Chinese Chemical Letters 33 (2022) 3451–3455

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Complexation between uranyl(VI) and CMPO in a hydroxyl-functionalized ionic liquid: An extraction, spectrophotography, and calorimetry study

Baihua Chen, Jun Liu, Hongyuan Wei, Yuchuan Yang, Xingliang Li, Shuming Peng*, Yanqiu Yang*

Institute of Nuclear Physics and Chemistry, CAEP, Mianyang 621900, China

ARTICLE INFO

Article history:
Received 4 November 2021
Revised 22 December 2021
Accepted 24 December 2021
Available online 29 December 2021

Keywords:
Uranyl(VI)
CMPO
Ionic liquid
Solvent extraction
Complexation
Thermodynamics

ABSTRACT

The extraction complexes of uranyl(VI) in HNO_3 to a hydroxyl-functionalized ionic liquid (IL) phase, $HOEtmimNTf_2$ bearing CMPO, were investigated. Three possibly successive extraction complexes, $UO_2\mathbf{L}^{2+}$ ($\mathbf{L}$ = CMPO), $UO_2\mathbf{L}_2{}^{2+}$ and $UO_2\mathbf{L}_3{}^{2+}$, were detected based on variable U/$\mathbf{L}$ ratios. Uranyl(VI) prefers to be extracted as complex $UO_2\mathbf{L}_3{}^{2+}$, combining with the ions from $HOEtmimNTf_2$ to construct a solid material through self-assembly. The thermodynamics of complexes, $UO_2\mathbf{L}_j{}^{2+}$ (j = 1-3), were studied by spectrophotometry and microcalorimetry. All the formation reactions are principally driven by entropy, although a small part of the driving force of complexes $UO_2\mathbf{L}_2{}^{2+}$ and $UO_2\mathbf{L}_3{}^{2+}$ comes from enthalpy. Based on the thermodynamic properties for complex $UO_2\mathbf{L}_3{}^{2+}$, we provide a possible coordination mode in $HOEtmimNTf_2$: the first CMPO molecule coordinates with $UO_2{}^{2+}$ in a bidentate fashion while the others do in a monodentate fashion. The results offer a thermodynamic insight into the formation behaviors of the uranyl(VI)/CMPO complexes involving the special IL $HOEtmimNTf_2$, which is of significance to advance the novel IL extraction strategy.

Liquid-liquid extraction is the most maturely popular separation technique for the reprocessing of spent nuclear fuels. Due to its unique physicochemical and solvation properties [1,2], ionic liquid (IL) is promising as an efficient and eco-friendly solvent to recover actinides from spent nuclear fuels. Extensive studies have been conducted over years on the extraction and complexation of actinides and lanthanides, replacing volatile molecular solvent dissolving the common ligands with ILs. Positive results on efficiency and selectivity have been achieved [2–6]. For example, uranyl(VI) in HNO_3 was more effectively extracted by trioctylphosphine oxide (TOPO) in butylmethylimidazolium bis(trifluoromethylsulfonyl)imide ($C_4mimNTf_2$) greatly elevated the extraction efficiency compared with the same extraction conducted with TOPO in dichloromethane [6].

Octylphenyl(*N,N*-diisobutylcarbamoylmethyl)phosphine oxide (CMPO) has received attention as one of the most widely studied phosphorous-based extractants to separate tri-, hexa- and tetravalent actinides from acidic solutions [7–9]. Schemes of actinides extraction from HNO_3 solutions by CMPO in ILs have been achieved recently [3,10–12]. Comparison studies illustrated the extraction efficiency enhances largely with ILs replacing molecular solvents as the diluent of ligands. Visser *et al.* using the mixture extractant of CMPO and TBP (tributyl phosphate), found that the distribution ratios for Am(III), Th(IV), Pu(IV) and U(VI) were all at least an order of magnitude higher when butylmethylimidazolium hexafluorophosphate (C_4mimPF_6) as the diluent of extracting phase than those when *n*-dodecane as diluent [10]. Rout *et al.* observed much larger D_{Am} values using TBP and CMPO in $C_4mimNTf_2$ than in *n*-dodecane [13].

