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Communication

Unusual complexation of nitrate with lanthanides in wet ionic liquid: A new approach for aqueous separation of trivalent *f*-elements using ionic liquid as solvent

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The energetics of lanthanide nitrate complexation in wet ionic liquid (IL; saturated with water as seen in aqueous separation process) differs entirely from that in dry IL. A new approach to design more effective strategies for separation of actinides and lanthanides using IL as a solvent has been revealed.

In recent years, room-temperature ionic liquids (IL) have gained the status of “design” solvents, where the properties of the solvent can be tailored through judicious choice of their cationic and anionic components.¹ With imidazolium-based cations and hydrophobic anions such as bis(trifluoromethane sulfonyl)amide, ILs are immiscible in water with desired physicochemical properties (e.g., viscosity) and, therefore, have been widely studied in the separation of metal ions from aqueous solutions.² Exciting results have been reported on the extraction of actinides (Ans) and lanthanides (Lns) with IL solvents containing extractants such as diglycolamides³, CMPO⁴ and malonamides.⁵ Very recently, DTPA (diethylene triamine pentaacetic acid) integrated with functionalized IL has been studied for group separation of Ans from Lns in TALSPEAK process.⁶ The most important property of ILs responsible for such a wide interest in separation studies is their unusual ability to dissolve ionic as well as neutral molecules, such as extraction ligands, which offers the exploration of a wide field of unexpected chemistry with this new class of solvents.

Studies on Ln-nitrate complexation in dry IL (in the absence of water) suggested the formation of $\text{Nd}(\text{NO}_3)_j^{(3-j)+}$, where $j = 1 - 6$, with very large $\log \beta$ values ranging from 7.88 to 35.68.⁷ Using spectrophotometry and thermodynamic approach, it was also found that UO_2^{2+} and nitrate formed very strong complexes in IL, more than five orders of magnitude higher than those in aqueous solutions.⁸ Similar large stability constants have been reported for the complexation of chloride with uranyl ions⁹ and with transuranic metal ions.¹⁰ It is worth mentioning that all the thermodynamic studies reported in the literature for metal complexation in IL medium have used dry IL, free from water. These data, while fundamental and insightful, do not provide information on the role of water that plays in the energetics of complexation in ILs in contact with water, a scenario encountered in most applications of ILs in separation processes.

To the best of our knowledge, no thermodynamic studies have been reported so far with the IL containing water. Because many ILs are highly hygroscopic, significant amounts of water (10-20 mg/g) could be uptaken depending upon the nature of the contacting aqueous solution.¹¹ As a result, the solvation sphere of the metal ions in wet IL is expected to be saturated with strong coordinating water molecules and, therefore, application of the thermodynamic data obtained in dry IL to the separation of metal ions from aqueous solutions is limited and, in some cases, could lead to erroneous or unrealistic conclusions. To bridge the gaps in the knowledge of metal complexation in wet ILs, and to help in designing the effective separation processes using ILs, we have studied the complexation of nitrate (a very weak ligand in aqueous solution but a commonly used anion in many separation process) with Lns in wet IL. To the best of our knowledge, this is the first report on metal-nitrate complexation in wet-IL, including the original direct determination of enthalpy of complexation by microcalorimetry and observation of a metal/nitrate complex in IL by ESI-MS.

In complex formation studies, it is very important to control the ionic strength of the solution, which is generally achieved by the addition of an inert salt in large quantities as compared to the ligand. If one assumes that the ILs are fully dissociated in the medium, the ionic strength in the present system should be about 3.4 mole/L (1-butyl-3-methyl imidazolium bis(trifluoromethane sulfonyl)imide; $\text{C}_4\text{mim-NTF}_2$: molar mass = 419.36; density = 1.422). Therefore, the complex formation occurring in our work should have a negligible impact on the total ionic strength as the Ln(III) concentration is in the range of 10^{-3} mol/L. Nevertheless, the stability constant obtained in the present work should be treated as “conditional stability constant” in the absence of activity coefficients of various species.

