Partial Molar Volume of NaCl and CsCl in Mixtures of Water and Methanol by Experiment and Molecular Simulation

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Abstract

Densities of solutions of NaCl and CsCl in mixtures of water and methanol are determined by experiment and molecular dynamics simulation. Both experiments and simulations cover the concentration range up to the solubility limit of the salt in the temperature range $288.15 \leq T$ / K ≤ 318.15 at ambient pressure. Non-polarizable molecular models from the literature are used for the ions and solvents. The partial molar volume of the salts at infinite dilution in the mixed solvent is determined from an empirical correlation of the data. The mixed solvent effects on the density and the partial molar volumes of the salts are well predicted by the molecular models.

Keywords: density measurement, molecular simulation, mixed solvent,

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electrolyte solution

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1. Introduction

A sound knowledge of thermophysical properties of electrolyte solutions is important for the understanding of natural processes and the design of a wide variety of industrial processes. Aqueous electrolyte solutions have been studied extensively, and more recently, also non-aqueous electrolyte solutions have drawn significant attention, because of their importance e.g. in energy storage. However, solutions of salts in mixed solvents have been studied only rarely up to now. In the present work, we therefore investigate the density and related volumetric properties in mixed solvent electrolyte solutions, where the electrolytes are either NaCl or CsCl and the solvent is a mixture of water and methanol.

Several experimental studies on densities of solutions of alkali halide salts in mixtures of water and methanol have been reported in the literature. Takenaka et al. [1–3] report densities of such solutions for seven of the 17 alkali halide salts that are soluble both in water and in methanol, namely LiCl, NaCl, KCl, NaBr, KBr, NaI, and KI. For solutions of NaCl, there are three additional investigations [4–6], and Ivanov and Abrosimov [7] study solutions of KBr. Furthermore, there is a detailed investigation by Raatschen [8] on solutions of LiBr in mixtures of water and methanol. Werblan [5] reports data on the cesium halides, however, inspection of these data shows considerable scatter, cf. Section 4.3.

Interestingly, densities of solutions of electrolytes in mixtures of water and methanol have hardly been studied with thermodynamic models. There are several modeling studies dealing with phase equilibria in such systems [9–19], however, most of the these works employ models for the excess Gibbs energy, so that solution densities cannot be obtained. Equations of state (EOS), which enable density calculations, have only very recently been extended towards the modeling of mixed solvent electrolyte solutions. This is e.g. the case for the ePC-SAFT EOS [17], the SAFT-VRE EOS [18] and the electrolyte CPA EOS [19]. Molecular simulations are particularly attractive for modeling mixed solvent electrolyte solutions due to the low number of adjustable parameters and a strong physical background. However, we are aware only of the work of Strauch and Cummings [12], who investigate the vapor-liquid equilibrium of solutions of NaCl in mixtures of water and methanol and also report the densities of the coexisting phases.

In contrast, solutions of a salt - in most cases NaCl - in pure water have been studied extensively with molecular simulations in the recent literature. In these studies, mainly the differences between polarizable and non-polarizable models were investigated. Models including polarizability, such as the alkali halide models developed around the polarizable water models SWM4-DP [20] and BK3 [21], were found to perform better than non-polarizable ones in some aspects, e.g. concerning the description of activity coefficients [22, 23]. Interestingly, this does not necessarily result in an improved prediction of the salt solubility [23]. When considering other properties such as the density, simple non-polarizable models are found to be of almost the same quality as the polarizable ones [23]. Furthermore, non-polarizable models can in principle describe a variety of properties of electrolyte solutions fairly well. However, the systematic assessment of Orozco et al. [24] shows that none of the existing model parameterizations is able to quantitatively describe several properties at once. This suggests that better model parameterizations can be found [25]. For a more detailed discussion of the recent advances in the field, see the comprehensive review by Nezbeda et al. [26].