Most recently, we provided a novel strategy for efficient capture of uranium from nitric acid solutions with CMPO in (1-hydroxyethyl-3-methyl)imidazolium bis(trifluoromethylsulfonyl) imide ($HOEtmimNTf_2$), a hydroxyl-functionalized ionic liquid [14]. The specific property of $HOEtmimNTf_2$ triggers the self-assembly of the uranyl(VI)/CMPO complex at the aqueous-IL interface to form a solid material, with the composition of 3/9/1/7 for $UO_2{}^{2+}$/CMPO/$HOEtmim^+$/$NTf_2{}^-$. Almost all aqueous uranium (95%) was transferred to the solid phase. However, the extraction species as well as the complexation of uranyl(VI) with CMPO involving $HOEtmimNTf_2$ still keep unknown. Herein, we describe the ther-

---

* Corresponding authors.
E-mail addresses: pengshuming@caep.cn (S. Peng), yan.qiu.yang@163.com (Y. Yang).

https://doi.org/10.1016/j.cclet.2021.12.066
1001-8417/

modynamic behaviors of complexation between uranyl(VI) and CMPO in HOEtmimNTf$_2$, investigated by biphasic extraction and monophasic titration. Based on the determined thermodynamics for complexes, we further discuss the chelation fashions of CMPO to uranyl(VI). The results and discussion are of significance in understanding the corresponding extraction behaviors and then optimizing the extraction systems.

It is generally accepted that ILs do not behave as inert diluents toward nitric acid [15,16]. As depicted in Fig. S1 (Supporting information), the HNO$_3$ concentration in HOEtmimNTf$_2$ increased linearly with the increase of the aqueous HNO$_3$ concentration. HNO$_3$ distribution ratio was calculated to be $D_{\text{HNO}_3} = 0.31$ by the linear slope, suggesting that strong interaction between HOEtmimNTf$_2$ and HNO$_3$ occurred. CMPO is of weak basicity and interacts with HNO$_3$. It has been demonstrated that HNO$_3$ can be extracted into the organic phase, using molecular solvents as the diluent of CMPO [17–19]. For example, equilibrating CMPO dissolved in NPHE (nitrophenylhexyl ether) with aqueous HNO$_3$ solution, HNO$_3$·CMPO was formed in the organic phase with the equilibrium constant $K = 3.1 \times 10^{-5}$ [18]. Given this, we conducted an additional experiment, equilibrating HOEtmimNTf$_2$ bearing CMPO with 0.1 mol/L HNO$_3$. As shown in Table S1 (Supporting information), in the concentration range of CMPO (0.024–0.064 mol/L), the equilibrium HNO$_3$ concentrations in the IL phases (0.0283–0.0274 mol/L) changed around 0.0277 mol/L (the equilibrium HNO$_3$ concentration in the IL phases without CMPO). Taking experimental uncertainty into account, we believe that the CMPO concentration in the IL phase affects the HNO$_3$ distribution little. In other words, the interaction of HNO$_3$ with CMPO is incomparable with that with HOEtmimNTf$_2$. It is the right reason for our previous observation that the HNO$_3$ concentration in the aqueous phase did not affect the uranium extraction efficiency [14]. Consequently, to simplify the experiment process and data treatment, the experimental solutions were prepared with the equal-volume equilibrated HOEtmimNTf$_2$ and 1.0 mol/L HNO$_3$, while the protonation of ligand CMPO was not considered.

The formation of extraction complexes in the biphasic extraction system is essential to produce solid assembly material. Firstly we conducted extractions on a constant-temperature water bath shaker, with the aqueous phase with UO$_2$(NO$_3$)$_2$ (no more than 1.0 mmol/L) in 1.0 mol/L HON$_3$. Pre-experiments showed that no observably solid assembly material appeared at the inter-surface of the biphasic system in a day time when the initial uranyl(VI) concentration in 1.0 mol/L HNO$_3$ solution was less than 1.0 mmol/L. Cation exchange has been presumed to be the partitioning mechanism for the biphasic metal extraction equilibrium with hydrophobic IL as diluent [1,20–22]. Considering the stoichiometric ratio of the solid material obtained at the interface of the biphasic system [14], we hypothesized three successive extraction complexes formed possibly in the IL phase, *i.e.*, $\text{UO}_2\mathbf{L}^{2+}$, $\text{UO}_2\mathbf{L}_2{}^{2+}$ and $\text{UO}_2\mathbf{L}_3{}^{2+}$. The uranium distribution ratio (D_U) should function as a cubic polynomial equation along with the CMPO concentration ($[\bar{L}]$) in the IL phase (Eq. S5 in Supporting information). Fig. 1 depicts the UO$_2$(NO$_3$)$_2$ extraction results by CMPO in HOEtmimNTf$_2$ at 25 °C. Fitting the extraction data with Eq. S5 based on the least square method, as shown the short dash line in Fig. 1a, the apparent equilibrium constants ($K_{ex}{}^{app}$) for the three successive extraction complexes were obtained to be $K_{ex,1}{}^{app} = 2.16 \pm 0.24$, $K_{ex,2}{}^{app} = 4.97 \pm 0.34$, and $K_{ex,3}{}^{app} = 8.53 \pm 0.03$, respectively. Interestingly that ($K_{ex,3}{}^{app}$-$K_{ex,2}{}^{app}$) > ($K_{ex,2}{}^{app}$-$K_{ex,1}{}^{app}$) > $K_{ex,1}{}^{app}$, suggests that, for this extraction system, uranium prefers to be extracted by the complexes of higher uranyl(VI) stoichiometric ratio, especially $\text{UO}_2\mathbf{L}_3{}^{2+}$. It can be interpreted that along with the uranyl(VI) stoichiometric ratio increasing, the extraction complexes become more hydrophobic, which facilitates their transfer into the organic phase [21]. As illustrated in Fig. 1b, in a dual logarithmic coordinate system a fine linearship we observed between D_U and $[\bar{L}]$ (2.6-4.5 mmol/L) with a slope of 2.93, suggesting complex $\text{UO}_2\text{L}_3{}^{2+}$ being the predominant extraction species [6].