Fig. 1 shows the representative spectrophotometric titrations of Nd(III) with nitrate ions. The absorption band at about 575 nm corresponds to the $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}, ^2\text{G}_{7/2}$ transition, which is the most hypersensitive band of Nd(III) ion.¹² The titration of Nd(III) by nitrate resulted in red-shift of the spectrum up to the $C_{\text{NO}_3}/C_{\text{Nd}}$ ratio of 5 with increase in the absorption band intensity. Further increase in the $C_{\text{NO}_3}/C_{\text{Nd}}$ ratio resulted in the formation of a new absorption band at around 580 nm with decrease in the intensity of the absorption band between 570 – 575 nm. The intensity of-

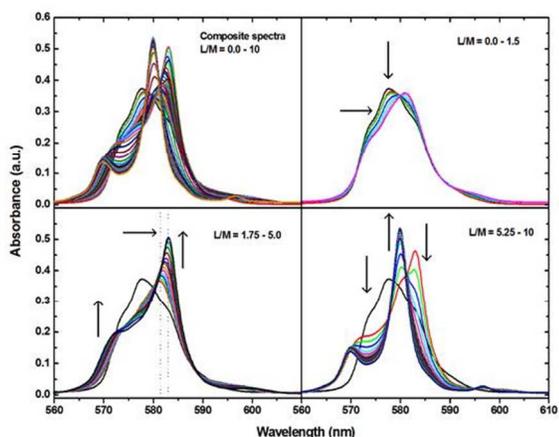


Fig. 1. Spectrophotometric titration of Nd(III) with nitrate at 25°C. Initial cuvette solution: 20 mmol/L Nd(NTF₂)₃; Titrant: 0.39 mol/L C₄mim·NO₃; L/M refers to the ratio of C_{NO₃}/C_{Nd}; The Nd(III) spectra in the absence of nitrate has been shown in all the four figures for comparison

the absorption band at 580 nm increased as the C_{NO₃}/C_{Nd} ratio was increased to 8, beyond which the 580 nm peak was unaffected even in the presence of excess ligand (C_{NO₃}/C_{Nd} ratio up to 20), suggesting the absence of any additional species.

A plot of total peak area of the hypersensitive band (⁴I_{9/2} → ⁴G_{5/2}, ²G_{7/2}) versus concentration of nitrate (Fig. S1 in SI) yielded four distinct break points, indicating the presence of four different species. The slope is almost zero after C_{NO₃}/C_{Nd} = 8, clearly indicating the ML₄ species as the limiting species. Analysis of the spectra by the Hyperquad program¹³ also confirmed the formation of four successive ML complexes. (The molar absorptivities of free Nd(III) and the four Nd(III)-nitrate complexes are shown in Fig. S2 in SI). The overall stability constants of Nd(III)-nitrate complexes in wet IL are several orders of magnitude higher than those in the aqueous medium, but lower than those observed in dry IL (Table 1). Based on the few studies on the complexation of nitrate with Ln/An in dry ILs,^{7,8} it is well accepted that, in the absence of water, the primary solvation sphere of Lns are occupied by the weakly solvating NTF₂⁻ anions, as has been evidenced by crystallography.¹⁴ The NO₃⁻ ions form complexes with Lns without spending much energy to de-solvate the NTF₂⁻ ions in the primary solvation sphere. As a result, the stability constants of Ln(III)/nitrate complexes in dry IL are high and the complexation is overwhelmingly driven by large exothermic enthalpy of complexation (Table 1). On the other hand, the water content of wet C₄mim·NTF₂ in the present work was calculated to be about 1 mol/L,¹³ so that the primary hydration sphere of Ln(III) was completely hydrated as confirmed by fluorescence measurements on Eu(III). The fluorescence lifetime of Eu(III) in wet IL was 111.7 ± 0.18 μs, similar to that observed in aqueous medium 110.5 ± 1.5 μs. Both lifetimes correspond to a primary hydration number of 9 for Eu(III). ($n_{H_2O} = 1.05/\tau - 0.70$, where τ is the fluorescence life time in ms.¹⁵ See Table S1 in SI). Therefore, Ln(III) in the wet IL may be represented as Ln(H₂O)₉³⁺, and nitrate needs to compete and replace water to form complexes with Ln(III). As a result, the stability constants in wet IL are a few orders of magnitude lower than those in dry IL. Use of these thermodynamic data will be more realistic for designing the Ln/An separation process, than using the data obtained in dry IL system.