In the present work, we first report new experimental density data for the systems water-methanol-NaCl and water-methanol-CsCl. Our experiments cover the entire concentration range up to the solubility limit of the salt, and we report data for the temperatures 288.15, 293.15, 298.15, 308.15, and

318.15 K. Second, we address the question whether simple non-polarizable molecular models based on Lennard-Jones (LJ) sites and partial charges can predict volumetric properties of the studied electrolyte solutions. In our discussion, the partial molar volume of the salt at infinite dilution is of particular interest, because it is a very sensitive property and provides a descriptive view of the salt-solvent interactions.

Throughout this work, the composition of a ternary solution of a salt CA, which completely dissociates into the ions C^+ and A^-, in a mixture of water and methanol is described by the methanol mole fraction of the salt-free solvent mixture χ_{MeOH}

$$\chi_{\mathrm{MeOH}} = n_{\mathrm{MeOH}}/(n_{\mathrm{MeOH}} + n_{\mathrm{W}}) \tag{1}$$

and the true mole fraction of the cation x_{C^+}

$$x_{\mathrm{C}^+} = n_{\mathrm{C}^+}/(n_{\mathrm{C}^+} + n_{\mathrm{A}^-} + n_{\mathrm{MeOH}} + n_{\mathrm{W}}), \tag{2}$$

where n_i are the mole numbers.

2. Experiments

Ultradry methanol ($\leq$ 50 ppm water) with a purity of $\geq$ 99.9 % was purchased from Roth. Deionized water was produced by an Elix Essential 5^{UV} of Merck Millipore and degassed by boiling before use. NaCl was purchased from Merck with a purity of $\geq$ 99.5 % and CsCl was purchased from Roth with a purity of $\geq$ 99.999 %. The salts were dried in a vacuum oven at 353 K for 24 h.

The electrolyte solutions were prepared gravimetrically (AE240, Mettler-Toledo) in a glovebox (GS Glovebox Technik). In case of mixed solvents, about 200 ml of a stock solution of water + methanol of the desired composition χ_{MeOH} was prepared first. All reported experimental data for one salt at one salt-free solvent composition χ_{MeOH} were obtained using one single stock solution. The solvent (pure or mixed) was then added to a known amount of salt to yield samples of about 20 ml. Uncertainties in the composition variables χ_{MeOH} and x_{C^+} were estimated from error propagation of the uncertainty of the balance. Thereby, the uncertainty of the salt-free solvent composition χ_{MeOH} is found to be better than ± 0.00002 mol mol^{-1}. The uncertainty of the mole fraction of the cation x_{C^+} is found to be better than ± 0.0002 mol mol^{-1} in most cases, except for the highly concentrated CsCl solutions, for which it is up to ±0.0009 mol mol^{-1}.

As a guide to the accessible concentration range in case of solutions of NaCl, the solubility data of Pinho and Macedo [14] were used. They proved to be reliable during the present experiments. In case of CsCl, the solubility is only known for the pure solvents water [27] and methanol [28], but not for mixed solvents. As an estimate, we assumed the same qualitative dependence of the solubility on the composition of the solvent mixture as for NaCl.

The densities of the samples were measured with a vibrating tube densimeter (DMA 4500 M, Anton Paar), which was calibrated with air and deionized water. Based on the repetition of several experiments and the resolution provided by the densimeter, the uncertainty of the reported densities is estimated to be better than ±0.0001 g cm^{-3}. The temperature was measured with the densimeter's built-in thermometer, for which the supplier claims an uncertainty of ±0.1 K.

To obtain the partial molar volume of the salt at infinite dilution v_{salt}^{∞} in the solvent from the measured densities, a simple empirical correlation is developed in the present work, cf. Sections 4.1 and 4.2. The uncertainty in the numbers for v_{salt}^{∞} obtained from that correlation was estimated by randomly disturbing the measured densities with their uncertainty and using these values for the fits. Thereby, the uncertainty in v_{salt}^{∞} is estimated to be better than ±0.5 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$ and thus of similar magnitude as the uncertainties reported by Takenaka et al. [1].

