Ionic liquids-based bitumen extraction: Enabling recovery with environmental footprint comparable to conventional oil

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Supporting Information

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Figure S1. ¹H NMR spectra (CDCl₃-*d*) of trihexyltetradecylphosphonium oleate ([P₆₆₆₁₄][Oleate]).



Protic IL	Density (g/cm ³)	
[C ₄ NH ₃][Oleate]	1.0048	
[C ₆ NH ₃][Oleate]	0.9964	
[C ₈ NH ₃][Oleate]	0.9933	
[HN ₂₂₂][Oleate]	0.9826	
[HN ₄₄₄][Oleate]	0.9707	
[HN ₈₈₈][Oleate]	0.9655	

Figure S2. (*Left*) Viscosity (by shear rate sweep test) and (*Right*) density (both determined at 25 °C) of the synthesized ionic liquids that are liquids at room temperature.



Figure S3. IL-water systems (1 g of IL added to 1 g water) show gel formation ([C4NH3][Oleate], [C8NH3][Oleate], [HN222][Oleate]) or immiscibility ([HN444][Oleate] and [HN888][Oleate])



Figure S4. Screening test for bitumen extraction from oil sands using trialkylammonium-based ILs show optimal separation for the tributylammonium IL under the experimental conditions.

Primary vs. Tertiary Amine-based ILs

It was previously reported that, when combining primary amines with carboxylic acids, the resulting protic ILs exhibit higher viscosity and lower thermal volatility than the starting components, evidence of proton transfer relatively close to complete and hence forming "true" salts.^{1,2} On the other hand, when tertiary amines are combined with carboxylic acids, the resulting protic ILs are less viscous and remained quite volatile, indicating incomplete proton transfer and hence systems in equilibrium between the ionized and non-ionized species.¹ Similar results were observed for us when primary and tertiary amines were mixed with oleic acid; for example, much higher viscosities (**Figure S1**), higher stability when exposed to vacuum (see below), and lower thermal volatility (see below) were observed for alkylammonium oleate ILs vs. trialkylammonium oleate ILs.

The difference between ionicity of the salts of the primary and tertiary amines was also evident in NMR spectra, when they were combined with oleic acid, stirred overnight, and then exposed to vacuum at 45 °C for 20 h. ¹H NMR spectra of the resulting liquids after mixing (before vacuum), after 10 h vacuum, and after an additional 10 h vacuum (20 h total) were collected (**Figures S5-S10**) and the ratio between cation and anion was calculated (**Table S1**). In addition, new peaks were observed in some of the ILs when exposed to vacuum over time (indicated in **Table S1** and **Figures S7-S8**).

Mixture	After mixing	After 10 h vacuum	After 20 h vacuum
[C ₄ NH ₂]:[Oleic acid]	1:1	1:1	1:1
[C ₈ NH ₂]:[Oleic acid]	1:1	1:1	1:1
[N ₂₂₂]:[Oleic acid]	1:1	0.3:1 ^a	0.25:1ª
[N ₄₄₄]:[Oleic acid]	1:1	0.3:1	0.3:1 ^a
[N ₈₈₈]:[Oleic acid]	1:1	1:1	1:1

Table S1. Amine:Oleic acid ratio composition after mixing and after 10 h and 20 h vacuum.

^a New peaks detected using 1H-NMR (Figures S7-S8).



Figure S5. ¹H NMR spectra (CDCl₃-*d*) of butylammonium oleate ([C₄NH₃][Oleate]) after (blue) mixing (1:1 amine:acid molar ratio), (green) 10 h vacuum, and (brown) 20 h vacuum.



Figure S6. ¹H NMR spectra (CDCl₃-*d*) of octylammonium oleate ([C₈NH₃][Oleate]) after (blue) mixing (1:1 amine:acid molar ratio), (green) 10 h vacuum, and (brown) 20 h vacuum.



Figure S7. (a) Full ¹H NMR spectra and (b) Expanded view of ¹H NMR spectra (CDCl₃-d) of triethylammonium oleate ([HN₂₂₂][Oleate]) after (blue) mixing (1:1 amine:acid molar ratio), (green) 10 h vacuum, and (brown) 20 h vacuum.



Figure S8. ¹H NMR spectra (CDCl₃-*d*) of tributylammonium oleate ([HN₄₄₄][Oleate]) after (blue) mixing (1:1 amine:acid molar ratio), (green) 10 h vacuum, and (brown) 20 h vacuum.



Figure S9. ¹H NMR spectra (CDCl₃-*d*) of trioctylammonium oleate ([HN₈₈₈][Oleate]) after (blue) mixing (1:1 amine:acid molar ratio), (green) 10 h vacuum, and (brown) 20 h vacuum.



Figure S10. TGA for the synthesized protic ILs. Difference in compositions are related to volatility, although the studied ILs are stable at room temperature, which we used in our bitumen extraction experiments.

References

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