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Effect of the Alkyl Chain Length of the Cation on the Interactions between Water and Ammonium-Based Ionic Liquids: Experimental and COSMO-RS Studies

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Supporting Information

ABSTRACT: To improve the understanding of the molecular interactions of water with tetraalkyl ammonium-based ionic liquids (ILs) such as tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, and tetrabutylammonium hydroxide, thermophysical properties such as density (ρ), speed of sound (u), viscosity (η) and refractive index (n_D) were measured and a computational study using COSMO-RS was performed. The derived properties such as excess volumes (V^E), deviation in isentropic compressibilities ($\Delta\kappa_s$), deviation in viscosities ($\Delta\eta$), and deviation in refractive indices (Δn_D) under the same experimental conditions for these systems were also estimated. The observed V^E and $\Delta\kappa_s$ values are negative over the entire composition of ILs at all investigated temperatures, whereas $\Delta\eta$ and Δn_D values are positive under the same experimental conditions. These results reveal that the ammonium-based ILs significantly affect the intermolecular interactions between the solvent molecules. The computational study allows a qualitative analysis of the results in terms of the ion−dipole interactions, ion-pair formation, and hydrogen bonding between ammonium-based ILs and water.

1. INTRODUCTION

The framework of thermophysical properties of ionic liquids (ILs) and their mixtures with water is quite interesting and important for the chemical industry as well as various scientific fields.[1−4] For the past 15 years, the importance of ILs has been increasing because of their low volatility, nonflammability, high potential for recycling, and solvating properties for diverse substances.[5−8] Meanwhile, ILs became popular as "green solvents" with a wide range of potential applications such as removal of pollutants (H_2S, CO_2, and heavier hydrocarbons) and metal separation.[9−13] To understand the nature of ILs and their applications, knowledge of their thermophysical properties is essentially needed. The thermophysical properties, such as density (ρ), ultrasonic sound velocity (u), viscosity (η), and refractive index (n_D), of ILs and molecular solvent mixtures at various temperatures are of great fundamental and practical importance. Although the applications of ammonium-based ILs are increasing,[14−19] there remains a lack of data on the thermophysical properties of these ammonium-based ILs with water.

Water is one of the most abundant and greenest solvent; it has crucial and significant importance in both chemical and biochemical processes. From the studies reported to date on the interactions between ILs and water it seems that water mainly binds to the anion, but the interaction also depends on the cation.[20−23] The presence of water can dramatically affect the physical properties of ILs, such as their polarity, viscosity, and conductivity, even at low concentrations.[24] As a consequence, absorbed water may alter rates of chemical reactions and efficiencies of various processes in ILs. Even small amounts of water have shown significant effect in membrane applications,[25] cellulose processing,[26] and capturing CO_2.[27] Studies of binary mixtures of water and ILs have been increasing because of their application in absorption cooling,[28−31] distillation,[29,32] and extraction and purification of biomolecules and other value-added compounds.[33−35]

Although some fluorinated ILs are poorly soluble in water, even in these cases the water is highly soluble in the IL. The dissolution of water in the IL induces a major effect on their physicochemical properties.[36,37] The detailed knowledge of the thermophysical properties of ILs with water is essential for clarifying the molecular interactions between water and the ions of ILs. During the past years, a variety of the experimental data of thermophysical properties of imidazolium$^+$,[38−51] pyridinium$^+$,[52−55] pyrrolidinium$^+$,[56−60] phosphonium$^+$,[61,62] and ammonium[34,63−68] based ILs and water have been studied by various researchers. Among them, ammonium-based ILs, a subset of protic ILs, have shown potential as promising solvents in many scientific studies.[69−72]

Although the number of works on water and different ILs is increasing, there is still a lack of data regarding thermophysical properties of ammonium-based ILs with water.[34,63−68] Very recently, Zarrougui et al.[63] examined transport and thermodynamic properties of ethylammonium nitrate [EAN] with water as a function of temperature. Later, thermophysical properties of aqueous solution of ammonium-based ILs such as diethylammonium acetate [DEAA], triethylammonium acetate [TEAA], diethylammonium hydrogen sulfate [DEAS], triethylammonium hydrogen sulfate [TEAS], trimethylammonium

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