3. Molecular Simulation

In the present work, rigid, non-polarizable molecular models for the solvents and ions are employed. The water model SPC/E is taken from the literature [29], the ion models and the methanol model are taken from previous work of our group. For methanol, we employ the molecular model of Schnabel et al. [30], which was optimized with respect to the vapor-liquid equilibrium of pure methanol. For the ions, molecular models of the Lennard-Jones (LJ) + point charge type from the ion model set of Reiser et al. [31] are used. The models of that set were trained together with the SPC/E water model mainly using density data of dilute aqueous solutions of all alkali halide salts [32]. Thus, the models used here for NaCl and CsCl were not optimized for describing the individual salts, but taken from an ion model set which includes all alkali and halide ions. Therefore, the Cl^- model is the same for both salts studied here.

Molecular dynamics (MD) simulations of methanol-water mixtures, employing the Schnabel et al. [30] model for methanol and several popular water models (including SPC/E) were previously conducted by Guevara-Carrión et al. [33, 34] and Pařez et al. [35], but with a focus on transport properties. In another previous study [36], the predictions obtained from combining the ion models of the set of Reiser et al. [31] with the methanol model of Schnabel et al. [30] using the Lorentz-Berthelot combining rules were already studied. Good agreement with experimental data for solutions of all alkali halide salts in methanol was found even though the ion models had only been trained with data on aqueous solutions. Altogether, these results from previous studies suggest that the employed models are suited as a starting point for modeling ternary solutions.

All models employ LJ sites and point or partial charges, so that the potential writes [37]

$$
\begin{aligned}
U &= U_{\mathrm{LJ}} + U_{\mathrm{C}} \\
&= \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \left\{ \sum_{a=1}^{n_i^{\mathrm{LJ}}} \sum_{b=1}^{n_j^{\mathrm{LJ}}} 4\epsilon_{ijab} \left[\left(\frac{\sigma_{ijab}}{r_{ijab}} \right)^{12} - \left(\frac{\sigma_{ijab}}{r_{ijab}} \right)^{6} \right] \right. \\
&\quad \left. + \sum_{c=1}^{n_i^e} \sum_{d=1}^{n_j^e} \frac{1}{4\pi\varepsilon_0} \frac{q_{ic} q_{jd}}{r_{ijcd}} \right\}, \qquad (3)
\end{aligned}
$$

where the indices a, b, c, and d refer to model interaction sites and i and j refer to molecules (including ions), ε_0 is the vacuum permittivity, ϵ_{ijab} and σ_{ijab} are the Lennard-Jones energy and size parameters, r_{ijab} and r_{ijcd} are site-site distances, and q_{ic} and q_{jd} are the magnitudes of the point charges. The interaction between unlike LJ sites is described by the modified Lorentz-Berthelot combining rules [38, 39]

$$\sigma_{ijab} = \eta_{ij} \, \frac{\sigma_{iiaa} + \sigma_{jjbb}}{2}, \tag{4}$$

$$\epsilon_{ijab} = \sqrt{\epsilon_{iiaa}\epsilon_{jjbb}}. \tag{5}$$

A binary interaction parameter η_{ij} different from 1 is only employed in the unlike interaction water-methanol and adjusted to experimental data of the molar excess volume at 298.15 K, cf. Section 4.1. This correction is introduced into the Lorentz rule here as the unlike size parameter obviously shows a much larger influence on densities than the unlike energy parameter, which is in line with a general theoretical analysis by Fischer et al. [40]. The adjustment was carried out to ensure a good description of the volumetric properties of the salt-free solvent mixture. It has only a minor impact on the results obtained for the properties of the electrolytes in the mixed solvent on which we focus here.

