

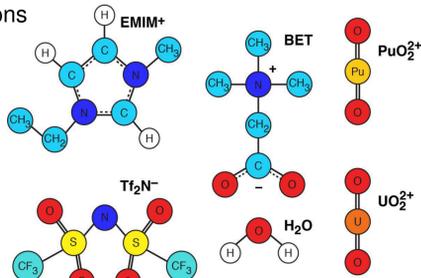
Uranyl(VI) and Plutonyl(VI) Coordination and Dynamics in a Task-Specific Ionic Liquid

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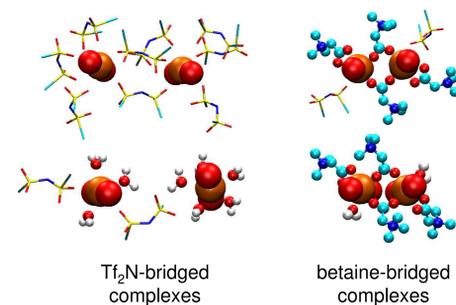
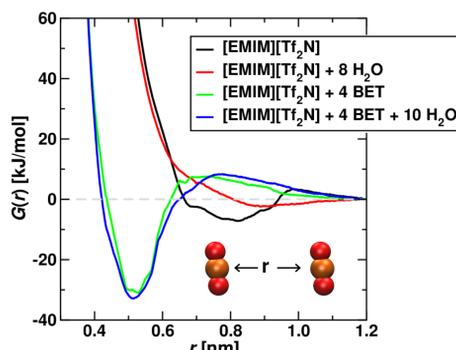
Introduction

- Ionic liquids (ILs) are unique solvents with many interesting properties
 - low volatility, large electrochemical window
- ILs are becoming of great interest for advanced nuclear fuel cycles
 - solvent extraction, electrochemical separations
- Many ILs complex very weakly with metals
 - not good for separations!
- Recently, Nockemann et al. designed a task-specific IL for complexing metals¹
 - betainium bis(trifluoromethylsulfonyl)imide
 - betainium deprotonates to form the zwitterion betaine when coordinating with a metal
- Molecular simulation can help us understand the interactions of actinides in ILs²
 - large scale classical simulations of uranyl(VI) and plutonyl(VI) in mixtures of 1-ethyl,3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf₂N]) with water and betaine (BET) using a recently developed actinyl(VI) force field³

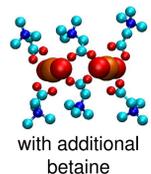


Dimeric Complexes

- In pure [EMIM][Tf₂N], Tf₂N-bridged dimeric (and trimeric) complexes can form²
 - just under half of the actinyl cations are found in multi-actinyl complexes
- The addition of even small amounts of water displaces Tf₂N from the first solvation shell and destroys the complexes
- The addition of betaine creates more strongly bound betaine-bridged complexes with shorter U-U separations
 - similar dimer found in the crystal structure⁴
- The addition of water has no significant effect on the betaine-bridged complexes

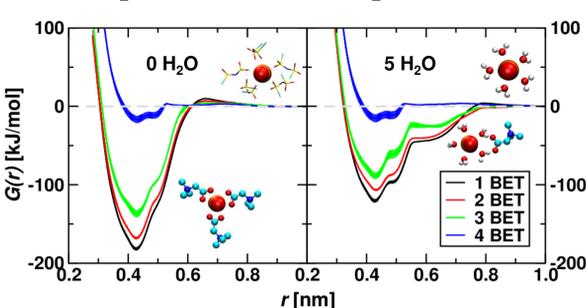
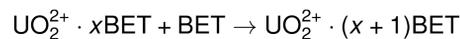
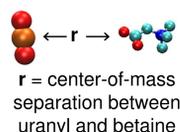


system	position [nm]	ΔG [kJ/mol]
[EMIM][Tf ₂ N]	0.8	-7 ± 1
[EMIM][Tf ₂ N] + 8 H ₂ O	0.9	-2 ± 1
[EMIM][Tf ₂ N] + 4 BET	0.5	-32 ± 7
[EMIM][Tf ₂ N] + 4 BET + 10 H ₂ O	0.5	-33 ± 6



Potential of Mean Force

- The potential of mean force (PMF) tells us the **relative free energy** change along a reaction coordinate, r
 - center-of-mass separation between uranyl and betaine
- Progressive addition of betaine to uranyl in bulk [EMIM][Tf₂N] in the presence and absence of water
 - betaine is a much stronger ligand than Tf₂N and water
 - relative free energy change 50-60 kJ/mol less in the presence of water

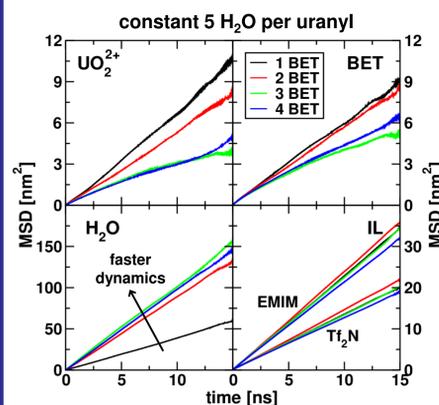


ΔG [kJ/mol]	0 H ₂ O	5 H ₂ O
1 BET	-182 ± 2	-120 ± 3
2 BET	-168 ± 2	-107 ± 2
3 BET	-137 ± 5	-89 ± 5
4 BET	-17 ± 5	-15 ± 5

relative free energy minima for the progressive addition of betaine to uranyl

Dynamics

- The mean square displacement (MSD) tells us about the dynamics of the system
 - calculate the diffusion coefficient using the Einstein relation
- $$\text{MSD}(t) = \langle |r(t) - r(0)|^2 \rangle \quad \lim_{t \rightarrow \infty} \text{MSD}(t) = 6Dt$$
- Addition of betaine slows the dynamics of uranyl and betaine
 - strongly correlated betaine and uranyl dynamics
 - faster water dynamics as water no longer coordinates with uranyl
 - little change in IL dynamics



