# Thermodynamic and Spectroscopic Study on the Solvation and Complexation behavior of Ln(III) in Ionic liquids: Binding of Ln(III) with CMPO in $C_4mimNTf_2$

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## Supporting Information

1. The fittings of absorbance at three representative wavelengths for the complexation of Nd with CMPO in ILs.
2. Revisit of the extraction data reported by Nakashima et al. (*Ind. Eng. Chem. Res.* 2005, 44, 4368-4372).
3. Influence of TBP on the complexation of CMPO with Ln(III) and Am(III) in IL-based extraction system.
4. Calculated Gibbs free energy for possible limiting Nd/CMPO complexes.
5. The full calorimetric titration thermograms for the complexation of Nd with CMPO in “dry” and “wet” ILs.

1. **The fittings of absorbance at three representative wavelengths for the complexation of Nd with CMPO in ILs.**

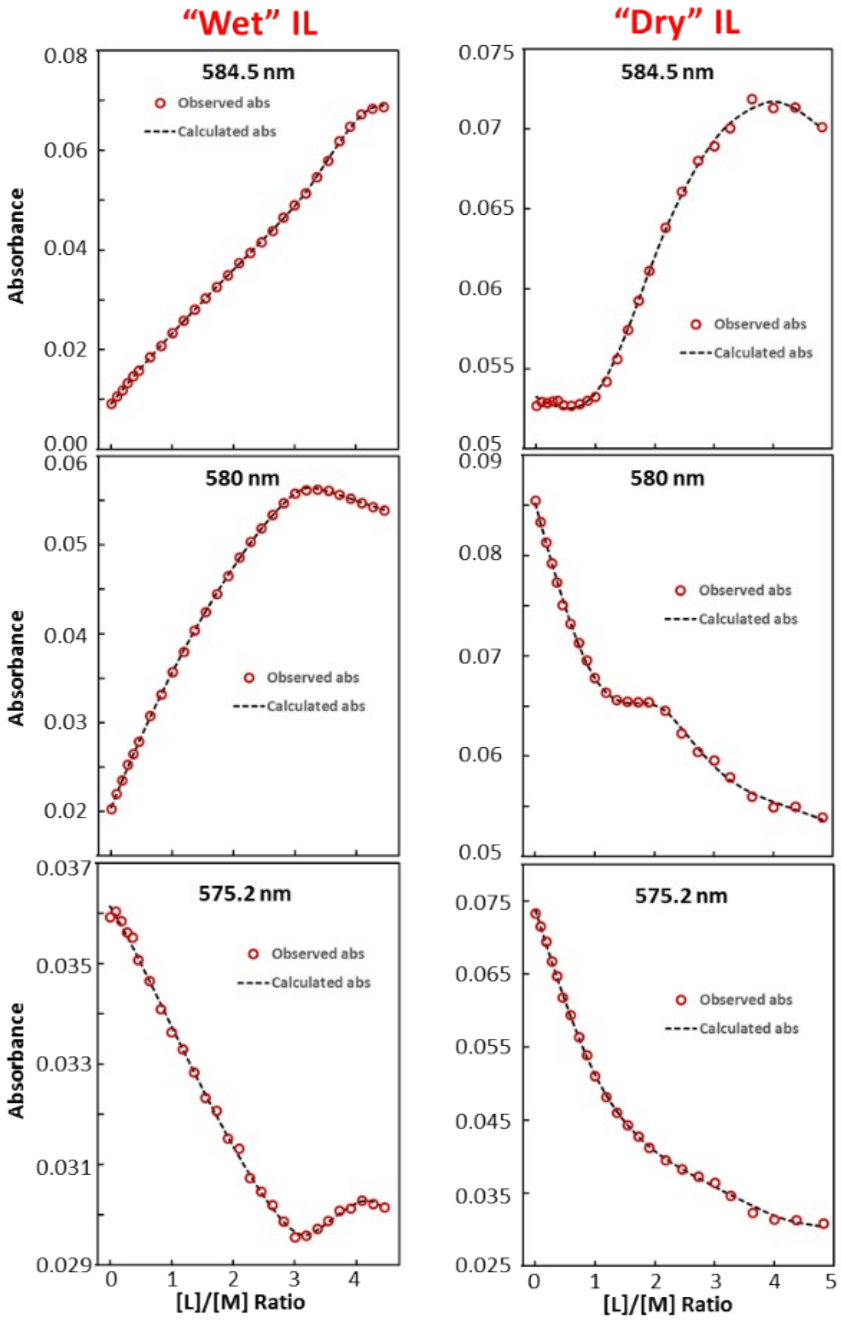


**Figure S1.** The fittings of absorbance at three representative wavelengths for the complexation of Nd with CMPO in ILs. (Cycles – observed absorbance, dashed line – calculated absorbance)

