



Density of ethanolic alkali halide salt solutions by experiment and molecular simulation



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ABSTRACT

The density of ethanolic electrolyte solutions of all soluble alkali halide salts (LiCl, LiBr, LiI, NaBr, NaI, and KI) is studied at 298.15, 308.15, 318.15, and 328.15 K at concentrations up to 0.05 mol/mol or 90% of the solubility limit both by experiment and molecular simulation. The force fields used for describing the ions are of the Lennard-Jones (LJ) plus point charge type, the ethanol force field is of the LJ plus partial charges type. All force fields were taken from previous work of our group and were adjusted to properties of aqueous solutions in case of the ions [J. Chem. Phys. 136 (2012) 084501, J. Chem. Phys. 140 (2014) 044504] and to pure component properties [Fluid Phase Equilib. 233 (2005) 134] in case of the solvent. The Lorentz–Berthelot combining rule is used to determine the mixed interactions between the ions and ethanol. The present simulations are hence predictions as no parameters are adjusted to properties of ethanolic electrolyte solutions. The predictions of the reduced density are found to be in good agreement with the experimental data. Furthermore, the radial distribution function of the ethanol sites around the ions, the solvation number and the residence time of ethanol molecules in the first solvation shell, the self-diffusion coefficient of the ions, and the electric conductivity are systematically studied by molecular simulation and compared to experimental data where available.

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1. Introduction

In the last decades, organic electrolyte solutions have become increasingly important in many industrial applications, especially in the field of electrochemistry [1,2]. They are used for example in the production and development of high-energy batteries [1], wet electrolytic capacitors [1], and photo-electrochemical cells [1] such as dye-sensitized solar cells with ethanol-based electrolytes [3]. The investigation of the thermodynamic properties of organic electrolyte solutions is therefore of particular interest [4].

We recently published a comprehensive molecular simulation study of thermodynamic properties of methanolic alkali halide salt solutions [5] with classical force fields, which were taken from previous work of our group. The ion force fields had been adjusted to properties of aqueous alkali halide salt solutions [6,7] and the solvent methanol to pure component properties [8]. No parameters were adjusted to properties of methanolic electrolyte solutions. The predictions of the reduced density, i.e. the density of the electrolyte solution divided by the density of the pure solvent at the same pressure and temperature, were found to be in very good agreement with experimental data over a wide temperature and concentration

range [5]. The same holds for other studied properties which include the first maximum in the radial distribution function (RDF) of the hydroxyl and the methyl group of the methanol molecule around the ions, the solvation number, the self-diffusion coefficient of ions in the solution, and the electric conductivity. Such a good agreement could not be expected a priori. To see whether the encouraging findings for the methanolic electrolyte solutions were just a lucky coincidence or whether our approach is capable of predicting thermodynamic properties of organic electrolyte solutions more generally, the present study extends the previous work to ethanolic alkali halide salt solutions. The methodology is largely unchanged and therefore only briefly described here.

The main focus was again on the reduced density of the electrolyte solutions. As there is a lack of experimental density data in the literature, the density of ethanolic electrolyte solutions of all soluble alkali halide salts (LiCl, LiBr, LiI, NaBr, NaI and KI) was studied systematically not only by molecular simulation but also by experiments at temperatures between 298.15 and 328.15 K and salt concentrations up to 0.05 mol/mol or 90% of the solubility limit. At 298.15 K, there are literature data in that concentration range for LiCl [9–13], NaBr [10,13], NaI [10,11,13–17], and KI [10], but not for LiBr [11,13] and LiI [11,13] salt solutions. At the other investigated temperatures, namely 308.15, 318.15 and 328.15 K, experimental

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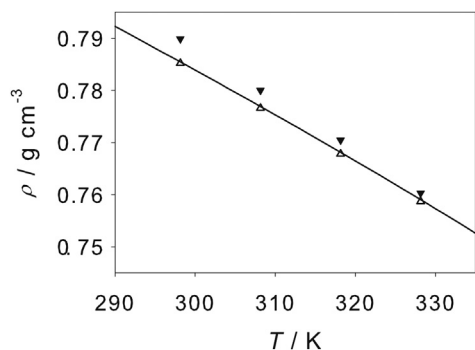


Fig. 1. Density of pure liquid ethanol as a function of temperature at 1 bar. Simulation results from the present work (\blacktriangledown) are compared to present experimental data (\triangle). The line indicates a correlation of experimental data from the literature [31].

density data of ethanolic alkali halide salt solutions were up to now entirely missing in the literature. The molecular simulations were carried out for the same temperature and composition as studied in the experiments of the present work.

