Ion-Solvent Interactions in 1:2 Lewis-Acidic Chloroaluminate Ionic Liquids

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Abstract: *Ionic liquids (ILs) formulated by mixing an organic chloride salt with AlCl₃ in a 1:2 molar ratio-classically, 1-ethyl-3-methylimidazolium chloride (EMImCl): AlCl₃ = 1:2- form Lewis-acidic "1:2 ionic liquids" in which the dominant anionic species is $Al_2Cl_7^-$ in equilibrium with $AlCl_4^-$. These liquids show distinctive ion–solvent interactions that govern transport, reactivity, and interfacial phenomena in catalysis and electrochemistry (e.g., Al battery electrolytes and Al electrodeposition). This review synthesizes how acidity and speciation control solvation thermodynamics and dynamics, surveys experimental and computational probes (NMR, vibrational spectroscopy, solvatochromic scales, conductivity) and distills design rules for tuning solvation via composition, cation identity, and purposeful dilution.[1][3]*

Keywords: ionic liquids, chloroaluminate, $Al_2Cl_7^-$, Lewis acidity, solvation, Kamlet–Taft, electrodeposition, catalysis

1. Introduction and Scope

Mixing organic chloride salts with AlCl₃ yields chloroaluminate ionic liquids whose acidity and speciation are set by the AlCl₃ mole fraction. At a 1:2 salt:AlCl₃ ratio (the "1:2 IL"), the liquid is Lewis-acidic and enriched in dimeric $Al_2Cl_7^-$ alongside $AlCl_4^-$. The balance of these anions controls reactivity and transport and is central to solvation of neutral and ionic solutes.[1][2]

In catalysis, this speciation orchestrates hydride/alkyl transfer and cracking–alkylation chemistry; in electrochemistry, it governs Al plating/stripping and conductivity. Understanding how solvent structure (the IL itself, with optional cosolvents) stabilizes charges and transition states is therefore essential.[1][5]

2. Conceptual Framework: Acidity, Speciation, and Solvatochromic Scales

Lewis acidity & anionic speciation. In 1:2 ILs, $AlCl_4^-$ (relatively inert) and $Al_2Cl_7^-$ (strongly Lewis-acidic) interconvert, and their ratio is sensitive to composition, temperature, water/impurity content, and cation identity. Larger, more weakly coordinating cations can stabilize larger (AlCl₃) n clusters, shifting speciation and viscosity-both of which feed back into solvation and ion mobility.[1][6]

Probing acidity with molecular bases. Spectroscopic probes such as pyridine distinguish Lewis/Brønsted acidity in chloroaluminate media; IR/NMR fingerprints track coordination to $Al_2Cl_7^-$ vs. $AlCl_4^-$ and provide a sensitive readout of "solvent" strength as seen by dissolved solutes.[1][5]

Solvatochromic parameters. Although originally developed for molecular solvents, Kamlet–Taft (α, β, π*) and related scales (Catalán; Reichardt's E_T^N) are increasingly used to parameterize IL solvation. π* in ILs acts as a polarizability-density descriptor; α/β trends capture H-bond acidity/basicity arising from the ionic network-useful when comparing neat 1:2 ILs versus cosolvent-modified systems.[1][8]

3. Experimental Probes of Ion–Solvent Interactions

NMR spectroscopy. Multinuclear NMR (¹H, ²⁷Al, ³⁵/³⁷Cl) resolves speciation ($AlCl_4^-$ vs. $Al_2Cl_7^-$), quantifies coordination to bases/nucleophiles, and accesses dynamics via relaxation and diffusion (DOSY). Recent reviews highlight how NMR connects local solvation structure with macroscopic transport in ILs, including those doped with metal salts.[10]

Vibrational spectroscopy. IR/Raman track Al–Cl stretching modes and their shifts upon solute coordination, revealing how donor molecules or trace water disrupt the $Al_2Cl_7^-$ network- often decreasing acidity and altering ion pairing. Pyridine/benzene probes remain particularly diagnostic.[6]