## 2. Revisit the extraction data reported by Nakashima et al. (*Ind. Eng. Chem. Res.* 2005, 44, 4368-4372).

We have revisited the extraction data reported by Nakashima et al. (*Ind. Eng. Chem. Res.* 2005, 44, 4368-4372) and found the CMPO/Eu stoichiometry in their work should also be close to 4:1, which is consistent with our results. Specifically, Nakashima et al. reported the extraction of trivalent metal ions by CMPO in $C_4mimPF_6$ in the absence of TBP. The experimental conditions are quite similar to those in our present work (the ionic liquids are different, but we have demonstrated that the complex stoichiometry is similar for the extraction of Eu/Am by CMPO in $C_4mimPF_6$ and $C_4mimNTf_2$, see *Solvent Extr. Ion Exch.*, 2017, 35, 408-422). The authors concluded from Figure S2 (Figure 3 in their original paper) that CMPO forms a 3:1 complex with all the metal cations. However, we found such a conclusion is not exactly the case after we reexamined their data. As shown in Figure S1, a slope of 3 in the ionic liquid system is only valid for $Y^{3+}$, which has smaller ionic radius than $Ce^{3+}$ and $Eu^{3+}$ and would accommodate less CMPO molecules around the first coordination sphere. For $Ce^{3+}$ and $Eu^{3+}$, the slopes are actually much larger. As we have marked out in the figure, the slope for $Eu^{3+}$ was found to be around 3.9, which agrees well with our results in the present work.

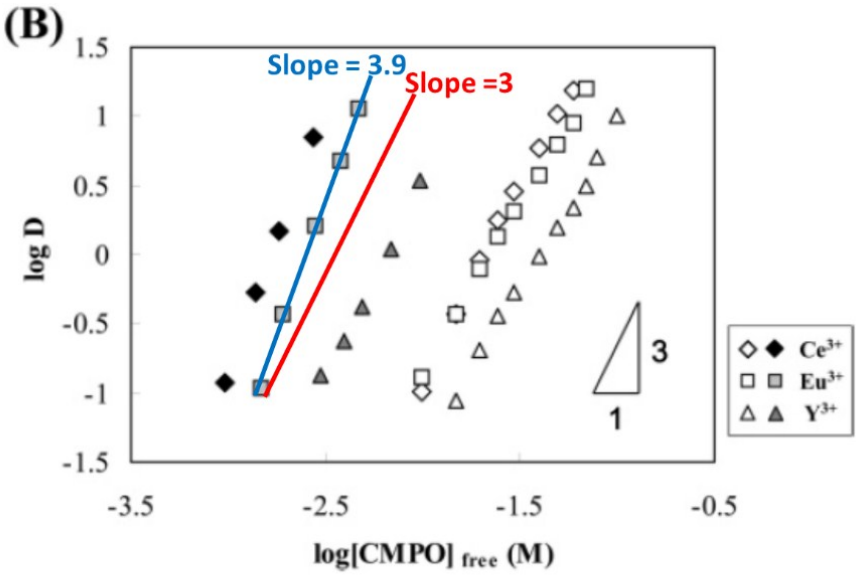


**Figure S2.** The extraction of trivalent metal ions from aqueous solution by CMPO in $C_4mimPF_6$ (Closed symbols) and *n*-dodecane (Open symbols). This figure was modified based on the original Figure 3 in *Ind. Eng. Chem. Res.* 2005, 44, 4368-4372.

## 3. Influence of TBP on the complexation of CMPO with Ln(III) and Am(III) in IL-based extraction system.

To explain the different stoichiometry of Ln/CMPO complex in IL-based extraction system with and without the presence of TBP, the extraction of Am and Eu from 0.1 M $HNO_3$ by CMPO in $C_4mimNTf_2$ in the presence and absence of 1.2 M TBP was conducted. The results are shown in Figure S3 (also see Figure 4 in our previously published paper *Solvent Extr. Ion Exch.*, 2017, 35, 408-422). It is clear from the results that the addition of TBP altered the dependency of *D* values on the concentration of CMPO. Less CMPO molecules were found to be associated with the metal ion during the extraction in the presence of TBP. This is why the stoichiometry value is lower in Rout et al.'s work (*Sep. Purif. Technol.*, 2011, 76, 238-243 and *J Radioanal. Nucl. Chem.*, 2011, 290:215–219) than that in our present work.

