Role of bis(trifluoromethanesulfonyl)imide anions in the ionic liquid extraction of europium(III) chelates

H. Okamura1), N. Aoyagi2), K. Shimojo1), H. Naganawa1) and H. Imura3)
1) : Interfacial reaction-field chemistry Gr., JAEA 2): Radiochemistry Gr., JAEA
3): Kanazawa Univ.

Liquid–liquid extraction is one of the separation methods based on the distribution of solutes between two immiscible solvents. Recently, ionic liquids (ILs) defined as room-temperature molten salts have been widely investigated as novel alternatives to conventional organic solvents. Application of ILs as extraction media in liquid–liquid extraction has many advantages [1]. In the IL system, not only neutral species but also charged species can be extracted by ion exchange *via* the cationic or anionic constituent of the ILs [2]. These unique mechanisms often lead to an enhancement in the extractability of a particular metal ion. However, the cause of the extraction enhancement except the ion-exchange has yet to be clarified.

Time-resolved laser-induced fluorescence spectroscopy (TRLFS) has been widely used as an analytical technique for the speciation of lanthanides(III). The fluorescence lifetime gives the information of the hydration state in the first coordination sphere of the metal ion. The number of coordinated water molecules can be determined by the fluorescence decay constants in H_2O- and D_2O-containing solvents.

In this study, the extraction of Eu(III) with 2-thenoyltrifluoroacetone (Htta) in 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C$_n$mim][Tf$_2$N]) was investigated to clarify the role of the Tf_2N^- anions in the IL extraction system [3]. The hydration state of neutral Eu(tta)$_3$ in a series of ILs was examined by TRLFS.

In the [C$_n$mim][Tf$_2$N] systems, Eu(III) was extracted as the neutral Eu(tta)$_3$ and the anionic Eu(tta)$_4^-$ chelates. The extraction constants of Eu(tta)$_3$ ($K_{\mathrm{ex},3}$) in [C$_n$mim][Tf$_2$N] are higher than those in conventional organic solvents. The two-phase stability constant of Eu(tta)$_3$ was calculated from $K_{\mathrm{ex},3}$, and was evaluated with the aid of the regular solution theory. The values against the solubility parameters in [C$_n$mim][Tf$_2$N] and in oxygen-containing organic solvents such as ketones, ethers, and esters show a large positive deviation from the linear relationship obtained for nonpolar or inert solvents. This deviation demonstrates the existence of specific solute–solvent interactions between Eu(tta)$_3$ and [C$_n$mim][Tf$_2$N], *i.e.*, inner- and/or outer-sphere solvation effects.

To clarify such specific solvation effect, the hydration state of Eu(tta)$_3$ in [C$_n$mim][Tf$_2$N] was examined by TRLFS using solid [Eu(tta)$_3$(H_2O)$_3$] synthesized (Fig. 1). The [Eu(tta)$_3$(H_2O)$_3$] complex was almost completely dehydrated in the series of [C$_n$mim][Tf$_2$N] saturated with water, whereas the hydrated chelate was observed in organic solvents. It was, therefore, plausible that the Tf_2N^- anions could coordinate to Eu(tta)$_3$ and replace the coordinated water molecules of [Eu(tta)$_3$(H_2O)$_3$].

Figure 2(a) shows the hydration number as a function of water concentration in 1-ethyl-3-methylimidazolium perchlorate ([C$_2$mim][ClO$_4$]) and [C$_2$mim][Tf$_2$N, ClO$_4$]. The Eu(tta)$_3$ chelate exists as di- or tri-hydrates in [C$_2$mim][ClO$_4$] containing 20 M water, indicating that the ClO_4^- anion does not give rise to the dehydration of Eu(tta)$_3$. In contrast, mono-hydrated Eu(tta)$_3$ chelate was formed in [C$_2$mim][Tf$_2$N, ClO$_4$] containing 0.50 M Tf_2N^- and 20 M water. This means that the Tf_2N^- anions displaced the coordinated water molecules of [Eu(tta)$_3$(H_2O)$_3$]. The hydration number in [C$_2$mim][Tf$_2$N, ClO$_4$] decreased with a decrease in water concentration. These observations prove the ligand displacement between water and Tf_2N^- in Eu(tta)$_3$ in ILs.

Figure 2(b) shows the effect of the Tf_2N^- concentration in 1,2-dichloroethane on the hydration number. Almost complete dehydration of [Eu(tta)$_3$(H_2O)$_3$] was observed more than 3.4×10^{-2} M Tf_2N^- (1.0 vol% [C$_4$mim][Tf$_2$N]). This result reveals that the coordination ability of Tf_2N^- to Eu(tta)$_3$ is stronger than that of water. A stable adduct species, [Eu(tta)$_3$(Tf$_2$N)]$^-$, was found by electrospray ionization mass spectrometry in the presence of [C$_4$mim][Tf$_2$N].

This study revealed that, in the IL extraction system, the hydrophobic metal chelate is effectively formed by the coordination of Tf_2N^-, resulting in the enhancement in the extractability of the neutral chelates. The knowledge obtained in this study can lead to the further progress in the development of IL extraction systems of metal ions.

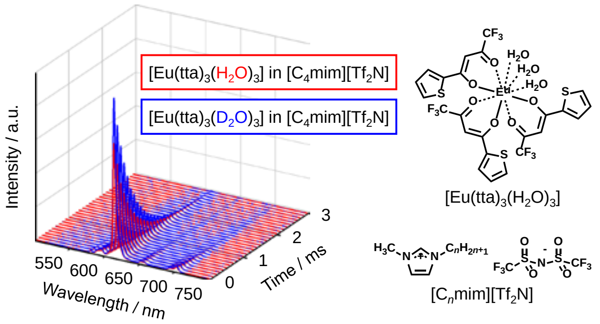

Fig.1 Fluorescence decay for [Eu(tta)$_3$(H_2O)$_3$] in [C$_4$mim][Tf$_2$N] saturated with H_2O (red) and D_2O (blue) following pulsed 394 nm excitation. Concentration of [Eu(tta)$_3$(H_2O)$_3$] was 1.0×10^{-4} M.

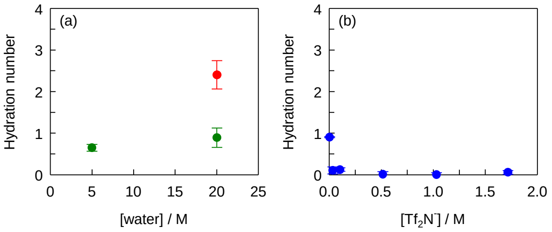

Fig.2 (a) Effect of water concentration in [C$_2$mim][ClO$_4$] (●) and [C$_2$mim][Tf$_2$N, ClO$_4$] (●) and (b) effect of Tf_2N^- concentration in 1,2-dichloroethane (●) on the hydration number of Eu(tta)$_3$. (a) Tf_2N^- concentration in [C$_2$mim][Tf$_2$N, ClO$_4$] was 0.50 M and (b) the solution was saturated with water. Concentration of [Eu(tta)$_3$(H_2O)$_3$] was 1.0×10^{-4} M.

References

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