Conductivity & transport metrics. Ionic conductivity and Walden plots respond strongly to speciation and viscosity. Methods that deconvolute species mobilities show how increasing $Al_2Cl_7^-$ or using bulkier cations reduces mobility, reflecting stronger cohesive ion–solvent interactions.[1][4]

Electrochemical signatures. Cyclic voltammetry and chronoamperometry in 1:2 ILs disclose plating/stripping kinetics and the role of solvation shells and ion aggregates at interfaces; mechanistic studies of Al reduction in EMImCl/AlCl₃ systems connect electrode processes to bulk solvation and speciation.[2]

4. Computational insights

Molecular simulations- from classical MD with polarizable force fields to reactive schemes-resolve ion coordination numbers, spatial heterogeneity, and the timescales of solvation. In chloroaluminate media, simulations capture the persistence of $Al_2Cl_7^-$ and its disruption by donor molecules; more broadly, MD connects local polarity/polarizability to solvatochromic observables that rationalize Kamlet–Taft trends.[11]

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5. Case studies

5.1 Catalysis in 1:2 ILs

Recent mechanistic work on polyolefin deconstruction in chloroaluminate ILs shows that while $Al_2Cl_7^-$ is a key marker of strong acidity, the catalytically competent ensemble can be more nuanced than a simple proportionality to $[Al_2Cl_7^-]$. The solvent environment stabilizes carbocationic intermediates and hydride transfer transition states; subtle solvation differences, controlled by composition and temperature, modulate rates and selectivity.[1][12]

5.2 Aluminium electrochemistry

For Al plating/stripping, ion–solvent structure determines overpotentials and Coulombic efficiency. Larger organic cations (e.g., pyrrolidinium vs. imidazolium) alter speciation, increase viscosity, and reduce the concentration/mobility of electroactive species, underscoring the coupling of solvation to transport. At the same time, fundamental reductions proceed via Al-chloro complexes whose interfacial desolvation is rate-limiting.[3][11]

6. Purposeful tuning of solvation

Composition (r = $AlCl_3$ mole ratio). Moving from 1:1 to 1:2 increases Lewis acidity by enriching $Al_2Cl_7^-$; small shifts in r and temperature can meaningfully change donor acceptance and, consequently, solute stabilization.[7]

Cation engineering. Bulky, weakly coordinating cations reduce lattice energy but can also favor larger chloroaluminate aggregates, raising viscosity and diminishing electroactive species-trade-offs that affect ion–solvent coupling and conductivity.[8]

Cosolvent/dopant strategies. Adding donor molecules (pyridine, ethers) or trace water decreases effective acidity by breaking $Al_2Cl_7^-$, shifting equilibria toward $AlCl_4^-$ and altering solvation shells; such dilution can improve kinetics but may suppress desired Lewis-acidic behavior. Probing with solvatochromic parameters (π^*, α, β) provides a practical map for these effects.[1][5]

7. Relation to Solvate Ionic Liquids (Context and Contrast)

Solvate ionic liquids (SILs)- stoichiometric complexes such as $Li(glyme)\_n^+$ paired with weakly coordinating anions- offer a useful contrast: they achieve strong, cation-centered solvation via ligand encapsulation, leading to high π^* and tunable α/β. While chemically distinct from 1:2 chloroaluminates, SIL studies illustrate how coordinated structures and polarizability density control ion–solvent interactions- concepts translatable to chloroaluminate design.[1][7]

8. Outlook and Open Questions

Open challenges include (i) quantitatively mapping $Al_2Cl_7^- \rightleftharpoons AlCl_4^-$ equilibria under operating conditions (current/potential, gas/liquid feeds), (ii) disentangling collective polarization from specific coordination in solvatochromic observables, and (iii) engineering cations/ligands that decouple high Lewis acidity from high viscosity. Progress will hinge on multi-modal approaches (operando NMR/vibrational spectroscopy + computation) tied to rigorous conductivity/kinetics models. [9][10]

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