Table 1. Comparison of thermodynamic data on complexation of Nd(III)-nitrate in water, wet IL and dry IL medium

Medium	Complex ^a	logβ	ΔH (kJ/Mol)	ΔS (J/Mol/K)
1 M NaClO ₄ ¹⁹	ML	-0.19 ± 0.02	1.50 ± 0.20	1.4 ± 1.0
Wet IL	ML	3.23 ± 0.18	26.15 ± 2.01	150 ± 7
	ML ₂	6.58 ± 0.53	10.49 ± 1.51	161 ± 5
	ML ₃	9.06 ± 0.38	107.7 ± 15.4	535 ± 52
	ML ₄	11.4 ± 0.47	21.45 ± 2.63	290 ± 9
Dry IL ⁷	ML	7.88 ± 0.10	-60.2 ± 9.1	-54 ± 31
	ML ₂	13.3 ± 0.10	-136 ± 5.1	-211 ± 18
	ML ₃	21.2 ± 0.15	-202 ± 7.5	-283 ± 26
	ML ₄	27.1 ± 0.20	-258 ± 10.8	-361 ± 37

^a: ML, ML₂, ML₃ and ML₄ denote the successive formation of Nd(NO₃)₂²⁺, Nd(NO₃)₂⁺, Nd(NO₃)₃ and Nd(NO₃)₄⁻ complexes.

Fig. 2 shows a representative calorimetric titration. Using calorimetric titration data in conjunction with the stability constants obtained by spectrophotometry, the enthalpies of complexation were calculated by Hyperquad program.¹³ This is the first demonstration that direct determination of complexation heat by microcalorimetry in wet IL is feasible. The overall enthalpy for each Nd(III)-nitrate complex was endothermic, accompanied by large positive entropy contributions (Table 1). This is in contrast to Nd(III)-nitrate complexation in dry IL, where exothermic enthalpy and negative entropy change was observed. Such difference in the enthalpy of complexation can be explained on the basis of strong solvating strength of water as compared to NTF₂⁻ anions of IL. Whereas little energy is needed to de-solvate Nd(III) in dry IL, much energy is needed for the same in wet IL where Nd(III) cations are strongly solvated by water, resulting in endothermic enthalpy contribution for the complexation. Positive entropy contribution is an indication of the release of water molecules from the primary coordination sphere of the metal ions. Significantly large entropy change for the third complex is probably due to a complete charge neutralization (Nd³⁺ + 3NO₃⁻ → Nd(NO₃)₃⁰) that could substantially increase the degree of disorder in the system.

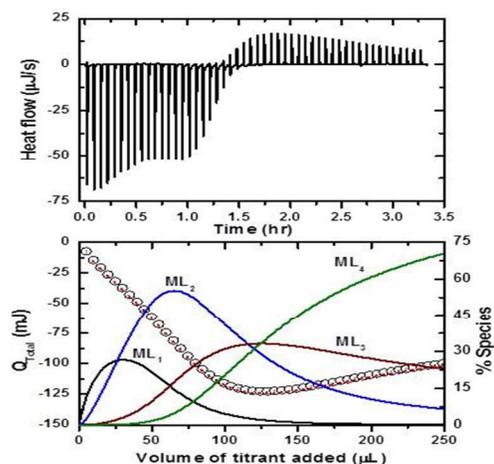


Fig. 2. Calorimetric titration of Nd(III)-nitrate at 25°C. Top: titration thermogram that are uncorrected for dilution heat. Bottom: Accumulated reaction heat and ML speciation (M = Nd, L = nitrate) as a function of titrant added. ○ -experimental; --- fit. Initial cup solution: 33.35 mmol/L Nd(NTF₂)₃; Titrant: 99.7 mmol/L C₄mim·NO₃

Further discussions can be made about the nature of complex (outer sphere or inner sphere) and the coordination mode of nitrate based on the thermodynamic data. As Choppin et al.¹⁶ pointed out, the thermodynamic parameters can be used to distinguish between the inner- and the outer-sphere complexes. Because significant energy is required to de-solvate the metal and ligand and the released solvent molecules increase the degree of disorder, endothermic enthalpy and positive entropy are usually associated with the formation of inner-sphere complexes. Data from present work indicate that, in wet IL, nitrate forms inner-sphere complexes with Lns.