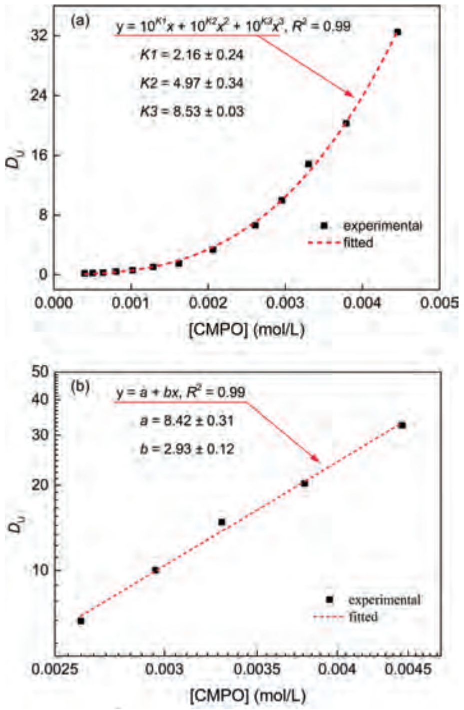

Fig. 1. $\text{UO}_2{}^{2+}$ in nitric acid extraction with CMPO in HOEtmimNTf$_2$ at ambient temperature. Aqueous phase: 0.91 mmol/L UO$_2$(NO$_3$)$_2$ in 1.0 mol/L HNO$_3$; organic phase: CMPO (0.5~4.5 mmol/L) in HOEtmimNTf$_2$ (equilibrated by 1.0 mol/L HNO$_3$).

As a result of the Laporte forbidden electronic transitions from ligand orbitals to empty 5*f* orbitals of central uranium, uranyl(VI) in the range of 485–380 nm behaves weak absorption bands which are mainly governed by the geometry of the equatorial coordination and only to a less extent affected by the chemical nature of the ligands [23,24]. In the present work, identification of the complex species between $\text{UO}_2{}^{2+}$ and CMPO, as well as the determination of the stability constants of the complexes, was achieved by spectrophotometric titrations of $\text{UO}_2{}^{2+}$ with CMPO in HOEtmimNTf$_2$ [25,26]. As shown in Fig. 2, additions of CMPO caused significant changes in the shape and location of the absorption bands. As the **L**/U ratio ($R = C_\text{L}/C_\text{U}$) increased to about 2.32, the series of absorption bands became sharper, well-defined, continuously red-shifted, and intensified. However, different changes were observed after R was higher than 2.32. The main absorption bands at about 402, 413, 425.5, and 438 nm were continued to red-shifted, accompanied by decreases in intensities, while the absorption band at about 390 nm changed little. For example, as shown in the insert picture of Fig. 3a, when R increased from 2.32 to 3.49, the peak center of the most intensive absorption band red-shifted from 425.5 to 426.0 nm, while its intensity reduced from 0.0432 to 0.0419; the absorption bands at about 452, 464, 481, and 498 nm increased slightly in intensity. The continuous changes of the absorption spectra in titration indicate the successive complexation of $\text{UO}_2{}^{2+}$ with CMPO.

Factor analysis by HypSpec program [27] suggested the presence of four absorption species in the system, *i.e.*, free $\text{UO}_2{}^{2+}$ and three successive complexes like $\text{UO}_2\mathbf{L}^{2+}$, $\text{UO}_2\mathbf{L}_2{}^{2+}$, and $\text{UO}_2\mathbf{L}_3{}^{2+}$. Fit converged well at the stability constants (logβ) of 4.82 (5), 9.39(12), and 12.98(5) for complex $\text{UO}_2\mathbf{L}^{2+}$, $\text{UO}_2\mathbf{L}_2{}^{2+}$, and $\text{UO}_2\mathbf{L}_3{}^{2+}$, respectively. The calculated molar absorption spectra of the species are depicted in Fig. 3b. The better-defined vibronic fine struc-