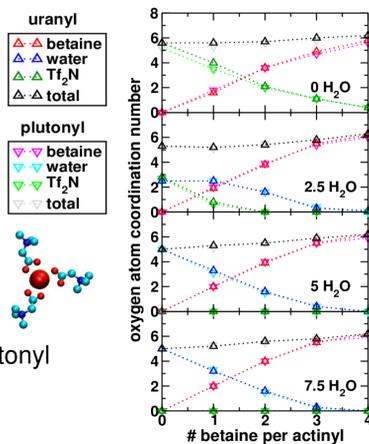
diffusion coefficients [$\times 10^{-9} \text{ m}^2/\text{s}$]

	uranyl	BET	H ₂ O
1 BET	0.12 ± 0.02	0.10 ± 0.04	0.65 ± 0.16
2 BET	0.09 ± 0.04	0.09 ± 0.04	1.50 ± 0.12
3 BET	0.06 ± 0.02	0.07 ± 0.02	1.66 ± 0.21
4 BET	0.05 ± 0.01	0.07 ± 0.02	1.64 ± 0.22

	EMIM	Tf ₂ N
1 BET	0.38 ± 0.01	0.22 ± 0.01
2 BET	0.40 ± 0.02	0.24 ± 0.02
3 BET	0.37 ± 0.02	0.22 ± 0.01
4 BET	0.35 ± 0.01	0.21 ± 0.01

Average Coordination Numbers

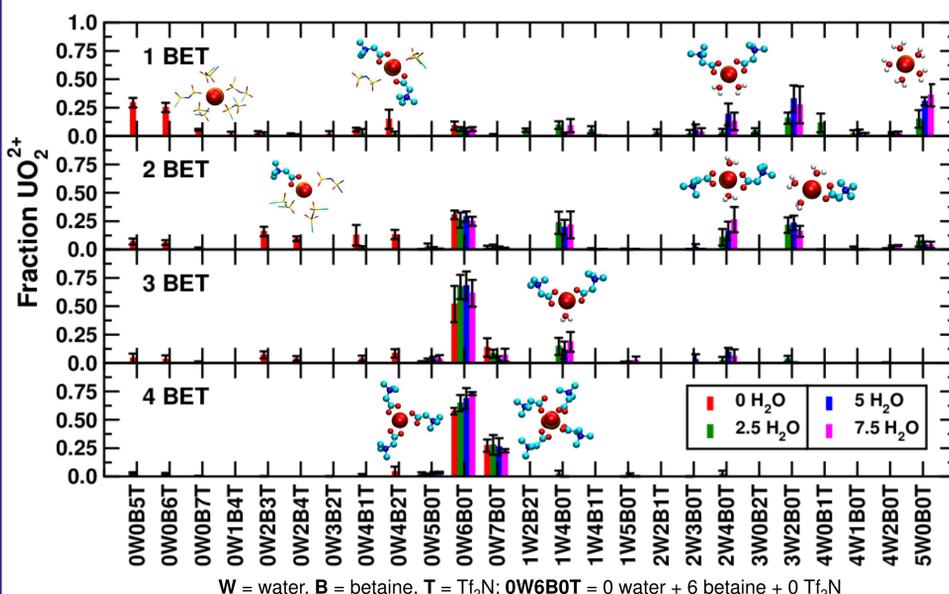
- Large scale simulations of 0.1 M actinyl(VI) solutions in [EMIM][Tf₂N] with varying amounts of betaine and water
 - betaine to actinyl ratios of 0, 1, 2, 3, and 4
 - water to actinyl ratios of 0, 2.5, 5, and 7.5
- Tf₂N only coordinates the actinyl in the absence of enough water and/or betaine to fill the first solvation shell
- Betaine displaces both Tf₂N and water
- Oxygen atom coordination number increases from 5 to 6 with increasing amounts of betaine
- No significant difference between uranyl and plutonyl



ligand strength:
betaine > water > Tf₂N

Distribution of Coordination Environments

- Broad distribution of coordination environments narrows with increasing betaine concentration



Conclusions and Acknowledgements

- Betaine coordinates strongly with uranyl(VI) and plutonyl(VI)
 - displaces both water and Tf₂N from the first solvation shell
 - a broad distribution of coordination environments at low betaine concentrations rapidly narrows with increasing amounts of betaine
- Little difference between uranyl(VI) and plutonyl(VI) in these mixtures
- Betaine-bridged dimeric complexes exist in solution
 - similar to the observed crystal structure
- Molecular simulation is a valuable tool for understanding the coordination and dynamics of actinyl cations in solution
 - molecular-level insight without difficult and/or dangerous experiments

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References

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