Densities were obtained by standard MD simulations in the NpT ensemble for the temperatures 288.15, 298.15 and 318.15 K. Simulation details are given in Appendix A. For each studied salt-free solvent composition, the simulations were carried up to the experimental solubility limit of the salt. To obtain the partial molar volume of the salt at infinite dilution in the solvent from the densities obtained in these simulations, the same correlation as for the measured densities was employed, cf. Sections 4.1 and 4.2.

4. Results and Discussion

The solution densities obtained from the experiments and the molecular simulations are reported in Tables 1 - 4. The densities of the studied salt-free solvents are reported together with the data for NaCl. To improve the readability of the plots, in most figures we only display the experimental results for 288.15, 298.15 and 318.15 K, and omit those for 293.15 and 308.15 K.

Table 1: Experimental data for the density of solutions of NaCl in mixtures of water and methanol at 1 bar. The uncertainties are: $u(\chi_{\mathrm{MeOH}}) = \pm 0.00002$ mol mol^{-1}, $u(\rho) = \pm 0.0001$ g cm^{-3}, $u(T) = \pm 0.1$ K. For $x_{\mathrm{Na^+}}$, the uncertainty of the last digit is given in parentheses, or omitted where it is below ± 0.0001 mol mol^{-1}.

		ρ / g cm^{-3}				
χ_{MeOH} / mol mol^{-1}	$x_{\mathrm{Na^+}}$ / mol mol^{-1}	T / K				
		288.15	293.15	298.15	308.15	318.15
0	0	0.9991	0.9982	0.9970	0.9940	0.9902
	0.0099(1)	1.0222	1.0210	1.0196	1.0162	1.0121
	0.0196(2)	1.0447	1.0432	1.0416	1.0378	1.0335
	0.0291(2)	1.0658	1.0641	1.0623	1.0582	1.0536
	0.0385(3)	1.0867	1.0848	1.0828	1.0785	1.0737
	0.0476(3)	1.1074	1.1054	1.1033	1.0987	1.0938
	0.0566(4)	1.1272	1.1250	1.1227	1.1180	1.1129
	0.0654(4)	1.1471	1.1448	1.1424	1.1374	1.1322
0.25	0	0.9421	0.9393	0.9364	0.9301	0.9234
	0.0040	0.9503	0.9475	0.9445	0.9382	0.9315
	0.0098(1)	0.9603	0.9574	0.9544	0.9480	0.9413
	0.0229(2)	0.9845	0.9815	0.9784	0.9719	0.9651
	0.0336(2)	1.0043	1.0012	0.998	0.9914	0.9845
0.5	0	0.8892	0.8854	0.8815	0.8736	0.8653
	0.0020	0.8921	0.8883	0.8844	0.8765	0.8682
	0.0049	0.8968	0.8930	0.8891	0.8811	0.8729
	0.0079(1)	0.9014	0.8975	0.8937	0.8857	0.8775
	0.0117(1)	0.9074	0.9036	0.8997	0.8917	0.8835
	0.0146(1)	0.9125	0.9087	0.9048	0.8968	0.8886
	0.0192(1)	0.9189	0.9150	0.9111	0.9031	0.8949

Table 1 continued.

		ρ / g cm^{-3}				
χ_{MeOH} / mol mol^{-1}	$x_{\mathrm{Na^+}}$ / mol mol^{-1}	T / K 288.15	293.15	298.15	308.15	318.15
0.75	0	0.8398	0.8355	0.8312	0.8224	0.8134
	0.0013	0.8418	0.8375	0.8332	0.8245	0.8155
	0.0027	0.8437	0.8395	0.8352	0.8264	0.8175
	0.0053	0.8471	0.8428	0.8385	0.8298	0.8209
	0.0079	0.8509	0.8467	0.8424	0.8337	0.8248
	0.0104(1)	0.8558	0.8516	0.8473	0.8387	0.8298
	0.0130(1)	0.8584	0.8541	0.8498	0.8412	0.8323
1	0	0.7959	0.7913	0.7866	0.7771	0.7675
	0.0010	0.7974	0.7927	0.7880	0.7786	0.7690
	0.0020	0.7989	0.7943	0.7896	0.7802	0.7707
	0.0030	0.8001	0.7955	0.7908	0.7814	0.7719
	0.0040	0.8014	0.7968	0.7921	0.7827	0.7733
	0.0050	0.8029	0.7983	0.7937	0.7843	0.7748
	0.0060	0.8041	0.7995	0.7949	0.7855	0.7761
	0.0070	0.8057	0.8011	0.7964	0.7871	0.7777

