Silylamine Reversible Ionic Liquids as Electrochemical Solvents

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Ionic liquids when used as electrochemical solvents serve as both the solvent and electrolyte¹. They are appealing for electrochemical purposes because of their wide electrochemical window, minimal volatility, and tunable solubility properties. Separation of products produced electrochemically can be difficult from ionic liquids, however.

Switchable solvents as electrochemical solvents offer the possibility to reduce or eliminate challenges of product separation while maintaining the desirable solvent/electrolyte properties of ionic liquids. Switchable solvents are solvents that can switch properties dramatically in a step-wise fashion with the introduction of an external stimulus such as light, heat or CO_2^2 Reversible ionic liquids (RevILs) are one type of switchable solvent^{3,4}. Reversible ionic liquids begin as molecular liquids with properties similar to those of traditional solvents (relatively non-polar, non-ionic and non-viscous). With the introduction of an external stimulus, commonly CO₂ at atmospheric pressures, the liquid switches to have properties similar to those of a traditional ionic liquid (relatively polar, ionic and viscous). Silylamines can be used as reversible ionic liquids where CO₂ reacts with the amine to form an ammonium-carbamate ion pair^{3,4}, as shown in Figure 1.

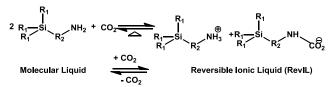


Figure 1. Silylamine reversible ionic liquids in molecular liquid and RevIL form. $R_1 = EtO$, MeO, Et, Pr, Hex; $R_2 = Pr$, Pr-CH₃.

By changing the R-groups around the Si, the properties of the RevIL change significantly including RevIL viscosity, reversal temperature, polarity and substrate solubilities. These silylamine RevIL systems have been used as reaction and extraction solvents³ and as CO_2 capture solvents⁴.

Silylamine RevILs have yet to be examined as electrochemical solvents. By using RevILs as electrochemical solvents, the desired ionic liquid properties in the electrochemical system can be achieved while also increasing the ease of product separation from the solvent and eliminating electrolyte contamination of the product. These RevILs can be especially useful in electro-organic syntheses where product separation is a concern as is electrolyte contamination and loss. The silylamine RevILs also have opportunities for improved performance in electrodeposition systems where the ammonium-carbamate ion pair can serve as a chelating system to support the metal cation in the solution prior to deposition.

The electrochemical properties and stability of

select silylamine RevILs will be reported along with model electrochemical reaction systems in the silylamine RevILs. Electrochemical properties examined include electrochemical window and conductivity. Both electroorganic and electrodeposition model reactions will be presented.

References

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