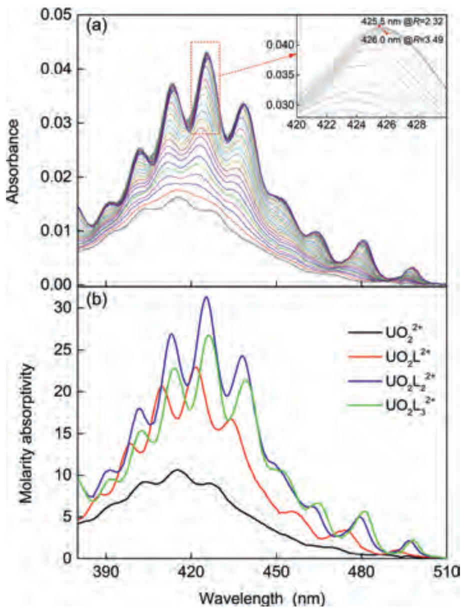

Fig. 2. Spectrophotometric titration of $UO_2(NO_3)_2$ with CMPO in HOEtmimNTf$_2$. Initial solution: $V^0 = 2.0$ mL, $C_U{}^0 = 1.5$ mmol/L, titrant: $C_L = 69.7$ mmol/L, 0.15 mL added. (a) Spectra of the titration system normalized to the initial concentration of U(VI); (b) molar absorptivity of the species found in the titration system.

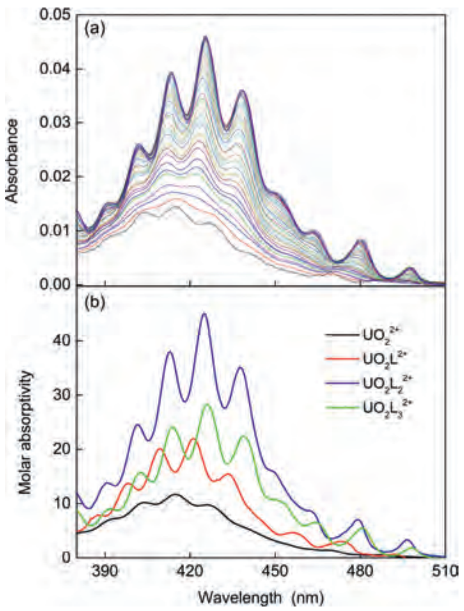

Fig. 4. Spectrophotometric titration of $UO_2(NTf_2)_2$ with CMPO in HOEtmimNTf$_2$. Initial solution: $V^0 = 2.0$ mL, $C_U{}^0 = 1.5$ mmol/L, titrant: $C_L = 97.4$ mmol/L, 0.096 mL added. (a) Spectra of the titration system normalized to the initial concentration of uranyl(VI); (b) Molar absorptivity of the species found in the titration system.

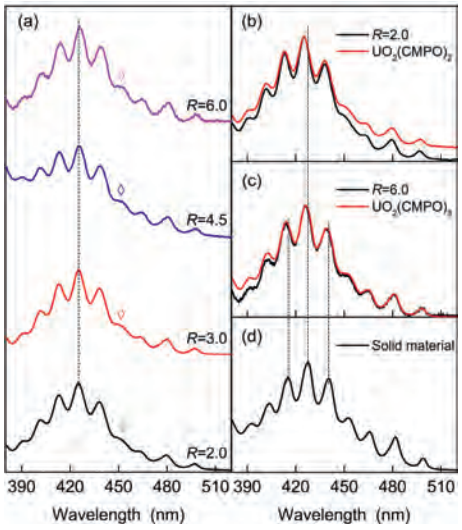

Fig. 3. (a) Absorption spectra of the IL phases after extraction; (b) Spectrum comparison of the IL phases after extraction ($R = 2.0$) with complex $[UO_2(CMPO)_2]^{2+}$; (c) Spectrum comparison of the IL phases after extraction ($R = 6.0$) with complex $[UO_2(CMPO)_3]^{2+}$; (d) Absorption spectrum of the solid assembly material.

ture and sharper absorption bands clued that uranyl(VI) complexed with CMPO in an ordered ligand field [25,28]. The spectrum changes of the titration system (Fig. 3a) can be interpreted with the quite different spectra of uranyl(VI) species and their concentration changes in the solution. For instance, Absorbancy of complex $UO_2\mathbf{L}_3{}^{2+}$ is weaker than that of complex $UO_2\mathbf{L}_2{}^{2+}$, responsible for the spectrum intensity decreased in the titration system when $R > 2.32$.

