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REVIEW

Calorimetric elucidation of ionic interactions in room temperature ionic liquid solutions

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Abstract Knowledge of thermal properties of room temperature ionic liquid (RTIL) solutions is essential in chemical process designing in addition to their application in understanding ionic interactions at molecular level. RTILs are considered to be substitutes for volatile organic compounds. While some experimental thermal data on these systems are available in a random manner, the modeling efforts to correlate enthalpy-concentration profiles of RTIL solutions are very scanty. In this review, an effort has been made to compare and discuss the experimental data of these RTIL solutions available in the literature. The readers are also made aware of the disappointing situation regarding the availability of any type of correlative models for the enthalpy-concentration data of the RTIL systems. An accurate knowledge of activity coefficients at infinite dilutions, Υ_i^{∞} acquired from thermal data will serve as inputs for the newer less polluting process designing and thus open opportunity for a cleaner environment.

Keywords Room temperature ionic liquids · Excess partial molar enthalpy · Calorimeters · Correlative models

Introduction

Considering the environment pollution caused by volatile organic compounds (VOCs) used in organic synthesis and other man-made processes, efforts are underway to replace these VOCs by a suitable solvent medium. This exercise is a part of 12 principles advanced by American Chemical Society (ACS) and US Environment Protection Agency (USEPA). The growing awareness about the need to use environmentally benign solvents has led to the increasing importance of room temperature ionic liquids (RTILs) in carrying out various chemical transformations. RTILs have found their applications in almost all the fields of science including the electrochemical devices (McEven et al. 1999; Egashira et al. 2005; Zheng et al. 2005, Lee et al. 2005), biological processes (Walker and Bruce 2004), lunar observatories (Borra et al. 2007), biodegradation (Ranke et al. 2007), medicinal chemistry as a pharmacophore (Coleman et al. 2012), food processing (Fu and Mazza 2011), waste management (Lapkin et al. 2006), storing solar thermal energy (Banqui et al. 2001), chemical processes (Wasserscheid and Welton 2003), etc. RTILs possess interesting physical and chemical properties, such as negligible vapor pressures, good solvent behavior, wide electrochemical window, and recyclability to name a few among others. RTILs are the organic salts that are liquid near ambient conditions (Earle and Seddon 2000; Wilkes 2002; Wasserscheid and Welton 2003). Ionic liquids are composed of relatively large organic cations and inorganic or organic anions. For example, the common ionic liquid cations are 1-alkyl-3-alkyl imidazolium, 1-alkyl pyridinium, or *N*-alkyl pyrrolidinium. Commonly used anions are hexafluorophosphate ($-PF_6$), tetrafluoroborate ($-BF_4$), bis(trifluoromethylsulfonyl)imide ($-NTf_2$), and various organic ions based on fluorinated amides, nitrides, and methides (see Fig. 1 for an example of structure of RTIL). Strikingly, different RTILs exhibit considerable variation in their stability in the presence of moisture and their solubility in water and other polar, non-polar solvents. Example of such ILs are 1-methyl-3-butylimidazolium tetrafluoroborate [BMIM][BF_4] and 1-methyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide [EMIM][NTf_2].

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