Ionic liquid extraction of rare earth metals

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Rare earth elements (REE) pertain to rare earth metals, which is now a days more essential to current industries. Rare earth metals have been widely used in various important products such as magnets, and catalysts etc. Therefore, the demand of rare earth metals has drastically increased in recent years.

Solvent extraction is the most effective method to enrich metal ions. The study on extraction of Neodymium (Nd), Dysprosium (Dy) and Praseodymium (Pr) etc. by an extractant in conventional organic solvents has been advanced. But, there is concern on increasing air pollution, human health and sometimes produces large volume of aqueous waste. A modern green metal processing technique will therefore have to take place at low temperatures in an eco-friendly environment which allows control of metal speciation, and tolerates impurities.

In recent times, ionic liquids (ILs) have received attention from many researchers for a wide range of applications. The majority of reports investigate their use as a replacement of volatile solvents owing to their non-volatilic properties but also because they often produce enhanced yields or reaction rates. Thus, the IL based extraction is more gracious and safe for environment compared to the volatile based extraction. ILs has also attracted considerable interest from electrochemical researchers because they tend to have a wide electrochemical window for metal deposition and also for application in a range of electrochemical devices such as solar cells, and lithium batteries.

In view of awareness of the deteriorating environment, it is necessary to develop an alternative environmental friendly system to replace the traditional. In this context, ILs was suggested as “green” solvents for metal extraction and separations. At the same time, ILs have extremely low vapor pressure, high thermal stability which offers advantages such as ease of containment, product recovery, recycling ability and suggested as the best solvent for extraction purposes.

For selection of the most effective ILs extraction solvents for Neodymium chloride (NdCl₃) and Dysprosium chloride (DyCl₃), we applied theoretical COSMO-RS model based on quantum chemistry and statistical thermodynamics of predefined Nd/DyCl₃-ILs systems. Up to 4,400 different IL systems have been considered as potential solvents. The quantum chemistry package of Turbo-mole was used to optimize geometries of all molecules, while solute-solvent interactions were calculated using the COSMOthermX software.

The chemical potentials of the metals salts in all ILs revealed significant decreases in values of the chemical potentials in systems with ionic liquids based on one specific cation of dodecyl-dimethyl-3-sulfopropylammonium, and three specific anions of bis(2,4,4-trimethylpentyl)phosphinate, decanoate, and benzoate.

Considering the additionally predicted physicochemical properties (KOW, viscosity) of the
ionic liquids containing the specific ions, most effective ILs extraction solvents for liquid-liquid extraction of NdCl₃ were selected which is shown in Table 1. Viscosities of ILs were estimated via a QSPR approach and approximated from the descriptors developed by Eiden et al., using the “Ionic Liquid Properties” panel of COSMOthermX.

### Table 1. Most effective ionic liquid solvents for liquid-liquid extraction of NdCl₃ and DyCl₃ selected on the base of COSMO-RS approach

<table>
<thead>
<tr>
<th>ILs</th>
<th>IL Cation</th>
<th>IL Anion</th>
<th>log₁₀Kₐw</th>
<th>Viscosity (298K) ln(mPaS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C1][A6]</td>
<td>trihexyl-tetradecyl-phosphonium [P6₃14]</td>
<td>bis(2,4,4-trimethylpentyl) phosphinate</td>
<td>16.1</td>
<td>10.2</td>
</tr>
<tr>
<td>[C1][A18]</td>
<td>trihexyl-tetradecyl-phosphonium [P6₃14]</td>
<td>decanoate</td>
<td>12.7</td>
<td>9.7</td>
</tr>
<tr>
<td>[C1][A28]</td>
<td>trihexyl-tetradecyl-phosphonium [P6₃14]</td>
<td>benzoate</td>
<td>10.0</td>
<td>8.6</td>
</tr>
<tr>
<td>[C19][A2]</td>
<td>dodecyl-dimethyl-3-sulfopropylammonium</td>
<td>tris(pentafluoroethyl) trifluorophosphate</td>
<td>9.1</td>
<td>7.8</td>
</tr>
</tbody>
</table>

Small amount of Toluene (C₆H₅CH₃) was used to overcome some of the drawbacks caused by the high viscosity of the ILs. At the same time the above solvent was chosen because its solubility in aqueous phases is negligible and it gives a high degree of phase separation. The experimental tests confirmed that, first three of the ILs are very efficient and fast extractants for Nd, from low to high concentrations aqueous solutions of the metal chlorides.

### Reference

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