In Fig. 3, we compared the absorption spectra of the IL phases after extraction with those of complexes $UO_2\mathbf{L}_2{}^{2+}$ and $UO_2\mathbf{L}_3{}^{2+}$ in HOEtmimNTf$_2$. The spectra of $UO_2\mathbf{L}_2{}^{2+}$ and $UO_2\mathbf{L}_3{}^{2+}$, as depicted in Fig. 2b, were obtained in the monophasic titration experiments. As shown in Fig. 3a, for the spectra of the post-extraction IL phases, along with the increase of **L**/U ratio, the position of absorption bands red-shifted continuously (depicted the short-dash line), and the relative intensity of the absorption band between 447 nm and 459 nm (marked with ◊) strengthened slowly. No matter in terms of the peak positions or the relative intensities among the peaks, the post-extraction spectrum of the IL phase when $R = 2.0$ was almost identical to that of complex $UO_2\mathbf{L}_2{}^{2+}$ (Fig. 3b), and that of the IL phase when $R = 6.0$ nearly overlapped that of complex $UO_2\mathbf{L}_3{}^{2+}$ (Fig. 3c). Such observations suggest that with the increase of the **L**/U ratio, the uranyl(VI) species in the post-extraction IL phase successively change in the order of $UO_2\mathbf{L}^{2+}$, $UO_2\mathbf{L}_2{}^{2+}$, and $UO_2\mathbf{L}_3{}^{2+}$, consistent with the trend of uranium distribution ratio with the CMPO concentration in the IL phase (Fig. 1). When CMPO extracts aqueous uranyl(VI) to the IL phase as complex $UO_2\mathbf{L}_2{}^{2+}$, and similarly when $R = 2.0$ the extraction complex is $UO_2\mathbf{L}_3{}^{2+}$ [24,25,29]. With the experimental techniques of our previous work [14], we collected some self-assembly material and determined its absorption spectrum (Fig. 3d). Compared with the absorption spectrum of complex $UO_2(CMPO)_3{}^{2+}$ in HOEtmimNTf$_2$ (Fig. 3c), significant redshifts occurred for the corresponding bands in the absorption spectrum of the assembly material. This is a common optical character resulting from the assembly of mono-molecules [30]. Typically two reasons can explain this phenomenon: one is related to an edge-to-edge (*J*-type) aggregation of complex monomers in self-assembly material, and the other is related to the state transition of complex monomers from the disordered dispersion in solution to the orderly tight arrangement the self-assembly material [30–32].

To check the effect of nitrate anions on the complexes formation, spectrophotometric titrations were also conducted with $UO_2(NTf_2)_2$ instead of $UO_2(NO_3)_2$, as shown in Fig. 4. Three successive uranyl(VI) complexes were also observed, which are of the same stability constants as the corresponding complexes of $UO_2(NO_3)_2$ (Table 1). Moreover, these species are of almost identical spectrum profiles (Fig. S2 in Supporting information). So, we believe that the species of uranyl(VI) are of the same coordination environments, no matter whether $UO_2(NO_3)_2$ or $UO_2(NTf_2)_2$ has been used as the initial substance. All the aforementioned results possibly explain why the counter ions detected in the solid

Table 1
Thermodynamic parameters of the complexation of uranyl(VI) with CMPO in ionic liquids.

Complex	Anion	logβ	ΔH (kJ/mol)	ΔS (J mol^{-1}K^{-1})	Ref.
$HOEtmimNTf_2$					
$UO_2\mathbf{L}^{2+}$	NO_3^-	4.82 (5)	7.5 (1.7)	120 (7)	pw
$UO_2\mathbf{L}_2{}^{2+}$		9.39 (12)	−3.4 (1.7)	168 (7)	pw
$UO_2\mathbf{L}_3{}^{2+}$		12.98 (5)	−13.2 (1.8)	201 (8)	pw
$UO_2\mathbf{L}^{2+}$	NTf_2^-	4.86 (4)	–	–	pw
$UO_2\mathbf{L}_2{}^{2+}$		9.12 (4)	–	–	pw
$UO_2\mathbf{L}_3{}^{2+}$		13.51 (5)	–	–	pw
$C_4mimNTf_2$					
$UO_2\mathbf{L}^{2+}$	NTf_2^-	4.61 (3)	12.1 (9)	129 (4)	[25]
$UO_2\mathbf{L}_2{}^{2+}$		8.78 (6)	31.2 (9)	273 (5)	[25]
$UO_2\mathbf{L}_3{}^{2+}$		11.8 (2)	17 (2)	283 (11)	[25]

