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Apparent Molar Volumes and Expansivities of Ionic Liquids Based on *N*-Alkyl-*N*-methylmorpholinium Cations in Acetonitrile

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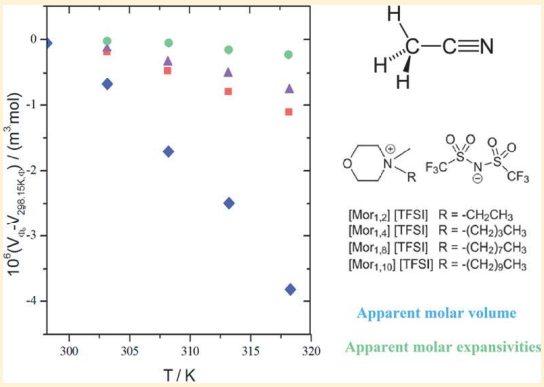
ABSTRACT: Densities of some acetonitrile solutions of ionic liquids based on *N*-alkyl-*N*-methyl-morpholinium cations, *N*-ethyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide, *N*-butyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide, *N*-methyl-*N*-octylmorpholinium bis(trifluoromethanesulfonyl)imide and *N*-decyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide were measured at T = (298.15–318.15) K and at atmospheric pressure. From density data the apparent molar volumes and partial molar volumes of the ILs at infinite dilution as well as the limiting apparent molar expansibilities and the Hepler's constant values have been evaluated. The results have been discussed in terms of the effect that alkyl chain length of the ILs and experimental temperature have on the ionic liquid–acetonitrile interactions occurring in the studied solutions.



1. INTRODUCTION

Over the past years ionic liquids have received much attention as potential green solvents or as materials for a wide range of applications in engineering. The main benefits of ionic liquids are their extremely low vapor pressure, nonflammability, high thermal and electrochemical stabilities, and wide liquid temperature range.[1−3] Nowadays ILs are widely used in organic synthesis, biocatalysis, nanotechnology, electrochemistry, and separation technologies, etc.[4−7]

Because of a growing interest in industrial applications of ionic liquids, various ILs have been subjected to studies of their structure–property relationships. Most of these studies concerned ionic liquids containing alkylimidazolium, alkyl pyrrolidinium, alkylpyridinium, phosphonium, and quaternary ammonium cations.[8−12] Recently, some work has been reported on the synthesis, thermal, electrochemical, and physicochemical characterization of morpholinium cation based ILs.[13−17] These ionic liquids can be conveniently synthesized because of their good product reproducibility, easy purification process, low cost, and short processing time. Morpholinium based ILs have been applied as catalysts, heat stabilizers, antioxidants for lubricating oils and as corrosion inhibitors.[18−20] Moreover, they have been considered as electrolytes for conventional lithium batteries.[21]

Despite its importance for process design, detailed knowledge of the thermodynamic and transport properties of mixtures of ionic liquids with other molecular solvents is limited. Existing studies mainly concern the density, viscosity, and speed of sound of mixtures of water or alcohols and ILs based on alkylimidazolium or alkylpyridinium cations.[22−26] However, in recent times data on the volumetric properties of systems involving ionic liquids with aprotic organic solvent have been published.[27−31] The results of density measurements have been used for the computation of excess molar volumes and interpreted in terms of ion–dipole interactions as well as the structural aspects of the ionic liquid and the investigated organic solvents. Only a few papers are focused on limiting molar quantities which may be determined by studying highly diluted solutions of ionic liquids.[32−35] Hence, in the present work we report the volumetric properties of some ionic liquids based on *N*-alkyl-*N*-methylmorpholinium cations in acetonitrile (AN) solutions. It is worth noting that so far the interactions of morpholinium cation-based ILs with nonpolar and dipolar solutes have been studied by Khara et al.[36,37] using the time-resolved fluorescence anisotropy measurements. Our interest in systems containing acetonitrile is due to the report of Chaban et al.[38] They found that acetonitrile decreases in an unprecedented way the viscosity of ILs and increases their ionic conductivity, which is not without significance for the application of IL/AN binary systems as advanced electrolyte solutions in electrochemistry. In our study, data on the densities of acetonitrile solutions of *N*-ethyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide, *N*-butyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)imide, *N*-methyl-*N*-octylmorpholinium bis(trifluoromethanesulfonyl)imide, and *N*-decyl-*N*-methylmorpholinium bis(trifluoromethanesulfonyl)-imide obtained at T = 298.15, 303.15, 308.15, 313.15, and 318.15 K are reported. From the experimental data, the apparent molar volumes and partial molar volumes of the ILs at infinite dilution as well as the limiting apparent molar expansibilities and the Hepler's constant values have been estimated. The results have been discussed in terms of the

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