flammability make this class of solvents safer and more environmentally friendly than molecular solvents. Since Rogers and his co-workers firstly reported the use of room temperature ionic liquids to

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separate substituted-benzene derivatives [1], ionic liquid as novel media for 'clean' liquid–liquid extraction has gained increasing attention in the field of the development of sustainable separation processes [2–6]. In particular, studies on the use ILs either as ion-type extractant or as suitable candidate for replacement of volatile organic solvent for separation of metal ions have been well documented [6]. As a kind of ion-type extractant, the extraction of metal ions often takes place via an ion-exchange mechanism [7–13]. This means that loss of ionic liquid components occurs inevitably upon extraction, which would hamper the regeneration of ionic liquids. What's more, it will contaminate the water, especially in the case of the ionic liquids containing fluoride. For example, PF_6^- of $[C_n mim][PF_6]$ can hydrolyze into toxic and corrosive PO_4^{3-}, HF, POF_3, H_2PO_3F, HPO_2F_2 at acidic media [14,15], and these compounds can pollute water body persistently.

Recently, task-specific ionic liquids (TSIL) with non-fluorinated anions and functional cation for task-specific purpose, such as tricaprylmethylammonium chloride (Aliquat 336, [A336][Cl]) [16] and tri(hexyl)tetradecylphosphonium chloride (Cyphos IL 101) [17], draw wide attention owing to the above reasons. As far as [A336][Cl] or $[A336][NO_3]$ is concerned, their application in the extraction of metal ions can be categorized in three aspects. Firstly, these ILs are used as single extractant or synergistic extractant in the traditional VOC-based extraction of metal ions [18–20]. In this case, the prominent advantage of using ionic liquids for extraction is lost. Secondly, these ILs have been employed to tailor new TSILs as efficient extractant [21–24], such as [A336][P507], [A336][P204], [A336][Cyanex272] and [A336][DGA]. Unfortunately, the synthetic TSILs usually exhibit high viscosity and limited solubility. Sometimes, these ILs are solely used as solvent [23,25]. Consequently, there are few reports on the use of [A336][Cl] or $[A336][NO_3]$ in a pure state as both extractant and solvent. These ILs can adopt ion association or anion-exchange mechanism during the extraction of metal ions, so that no organic ligand (cation component of IL) is lost. In this viewpoint, their toxicities are lower than those of imidazolium-type ILs. It is worth mentioning that their costs are much cheaper than those of $[C_n mim]^+$-type ILs. Undoubtedly, such advantages are much preferred for IL-based extraction.

Vanadium is an important metal for high-tech fields such as aerospace, catalyst, steel and iron industries. [26] Furthermore, vanadium and chromium are a pair of adjacent transition metals and co-exist in nature. It is not an easy task for the separation of vanadium from chromium due to their similarly physicochemical properties. In the past decades, the separation of V(V) from Cr(VI) has drawn considerable attention. Although successful separation of V(V) from Cr(VI) could be achieved by traditional liquid–liquid extraction by amines [27–30], environmental problems as well as generation of interfacial emulsion and crud caused by the use of huge amount of VOCs as diluents have been long realized [29,30]. Moreover, Cr(VI) is a well-known strong oxidant. It can cause the oxidation of alcohols [31], alkynes [32], aldehydes [33] and amines [34], which takes place more readily under acidic conditions. Currently, most of the V–Cr separation are performed in the acidic or neutral aqueous solution. As a result, the extractants (amines) could be destroyed by Cr(VI). Indeed, in our preliminary experiments, it has been observed that the organic extractant phase became darker and darker from the light yellow if contacting the Cr(VI) aqueous phase in acid media for a longer time.

