

SUPPORTING INFORMATION

Mechanism of ionic liquid-based acidic aqueous biphasic systems formation

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Table

Table S1. Ability of commercially available ILs to form acidic ABS with four acids. DEN indicates visible IL denaturation (color change, emission of gases, precipitate formation). As all these determinations were performed visually, some degree of uncertainty is involved, and this is represented by MAYBE (some systems have a very weak cloud point, others form a gel like phase and some slightly change color upon phase separation).

IL class	IL		Acids			
	Cation	Anion	H ₂ SO ₄	HCl	HNO ₃	H ₃ PO ₄
Imidazolium	[C ₄ mim]	[N(CN) ₂]	DEN	DEN	DEN	NO
		[BF ₄]	NO	NO	NO	NO
		[Br]	NO	NO	DEN	NO
		[Tos]	NO	NO	NO	NO
		[SCN]	DEN	NO	DEN	NO
		[CH ₃ CO ₂]	NO	NO	NO	NO
		[CF ₃ CO ₂]	NO	NO	NO	NO
		[CF ₃ SO ₃]	NO	NO	NO	NO
		[CH ₃ SO ₃]	NO	NO	NO	NO
		[C ₂ H ₅ PO ₄]	NO	NO	NO	NO
		[NO ₃]	NO	NO	NO	NO
		[CH ₃ SO ₄]	NO	NO	NO	NO
[C ₂ H ₅ SO ₄]	NO	NO	NO	NO		
Effect of imidazolium	[C ₂ mim]	[Cl]	NO	NO	NO	NO

cationic chain	[C ₄ mim]		NO	NO	NO	NO
	[C ₆ mim]		NO	NO	NO	NO
	[C ₈ mim]		NO	NO	NO	NO
	[C ₁₀ mim]		NO	NO	NO	NO
	[C ₁₂ mim]		NO	NO	NO	NO
	[C ₁₄ mim]		NO	NO	NO	NO
Pyridinium, pyrrolidinium, piperidinium	[C ₄ mpy]	[Cl]	NO	NO	NO	NO
	[C ₄ mpip]		NO	NO	NO	NO
	[C ₄ mpyrr]		NO	NO	NO	NO
	[C ₄ -2-mpy]		NO	NO	NO	NO
Phosphonium	[P ₁₄₄₄]	[CH ₃ SO ₄]	NO	NO	YES	NO
	[P _{1i(444)}]	[Tos]	NO	NO	YES	NO
	[P ₄₄₄₂]	[(Et) ₂ PO ₄]	NO	NO	YES	NO
	[P ₄₄₄₄]	[Cl]	YES	NO	YES	NO
		[Br]	DEN	NO	YES	NO
	[P ₈₈₈₈]	[Br]	YES	MAYBE	DEN	NO
	[P ₁₁₁₁₄]	[Br]	NO	NO	DEN	NO
[P ₄₄₄₁₄]	[Cl]	YES	YES	YES	NO	
Ammonium	[N ₁₁₁₁]	[Cl]	NO	NO	NO	NO
	[N ₂₂₂₂]	[Cl]	NO	NO	NO	NO
	[N ₃₃₃₃]	[Cl]	NO	NO	YES	NO
	[N ₄₄₄₄]	[Cl]	NO	NO	YES	NO
		[Br]	DEN	NO	DEN	NO
	[N ₅₅₅₅]	[Cl]	YES	NO	YES	NO
	[N ₈₈₈₈]	[Br]	DEN	MAYBE	YES	NO
	[N ₁₁₁₁₄]	[Br]	DEN	NO	DEN	NO
	[NB ₁₁₁]	[Cl]	NO	NO	NO	NO
	[NB ₂₂₂]	[Cl]	NO	NO	NO	NO
	[NB ₄₄₄]	[Cl]	NO	NO	YES	NO
[NB _{22(2OH)}]	[Cl]	NO	NO	NO	NO	
Choline	[Ch]	[Cl]	NO	NO	NO	NO
	[Ch]	[H ₂ PO ₄]	NO	NO	NO	NO
	[Ch]	[C ₂ H ₃ O ₂]	NO	NO	NO	NO