Data in the literature show that bidentate nitrate coordination is dominant in solid compounds of Lns such as $[\text{Nd}(\text{NO}_3)_3(18\text{-crown-6})]$.¹⁷ EXAFS studies have also shown that the nitrate is bidentate in Nd(III) complex obtained in aqueous solutions, with the N atom at about 2.5 Å from the metal atom.¹⁸ However, it remains unclear whether nitrate is mono- or bi-dentate in the Ln(III) complexes in wet IL. Our attempt to obtain the crystal of Nd(III)-nitrate complex in IL has not been successful, but the fluorescence lifetime data provided insightful information. As mentioned previously, the Eu(III) in wet IL in the absence of nitrate is fully hydrated ($N_{\text{H}_2\text{O}} \approx 9$). In comparison, the fluorescence lifetime of Eu(III) was found to increase as the ratio of $C_{\text{NO}_3}/C_{\text{Eu}}$ increased, indicating the replacement of water by nitrate (Table S1 in SI). At $C_{\text{NO}_3}/C_{\text{Eu}}$ ratio of 8, where the limiting ML_4 species dominates, the lifetime was 911 μs suggesting the absence of water molecules in the primary hydration sphere of Eu(III) in ML_4 species. Intuitively, it is very reasonable to conclude that the nitrates coordinate to Eu(III) in bidentate mode.

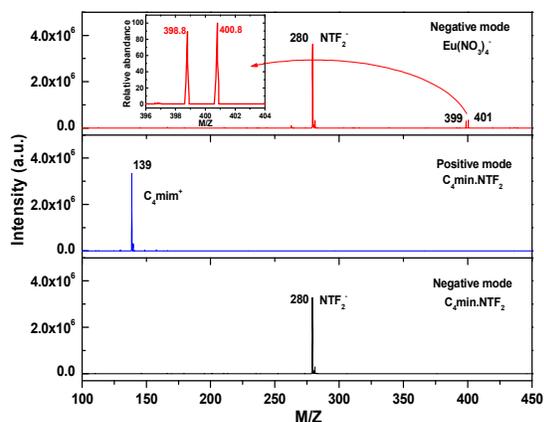


Fig. 3. ESI-MS spectra of IL and Eu(III)-nitrate complex recorded in acetonitrile medium. M/Z refers to mass to charge ratio.

Data from ESI-MS provided direct observation of the limiting ML_4 species in wet IL (Fig. 3). Injection of pure IL (~50 μmol/L in acetonitrile) resulted in two peaks corresponding to the IL cation (C_4mim^+) at mass/charge = 139 and anion (NTF_2^-) at mass/charge = 280. Then we measured the ESI-MS spectra of Eu(III)-nitrate complex at $C_{\text{NO}_3}/C_{\text{Eu}}$ ratio of 9, where the formation of ML_4 anionic species is complete. Presence of peaks at mass/charge 399 and 401 confirmed the formation of $\text{Eu}(\text{NO}_3)_4^-$ anionic complex without water molecules. The result of ESI-MS agrees with above discussions on the nature and coordination modes of Ln(III)/nitrate complexes in wet IL based on thermodynamic measurements and fluorescence lifetime.

Conclusions

We have demonstrated for the first time that the energetics of the metal-nitrate complexation in wet IL is entirely different from those observed in commonly studied dry IL system. Trivalent f -elements form ML , ML_2 , ML_3 and ML_4 complexes with nitrate in wet IL. Their stability constants are several orders of magnitude higher than those in aqueous solution, but much lower than those observed in dry IL. In addition, the enthalpies of complexation are endothermic in wet IL, completely opposite to the exothermic enthalpies in dry IL. The present work gives perspective to obtain thermodynamic data under the prevailing conditions of aqueous metal separation using ILs. It is anticipated that this study will help in development of more effective strategies to design aqueous separation processes using ILs as solvent.

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Notes and references

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 † Electronic Supplementary Information (ESI) available: [Experimental details, Table S1 and Figs. S1 and S2]. See DOI: 10.1039/b000000x/
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Graphic Abstract