Recently, we reported the separation of V(V) from Cr(VI) using $[C_8mim][PF_6]$ [35]. Although this separation is efficient, $[C_8mim][PF_6]$ suffers from the loss of anion PF_6^- due to an anion exchange mechanism between PF_6^- and vanadate. In this work, a novel V(V)–Cr(VI) extraction and separation strategy from near-alkaline solution was designed by using pure $[A336][NO_3]$ containing a commercial extractant N1923 as mixed extractants. Where, it is expected that $[A336][NO_3]$ plays not only a kind of solvent for the ionic extracted species but also an efficient extractant for vanadate. Moreover, since ion liquids are ready to be stable for large cation or large anion [36], it is expected that the big cation $[A336]^+$ has a stronger affinity to the larger vanadate than that to the smaller chromate. Due to the solubilization of IL for the ionic species, the extraction and separation performance of V(V) and Cr(VI) should be enhanced. Hence, it can be expected that the novel IL-based extraction system consisting of quaternary ammonium nitrate IL containing a commercial extractant is an efficient and sustainable strategy for the separation of vanadate and chromate.

2. Materials and methods

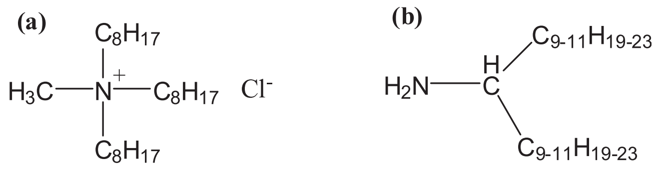
2.1. Materials

Aliquat 336 ([A336][Cl]), tricaprylmethylammonium chloride is a mixed quaternary ammonium salt containing mainly trioctylmethylammonium chloride (Aldrich, 97%). Primary amine N1923 (93%) was kindly supplied by Shanghai Rare-earth Chemical Co., Ltd. Their structures of the main components were shown in Scheme 1. The stock solutions of V(V) and Cr(VI) were prepared by dissolving $NaVO_3$ (analytical grade, Sinopharm Chemical Reagent Co. Ltd. China) and Na_2CrO_4 (analytical grade, TianJin GuangFu Fine Chemical Research Institute, China) in deionized water, respectively. The other chemicals, such as KNO_3, NaCl, Na_2SO_4, $NaNO_3$ and Na_3PO_4, are analytical grade reagents. All chemicals were used as received, without further purification.

Many developed ionic liquids including Aliquat 336 had relatively high viscosity, which is disadvantageous to industrial application. To decrease the viscosity of Aliquat 336 and to improve mass transfer and kinetics, [A336][Cl] was replaced by $[A336][NO_3]$ in this work. In order to prepare $[A336][NO_3]$, 100 g of [A336][Cl] was pre-equilibrated 4 times with each 200 ml 2.5 M KNO_3 solution to exchange the chloride ions to be nitrate ions. The decline in chloride concentration after each equilibration is shown in Table S1. After the fourth equilibration, chloride levels remained a very low extent and almost unchanged, which shows that most of [A336][Cl] has been changed to be $[A336][NO_3]$. In order to control extraction equilibrium acidity, N1923 was pre-equilibrated with 0.5 M HNO_3 according to a stoichiometric ratio of 1.05 between HNO_3 and $-NH_2$, then the obtained acidified N1923 (abbreviated as $[RNH_3][NO_3]$) was washed till neutral by deionized water. Physical properties of Aliquat 336, $[A336][NO_3]$, N1923 and $[RNH_3][NO_3]$, including density (g/cm^3), viscosity (mPa s) and average molecular weight, were listed in Table S2. As shown in Table S2, the viscosity of [A336][NO_3] was much less than that of [A336][Cl], which would thus improve the extraction and save energy.

2.2. Instruments and measurements

The pH measurements were performed using HANNA pH211 digital pH meter (Italy). The concentrations of metal ions in aqueous phase were determined by OPTIMA 7000DV inductively coupled plasma-optical emission spectrometer (ICP-OES)



Scheme 1. Structures of main components for ionic liquid Aliquat 336 and extractant N1923 used in this study.