In the literature, there are only a few simulation studies on the thermodynamic properties of ethanolic alkali halide salt solutions [13,18–20]. Held et al. [13] modeled the liquid densities, the osmotic coefficient, and the mean ionic activity coefficients of ethanolic electrolyte solutions with the ePC-SAFT equation of state and validated the results against own measurements. Zeng and co-workers [19,20] investigated the structure of the solvent around Li^+ and Na^+ and dynamic properties like auto-correlation functions of these ions in ethanolic solutions by Car–Parrinello molecular dynamics simulations. Yan et al. [18] used molecular simulations with classical force fields to study osmotic effects in ethanolic NaBr salt solutions with a membrane simulation method [18]. The force field for ethanol was taken from Jorgensen [21], that for the ions (Na^+ and Br^-) from Jorgensen et al. [22]. A geometric mixing rule was used, and no interaction parameters were adjusted [18]. To the best of our knowledge, no other reports on molecular simulation with classical force fields of thermodynamic properties of ethanolic alkali halide salt solutions are available in the literature.

Several ethanol force fields are available in the literature [21,23–26]. From these, we have chosen one developed previously in our group by Schnabel et al. [26] which is known to give good results both for thermodynamic properties of pure ethanol and ethanol-containing non-ionic mixtures [26–30]. The parameters of the ethanol model were adjusted to the vapor–liquid equilibrium of pure ethanol [26], namely the saturated liquid density and the vapor pressure. The temperature dependence of the density of pure liquid ethanol at 1 bar is shown in Fig. 1. The density of pure ethanol is slightly overestimated by the model over the entire investigated temperature range. The highest deviation from experimental data of about 0.6% is found at 298.15 K. With increasing temperature, the deviations decrease.

The force fields used for the ions [6,7] were taken from previous work of our group. Their parameters were adjusted with SPC/E water [32] to properties of aqueous electrolyte solutions, namely the reduced density, the self-diffusion coefficient of the ions in the solution, and the first maximum in the RDF of water around the ions at 293.15 and 298.15 K, respectively, and 1 bar [6,7]. They describe many thermodynamic properties of aqueous alkali halide salt solutions well, also outside the range they were adjusted to [6,7,33]. As in our study on methanolic electrolyte solutions [33], Lorentz–Berthelot combining rules are used here to determine the mixed interactions between ions and solvent molecules, and no parameters were adjusted to the properties of ethanolic alkali halide salt solutions so that all simulation results presented here are predictions.

A focus of the present study was to evaluate predictions for the reduced density of the solution which is defined as

$$\tilde{\rho} = \frac{\rho}{\rho_{\text{EtOH}}}, \quad (1)$$

where ρ_{EtOH} is the density of pure ethanol at the same temperature and pressure as the density of the solution ρ . It is used as reference property to minimize the influence of the error in the ethanol model on the simulation results, cf. Fig. 1. For the calculation of the reduced density, the density of pure ethanol has to be known. In the case of experimental data, it is taken from the present measurements of pure ethanol, in the case of simulation results, it is determined in present pure ethanol simulations.

Besides the reduced density, also structural, dynamic, and transport properties of ethanolic alkali halide salt solutions were systematically studied in the present work by molecular simulation at 298.15 K and compared to experimental literature data where available.

Throughout this study all properties were investigated at 1 bar and the composition is given in terms of the ion mole fraction x_i , which is defined as

$$x_i = \frac{n_i}{2 \cdot n_i + n_{\text{EtOH}}}, \quad (2)$$

where n_i is the mole number of each ion type and n_{EtOH} the mole number of ethanol molecules in the electrolyte solution. For the 1:1 salts studied here, the ion mole fraction of the anions and the cations is x_i each. Some other studies quantify the salinity in terms of the overall salt mole fraction, regarding the salt as a single component. The ion mole fraction x_i is related to the overall salt mole fraction

$$x_S = \frac{n_S}{n_S + n_W} \quad (3)$$

by

$$x_S = \frac{x_i}{1 - x_i}, \quad (4)$$

as the mole number of salt in the solution is $n_S = n_i$ here.

In Section 2 of the present paper, the experiments are described. The employed force fields and the simulation methods are introduced in Section 3. In Section 4, the experimental data and the simulation results are presented and discussed. Section 5 summarizes the main statement from the present work.

2. Experiments

For the preparation of the ethanolic alkali halide salt solutions pure ethanol ($\geq 99.9\%$, ROTISOLV Roth) was used. The purity and the supplier of the alkali halide salts are shown in Table 1. The treatment of the salts, the preparation of the samples of electrolyte solutions and the density measurements are identical to the procedures described in detail in recent work [5]. The uncertainty of

Table 1
Purity and supplier of the alkali halide salts.

Salt	Purity	Supplier
LiCl	$\geq 99\%$	Merck
LiBr	$\geq 99.999\%$	Roth
LiI	$\geq 99\%$	AlfaAesar
NaBr	$\geq 99\%$	Merck
NaI	$\geq 99.5\%$	Roth
KI	$\geq 99\%$	Fluka

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