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Tuning the selectivity of non-aqueous liquid-liquid extraction systems by addition of hydrophilic ionic liquids as second extractant to the more polar phase

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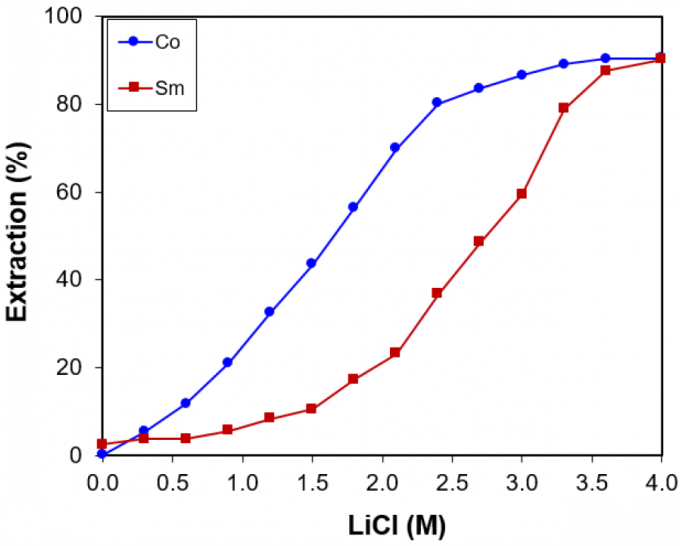
PURPOSE OF THE ABSTRACT

Liquid-liquid extraction (solvent extraction) is one of the most widely used techniques for metal separations. Conventionally, a liquid-liquid extraction system consists of an aqueous phase (more polar) that contains the metals to be separated and an organic phase (less polar) that contains extractants, a diluent and sometimes a modifier. The extractants always reside in the less polar phase due to their high hydrophobicity, which minimizes the loss of extractants to the aqueous solution. The separation of metals is achieved by the difference in the affinity of metals to the extractants. The optimization of metal separations is largely dependent on the composition of the less polar phase, such as the type and concentration of extractant, the property of diluent, and sometimes a second extractant can be used as a synergist to enhance separation. To a less extent, adjustment of the aqueous pH for acidic extractants and addition of salts to the more polar phase for adducting metals could also effectively optimize separations. However, for a specific extractant, its affinity to metals (the distribution ratio of metals) has a specific sequence that is independent of the extractant concentration in the less polar phase and the pH and salt concentration of the aqueous phase. These parameters deal with the coordination of metals with the extractants in the less polar phase and have limitation in the selectivity of metals.

Until now, extractants in liquid-liquid extraction systems exclusively reside in the less polar phase, no study has reported the use of an extractant in the more polar phase, to the best of our knowledge. This fact might be explained by the relative solubility of extractants: it is easy to keep extractants in the less polar phase by making them hydrophobic, but difficult to keep extractants in the more polar phase, because even hydrophilic molecules can be soluble in the less polar phase.

Ionic liquids (ILs) are a group of special material that consists entirely of ions. ILs containing chelating functional groups can coordinate with metals and some hydrophobic ILs have been used as extractants (residing in the less polar phase). In principle, hydrophilic ILs containing the same functional groups as hydrophobic ILs should have similar metal extracting capability. Moreover, ILs have high polarity because they are composed of discrete cations and anions, which would make hydrophilic ILs insoluble in the less polar phase. Therefore, hydrophilic ILs are potential extractants that can reside in the more polar phase. In this study, we demonstrate the use of hydrophilic ILs as extractants in the more polar phase while the less polar contains an ordinary extractant. As an example, both trialkyl phosphine oxides and quaternary ammonium chlorides extract $CoCl_2$ more efficiently than $SmCl_3$, but when they are concurrently dissolved in the less polar phase and the more polar phase respectively, more efficient extraction of $SmCl_3$ can be achieved with a high separation factor. The mechanism of the unusual metal separation is the competition of metal coordination with the two extractants in the two immiscible phases. With two extractants concurrently in the two immiscible phases, coordination of metals respectively with two extractants can be regulated simultaneously, therefore the selectivity of metals is much more flexible and controllable, leading to unusual metal separations. In principle, the method of metal extraction with two extractants together could significantly enhance the selectivity of many kinds of metal separations using a variety of hydrophilic ionic liquids in the more polar phase.

FIGURES



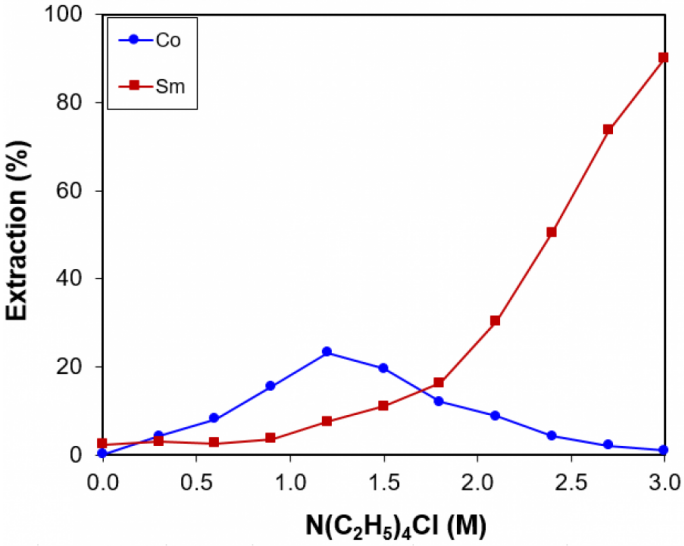


FIGURE 1

Extraction of Co and Sm by Cyanex 923 with LiCl in the more polar phase

Blue circle is Co;

Red square is Sm.

FIGURE 2

Extraction of Co and Sm by Cyanex 923 with tetraethylammonium chloride in the more polar phase

Blue circle is Co;

Red square is Sm.

KEYWORDS

liquid-liquid extraction | hydrophilic ionic liquid | two-extractant | cobalt and samarium

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