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Theory of Electrosorption of Water from Ionic Liquids

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Abstract

We propose and develop a classical density functional theory for the description of a minor amount of water dissolved in ionic liquid in the vicinity of an electrode. In addition to the electrostatic energy and lattice-gas mixing entropy terms, the utilised grand canonical potential contains several phenomenological terms/parameters that describe short-range interactions between ions of ionic liquid, water molecules and the electrode. Some of these have been earlier introduced in the theory of electrical double layer in pure ionic liquids. Based on this, we investigate the role of the remaining 'specific interaction' parameters – those that characterize possible (i) specific interaction of ions and molecules with the electrode, which are responsible for their specific adsorption; and (ii) hydrophilicity/hydrophobicity of ions. As a result we obtain water electrosorption isotherms as a function of the potential drop across the electrical double layer, investigate its asymmetry with respect to the sign of electrode potential, and establish the relationship between the sign of this asymmetry and hydrophobicity/hydrophilicity of cations and anions. We also calculate the effect of water electrosorption on the double layer differential capacitance which brings clear new features

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