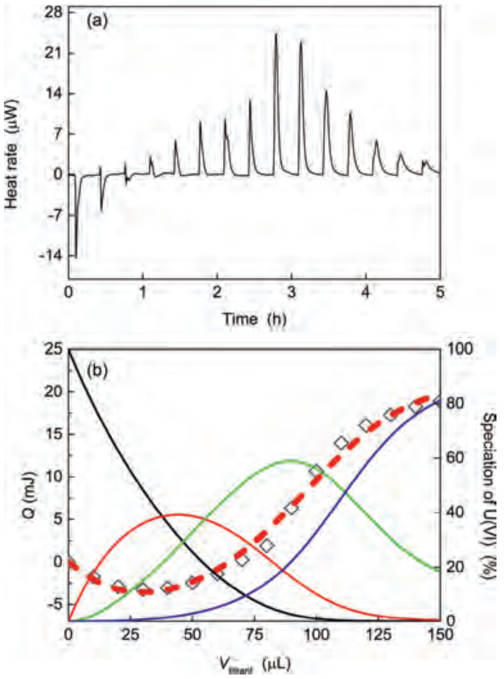

Fig. 5. Representative microcalorimetric titration of uranyl(VI)/CMPO complexation in $HOEtmimNTf_2$. (a) Titration thermograms; (b) cumulative reaction heat (black ◇ for experimental data (left y-axis), and: the red short dash line for the calculated results) and the uranyl(VI) species (right y-axis, black line: $UO_2{}^{2+}$, red line: $UO_2\mathbf{L}^{2+}$, green line: $UO_2\mathbf{L}_2{}^{2+}$, and blue line: $UO_2\mathbf{L}_3{}^{2+}$) as a function of the titrant volume ($V_{titrant}$, μL). Initial solution in the cup: 0.800 mL of $UO_2(NO_3)_2$ solution (2.19 mmol/L) in $HOEtmimNTf_2$, titrant: 40.0 mmol/L CMPO in $HOEtmimNTf_2$.

material collected from the extraction system are NTf_2^- rather than NO_3^-.

Fig. 5 shows a representative microcalorimetric titration of U(VI)/CMPO complexation in $HOEtmimNTf_2$. At the beginning of titration, the heat-rate curve consisted of negative peaks; with the addition of ligand solution, the negative peaks decreased rapidly in turn and then changed to positive peaks (Fig. 5a). This phenomenon indicated that the complexation system was endothermic in the early stage with lower **L**/U ratios, while rapidly changing to be exothermic with the increase of **L**/U ratio. In conjunction with the stability constants determined by spectrophotometry, the enthalpies for the U(VI)/CMPO complexes were calculated with HypDeltaH [33] and summarized in Table 1. The formation reactions of complexes $UO_2\mathbf{L}^{2+}$, $UO_2\mathbf{L}_2{}^{2+}$ and $UO_2\mathbf{L}_3{}^{2+}$ are of small enthalpy and large positive entropy, in agreement with the normal characters of the inner-sphere complexation between a hard Lewis acid and hard Lewis base [34,35]. The formation of $UO_2\mathbf{L}^{2+}$ is endothermic and entirely driven by entropy; the formations of $UO_2\mathbf{L}_2{}^{2+}$ and $UO_2\mathbf{L}_3{}^{2+}$ are weakly exothermic and driven by both enthalpy and entropy, whereas enthalpy only accounts for a small portion of the driving force. Positive enthalpy for complex $UO_2\mathbf{L}^{2+}$ indicates that the consumed energy in uranyl(VI) desolvation overrides the release in uranyl(VI)/CMPO coordination, whereas the opposite situation for complexes $UO_2\mathbf{L}_2{}^{2+}$ and $UO_2\mathbf{L}_3{}^{2+}$ [28,36,37].