Figures

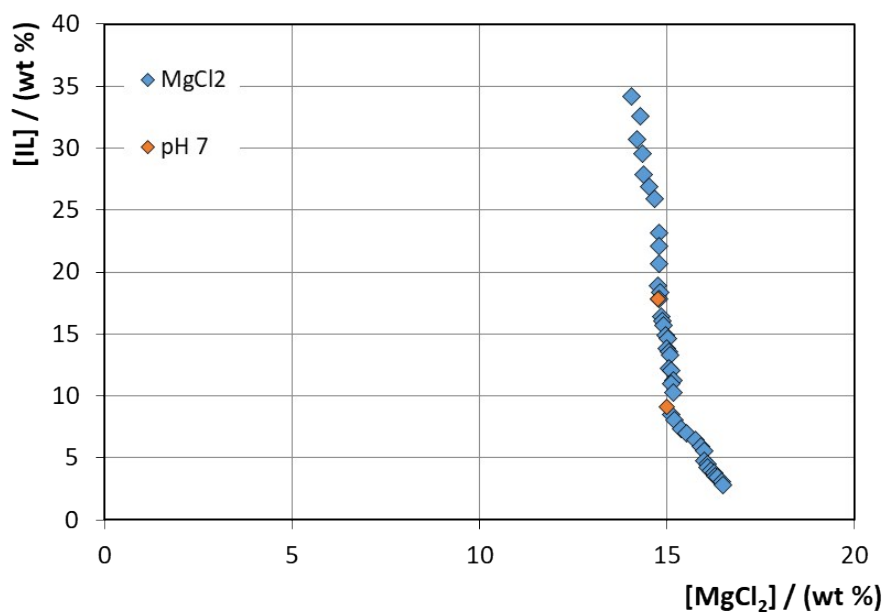


Figure S1. Binodal curves and binodal mixture points for the $[P_{44414}]Cl$ - $MgCl_2$ - H_2O systems at 298 K without and with pH control respectively

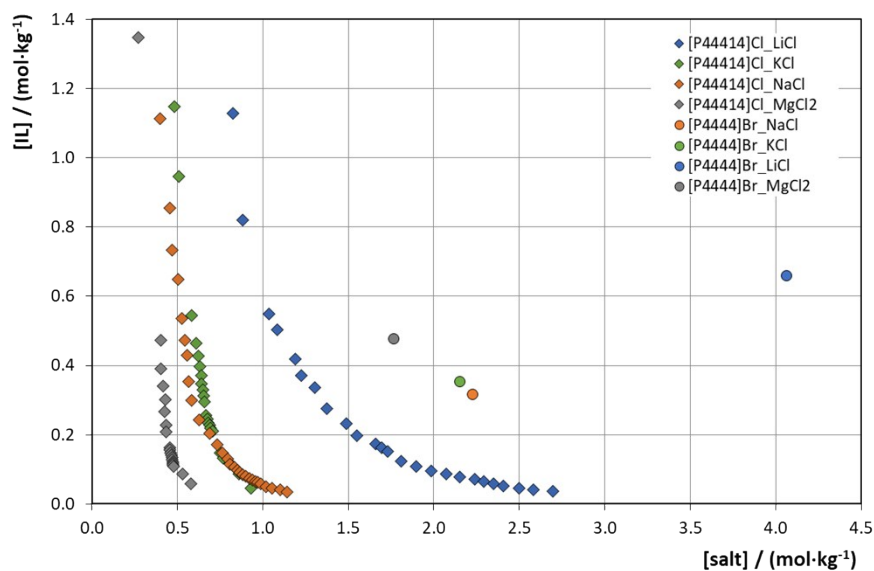


Figure S2. Binodal curves and binodal mixture points for the ABS composed of LiCl, NaCl, KCl, and $MgCl_2$ with $[P_{44414}]Cl$ and $[P_{4444}]Br$ respectively at 323 K

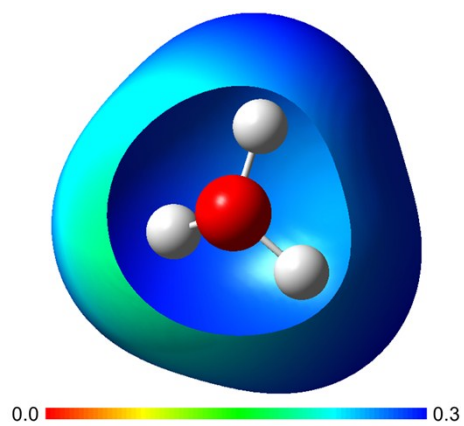


Figure S3. Comparison of the charge distribution at the molecular surface of H_3O^+ cation computed at the B3LYP/6-311+G(d,p) level of theory. Blue color illustrates positively charge segments while red color illustrates neutrally charged segments.