Interfacial Enrichment and Reaction Mechanisms of Organic Molecules in Ionic Liquids

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Tailoring the surface composition of ionic liquids (ILs) is a key strategy for enhancing the performance of supported ionic liquid phase (SILP) catalysts. In addition, understanding and controlling the surface composition of metalloporphyrins in ionic liquids is crucial for designing photoactive materials. In this work, we first investigate the interfacial behavior of fluorine-free Ru polypyridyl complexes functionalized with n-nonyl side chains (Ru-C_9) dissolved in two ILs with contrasting physicochemical properties, such as hydrophobicity and surface tension, namely $[C_4C_1Im][PF_6]$ and $[C_4C_1Im][OAc]$[1]. Using angle-resolved X-ray photoelectron spectroscopy (ARXPS), we show that Ru-C_9 complexes undergo pronounced surface enrichment in $[C_4C_1Im][PF_6]$, adopting a buoy-like orientation at the IL/vacuum interface. Surface saturation is achieved at a bulk concentration of 0.12 $\%_{mol}$, a regime relevant for efficient SILP catalysis. In contrast, no interfacial enrichment is observed in $[C_4C_1Im][OAc]$, highlighting the critical role of IL composition, particularly anion identity and surface tension, in governing the surface distribution of metal complexes. These findings provide molecular-level insights into the design of IL-based catalytic systems with optimized interfacial properties. Consequently, we investigate the interfacial behavior of zinc-didodecylporphyrin molecules (Zn-DDP) dissolved in the hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate $[C_4C_1Im][PF_6]$ using ARXPS.[2] Upon mild heating, Zn-DDP undergoes spontaneous demetallation, evidenced by the appearance of aminic (–NH) and iminic (=N–) nitrogen XPS signals characteristic of the free-base porphyrins. Partial hydrolysis of $[PF_6]^-$ anions produces phosphate species that contribute to the demetallation process. Concentration-dependent measurements reveal extremely high surface enrichment of porphyrins at the IL/vacuum interface, reaching surface saturation already at about 0.50 $\%_{mol}$ Zn-DDP content in the bulk. Temperature-dependent ARXP spectra reveal that for unsaturated interfaces, surface enrichment increases with increasing temperature. Our findings provide molecular-level insights to guide the design of porphyrin-based photoactive interfaces in ionic liquid systems.

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References

[1] Ceccatto, A. et al. *Influence of ionic liquid composition on surface enrichment of fluorine-free Ru complexes.* **RSC Adv.**, 2025,**15**, 36137-36144

[2] Ceccatto, A. et al. *Interfacial Enrichment and Demetallation of a Zinc Porphyrin in the Ionic Liquid $[C_4C_1Im][PF_6]$.* **ChemPhysChem.** *Under review.*