In molecular solvents, the coordination number of linear $UO_2{}^{2+}$ is five or six (CN = 5 or 6), forming pentagonal or hexagonal bipyramidal complexes with ligands [26,38–42]. However, in ILs such as C_4mimPF_6 and $C_8mimNTf_2$, extended X-ray absorption fine structure (EXAFS) measurements showed that $UO_2{}^{2+}$ behaves lower CN (CN = 4.0-4.5) than in molecular solvent [43,44]. The entropy for complex $UO_2\mathbf{L}^{2+}$ in $HOEtmimNTf_2$ (120(7) J mol^{-1}K^{-1}) is equivalent to that in wet $C_4mimNTf_2$ (129(4) J mol^{-1}K^{-1}) [25], indicating that in $HOEtmimNTf_2$, the first CMPO molecule chelates to $UO_2{}^{2+}$ in the same bidentate fashion as in $C_4mimNTf_2$ [25]. Such coordination mode has been confirmed by the solid crystallographic data of the corresponding complex [38,39]. The stepwise enthalpy and entropy for complex $UO_2\mathbf{L}_2{}^{2+}$ (reaction $UO_2\mathbf{L}^{2+} + \mathbf{L} \rightarrow UO_2\mathbf{L}_2{}^{2+}$, $\Delta H_2 = -10.9 \pm 2.0$ kJ/mol, $\Delta S_2 = 48 \pm 8$ J mol^{-1}K^{-1}) and for complex $UO_2\mathbf{L}_3{}^{2+}$ (reaction $UO_2\mathbf{L}_2{}^{2+} + \mathbf{L} \rightarrow UO_2\mathbf{L}_3{}^{2+}$, $\Delta H_3 = -9.8 \pm 2.0$ kJ/mol, $\Delta S_3 = 33 \pm 9$ J mol^{-1}K^{-1}) are of equivalent values in error ranges, suggesting the second and third CMPO molecule most likely chelate to $UO_2{}^{2+}$ in the same fashion. Consequently, we herein hypothesize that the second and the third CMPO would act as a monodentate ligand to coordinate with $UO_2{}^{2+}$ [45]. The thermodynamic results can be interpreted perfectly with such a complexation assumption. One donor of CMPO (possibly the O-donor of P=O moiety because of its stronger basicity than that of the N-O moiety [46]) coordinates with $UO_2{}^{2+}$, which is convenient to disperse the steric hindrances and coordination tensions. As consequence, less difference occurs in the energy needed to remove the inner-sphere solvent molecules of $UO_2{}^{2+}$ in the last two complexations.

In summary, the complexation of uranyl(VI) with CMPO in a hydroxyl-functionalized ionic liquid $HOEtmimNTf_2$ has been investigated by solvent extraction, spectrophotometry, and calorimetry. Three successive complexes $UO_2\mathbf{L}^{2+}$, $UO_2\mathbf{L}_2{}^{2+}$ and $UO_2\mathbf{L}_3{}^{2+}$ form in $HOEtmimNTf_2$. Though $UO_2\mathbf{L}^{2+}$ and $UO_2\mathbf{L}_2{}^{2+}$ are the possible extraction species under a lower **L**/U ratio, complex $UO_2L_3{}^{2+}$ is the preferable extraction species of uranyl(VI) in the IL phase, assembling its neutral molecules at the inter-surface of the biphasic system to yield a solid material [14]. In homogeneous $HOEtmimNTf_2$ solution, the stability constants of complexes $UO_2\mathbf{L}^{2+}$, $UO_2\mathbf{L}_2{}^{2+}$ and $UO_2\mathbf{L}_3{}^{2+}$ are 4.82(5), 9.39(12) and 12.98(5), respectively. All formation reactions are predominantly driven by entropy, although a small part of the driving force of complexes $UO_2\mathbf{L}_2{}^{2+}$ and $UO_2\mathbf{L}_3{}^{2+}$ comes from enthalpy. The thermodynamics of the $UO_2{}^{2+}$/CMPO complexes is interpreted by hypothesizing that the first CMPO molecule coordinates with $UO_2{}^{2+}$ in a bidentate fashion, and the others in a monodentate fashion.

Declaration of competing interest

The authors declare no conflict of interest.

Acknowledgment

This work was supported by the National Science Foundation of China (Nos. 22076175, 11675156, U1830202 and 21976165).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2021.12.066.