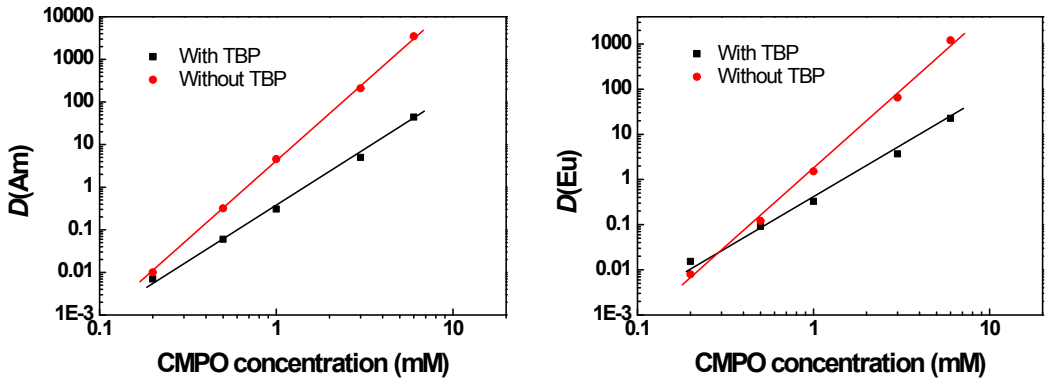


**Figure S3.** The dependence of the extraction of $Am^{3+}$ and $Eu^{3+}$ on the concentration of CMPO in $C_4mimNTf_2$ in the presence and absence of TBP. The initial concentration of nitric acid in the aqueous phase was 0.1 M and TBP concentration in $C_4mimNTf_2$ was 1.2 M.

## 4. Calculated Gibbs free energy for possible limiting Nd/CMPO complexes

**Table S1.** Calculated Gibbs free energy for possible limiting Nd/CMPO complexes

| Complex | $NdL_3$ | $NdL_4$ | $NdL_3 \cdot H_2O$ | L | $H_2O$ |
|---|---|---|---|---|---|
| Gibbs free energy (kcal/mol) | -25938.39 | -34668.98 | -26255.31 | -8715.73 | -319.86 |

## 5. The full calorimetric titration thermograms for the complexation of Nd(III) with CMPO in "dry" and "wet" ILs

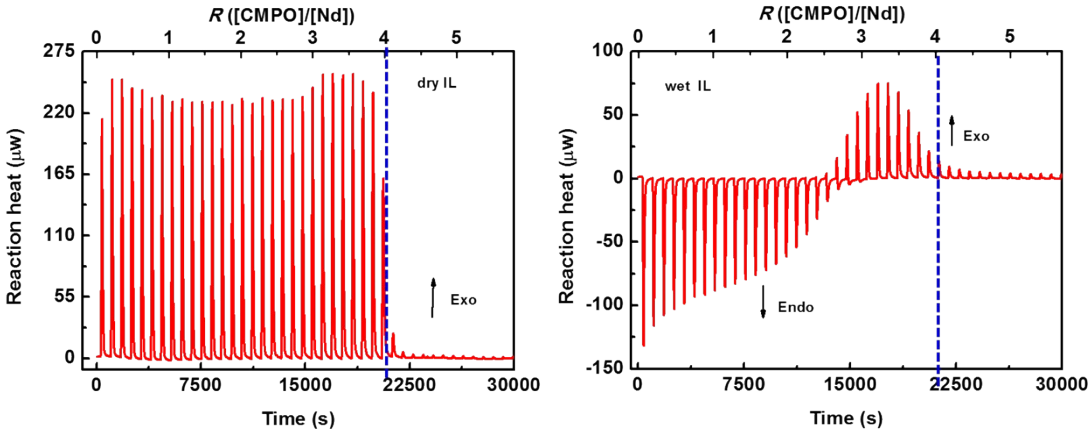


**Figure S4.** The full calorimetric titration thermograms for the complexation of Nd(III) with CMPO in "dry" and "wet" ILs. The [CMPO]/[Nd] ratio was shown in the up-axis for reference.