Organic electrolyte solutions: Modeling of deviations from ideality within the binding mean spherical approximation

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Organic electrolyte solutions: Modeling of deviations from ideality within the binding mean spherical approximation

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Abstract

Deviations from ideality in organic electrolyte solutions are described within the Binding Mean Spherical Approximation (BiMSA) theory, in which ions are regarded as charged hard spheres and unlike ions may associate to form an ion pair. Association is modeled within the Wertheim theory (as done in SAFT-type models). The model includes a mass action law with a thermodynamic association constant. The literature about the thermodynamic properties of this type of solution is reviewed. Besides, it is attempted to gain some insight into the solvation of ions by computing their Stokes hydrodynamic diameters from conductivity experiments, and by employing an original analysis introduced by Fawcett. The BiMSA model is used to represent the osmotic coefficient of 1-1 electrolytes in pure methanol, ethanol, 2-propanol, acetone and acetonitrile. The optimized cation sizes in the solvents are compared with their hydrodynamic diameters. The regressed association constants are compared with literature values derived from conductivity and vapor pressure experiments.

Keywords: Electrolytes, Organic solutions, Thermodynamics, Binding Mean Spherical Approximation (BiMSA), MSA.

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1. Introduction

Mixed solvent (aqueous-organic) electrolytes have been used for some time now in many industrial processes, for example in order to optimize crystallization [1] and other separation processes in the chemical and pharmaceutical industries, such as water-alcohol distillation [2]. In probably more recent times, solutions of salts in *pure* organic solvents have been used increasingly in industrial processes and devices as, e.g., in the fabrication of lithium-ion batteries involving different types of carbonates as the solvent [3], of wet double-layer capacitors and supercapacitors, and in electrodeposition, electroplating, etc. [4].

Experimental data about deviations from ideality in binary organic electrolyte solutions are by far not as plentiful as in the case of aqueous electrolytes. This is likely partly due to the fact that this type of solution is not found in nature. Moreover careful experiments require the use of absolutely dry salts and solvents, which may not be easy to achieve. Furthermore the solubility of common salts is generally limited in organic solvents. They are not as good solvents as water for salts.

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