References

[1] X. Sun, H. Luo, D. Sheng, Chem. Rev. 112 (2012) 2100–2128.
[2] Z. Kolarik, Solvent Extr. Ion Exch. 31 (2013) 24–60.
[3] M. Lqbal, K. Waheed, S.B. Rahat, T. Mehmood, M.S. Lee, J. Radioanal. Nucl. Chem. 325 (2020) 1–31.
[4] K. Takao, T.J. Bell, Y. Ikeda, Inorg. Chem. 52 (2013) 3459–3472.
[5] L. Maria, A. Cruz, J.M. Carretas, et al., Sep. Purif. Technol. 237 (2019) 116354.
[6] L. Yuan, M. Sun, X. Liao, et al., Sci. China Chem. 57 (2014) 1432–1438.
[7] S.A. Ansari, P. Pathak, P.K. Mohapatra, V.K. Manchanda, Sep. Purif. Rev. 40 (2011) 43–76.
[8] C.Z. Wang, W.Q. Shi, J.H. Lan, et al., Inorg. Chem. 52 (2013) 10904–10911.
[9] C.Z. Wang, J.H. Lan, Y.L. Zhao, et al., Inorg. Chem. 52 (2013) 196–203.
[10] A.E. Visser, R.D. Rogers, J. Solid State Chem. 171 (2003) 109–113.
[11] A.N. Turanov, V.K. Karandashev, A.N. Yarkevich, Russ. J. Inorg. Chem. 63 (2018) 406–413.
[12] J. Shi, W. Yuan, Z. Dong, L. Zhong, F. Tang, Chin. J. Inorg. Chem. 32 (2016) 414–420.
[13] A. Rout, K.A. Venkatesan, T.G. Srinivasan, P. Rao, Radiochim. Acta 97 (2009) 719–725.
[14] B. Chen, K. Wu, Y. Yang, et al., Chem. Commun. 55 (2019) 6894–6897.
[15] M.P. Jensen, J. Neuefeind, J.V. Beitz, S. Skanthakumar, L. Soderholm, J. Am. Chem. Soc. 125 (2003) 15466–15473.
[16] Z. Kolarik, Solvent Extr. Ion Exch. 31 (2013) 24–60.
[17] S.A. Ansari, P.N. Pathak, V.K. Manchanda, et al., Solvent Extr. Ion Exch. 23 (2005) 463–479.
[18] S. Belair, A. Labet, C. Mariet, P. Dannus, Solvent Extr. Ion Exch. 23 (2005) 481–499.
[19] F. McLachlan, K. Greenough, A. Geist, et al., Solvent Extr. Ion Exch. 34 (2016) 334–346.
[20] M.P. Jensen, J.A. Dzielawa, P. Rickert, M.L. Dietz, J. Am. Chem. Soc. 124 (2002) 10664–10665.
[21] A.N. Turanov, V.K. Karandashev, A.N. Yarkevich, Radiochemistry 59 (2017) 360–364.
[22] A. Rout, K.A. Venkatesan, T.G. Srinivasan, P.R. Vasudeva Rao, Sep. Purif. Technol. 97 (2012) 164–171.
[23] J.T. Bell, R.E. Biggers, J. Mol. Spectrosc. 18 (1965) 247–275.
[24] C.C. Görller-Walrand, S.D. Jaegere, Spectrochim. Acta A Mol. Spectrosc. 27 (1972) 257–268.
[25] Q. Wu, T. Sun, X. Meng, J. Chen, C. Xu, Inorg. Chem. 56 (2017) 3014–3021.
[26] L. Lv, B. Chen, J. Liu, et al., Dalton Trans. 48 (2019) 566–577.
[27] P. Gans, A. Sabatini, A. Vacca, Talanta 43 (1996) 1739–1744.
[28] P. Nockemann, K. Servaes, R.V. Deun, et al., Inorg. Chem. 46 (2007) 11335–11344.
[29] D. Ternova, A. Ouadi, V. Mazan, et al., J. Solution Chem. 47 (2018) 1309–1325.
[30] B. Kopainsky, J.K. Hallermeier, W. Kaiser, Chem. Phys. Lett. 83 (1981) 498–502.
[31] Y. Chen, Y. Kong, Y. Wang, et al., J. Colloid Interface Sci. 330 (2009) 421–427.
[32] J. Roden, W.T. Strunz, A. Eisfeld, Int. J. Mod. Phys. B 24 (2010) 5060-5060.
[33] P. Gans, A. Sabatini, A. Vacca, J. Solut. Chem. 37 (2008) 467–476.
[34] W.A. Reed, L. Rao, P.L. Zanonato, A.Y. Garnov, K.L. Nash, Inorg. Chem. 46 (2007) 2870–2876.
[35] Y. Yang, S.J. Teat, Z. Zhang, S. Luo, L. Rao, Dalton Trans. 45 (2016) 384–391.
[36] I. Billard, C. Gaillard, C. Hennig, Dalton Trans. 37 (2007) 4214–4221.
[37] C. Gaillard, A. Chaumont, I. Billard, et al., Inorg. Chem. 46 (2007) 4815–4826.
[38] R.N. Kapoor, P. Guillory, L. Schulte, et al., Appl. Organomet. Chem. 19 (2005) 510–517.
[39] E.V. Sharova, O.I. Artyushin, K.A. Lyssenko, M.P. Passechnik, I.L. Odinets, Russ. Chem. B 57 (2008) 1890–1896.
[40] Y. Yang, Z. Zhang, L. Yang, et al., Inorg. Chem. 58 (2019) 6064–6074.
[41] J. Liu, X. Wang, B. Chen, et al., Inorg. Chem. Front. 7 (2020) 3412–3423.
[42] C. Xu, G. Tian, S.J. Teat, L. Rao, Inorg. Chem. 52 (2013) 2750–2756.
[43] V. Cocalia, K. Gutowski, R. Rogers, Coordin. Chem. Rev. 250 (2006) 755–764.
[44] K. Servaes, C. Hennig, I. Billard, et al., Eur. J. Inorg. Chem. 2007 (2007) 5120–5126.
[45] L. Rao, Chem. Soc. Rev. 36 (2007) 881–892.
[46] A. Chaumont, G. Wipff, Phys. Chem. Chem. Phys. 8 (2006) 494–502.