Table 2: Experimental data for the density of solutions of CsCl in mixtures of water and methanol at 1 bar. The uncertainties are: $u(\chi_{\mathrm{MeOH}}) = \pm 0.00002$ mol mol^{-1}, $u(\rho) = \pm 0.0001$ g cm^{-3}, $u(T) = \pm 0.1$ K. For x_{Cs^+}, the uncertainty of the last digit is given in parentheses, or omitted where it is below ± 0.0001 mol mol^{-1}.

		ρ / g cm^{-3}				
χ_{MeOH} / mol mol^{-1}	x_{Cs^+} / mol mol^{-1}	T / K				
		288.15	293.15	298.15	308.15	318.15
0	0.0099(1)	1.0697	1.0684	1.0670	1.0635	1.0592
	0.0196(2)	1.1373	1.1358	1.1341	1.1301	1.1255
	0.0292(2)	1.2033	1.2016	1.1996	1.1952	1.1902
	0.0385(3)	1.2662	1.2642	1.2620	1.2573	1.252
	0.0536(7)	1.3670	1.3646	1.3621	1.3567	1.3509
	0.0690(9)	1.4669	1.4641	1.4613	1.4553	1.4486
0.25	0.0192(3)	1.0661	1.0650	1.0623	1.0564	1.0501
	0.0370(5)	1.1664	1.1635	1.1604	1.1540	1.1471
	0.0536(7)	1.2534	1.2501	1.2466	1.2395	1.2311
0.5	0.0074	0.9248	0.9208	0.9169	0.9088	0.9004
	0.0146(1)	0.9597	0.9557	0.9517	0.9435	0.9350
	0.0215(1)	0.9916	0.9876	0.9835	0.9751	0.9665
	0.0283(2)	1.0241	1.0200	1.0158	1.0073	0.9986
	0.0349(2)	1.0564	1.0522	1.0480	1.0394	1.0305
0.75	0.0025	0.8511	0.8468	0.8424	0.8336	0.8246
	0.0050	0.8611	0.8568	0.8524	0.8436	0.8346
	0.0074	0.8712	0.8669	0.8625	0.8536	0.8445
	0.0098(1)	0.8808	0.8764	0.8720	0.8631	0.8540
	0.0122(1)	0.8901	0.8857	0.8813	0.8723	0.8632
1	0.0012	0.8008	0.7961	0.7913	0.7818	0.7723
	0.0025	0.8055	0.8008	0.7960	0.7865	0.7769
	0.0037	0.8099	0.8052	0.8005	0.7910	0.7814
	0.0049	0.8145	0.8098	0.8051	0.7955	0.7859

Table 3: Molecular simulation data for the density of solutions of NaCl in mixtures of water and methanol at 1 bar. For the density, the uncertainty of the last digit is given in parentheses.

		ρ / g cm^{-3}		
χ_{MeOH} / mol mol^{-1}	$x_{\mathrm{Na^+}}$ / mol mol^{-1}	T / K 288.15	 298.15	 318.15
0	0	1.0042(2)	0.9996(2)	0.9879(2)
	0.02	1.0407(2)	1.0357(2)	1.0232(2)
	0.04	1.0762(2)	1.0708(2)	1.0577(2)
	0.06	1.1107(2)	1.1045(2)	1.0907(2)
0.25	0	0.9493(2)	0.9407(2)	0.9237(2)
	0.01	0.9646(2)	0.9559(2)	0.9385(2)
	0.02	0.9789(2)	0.9710(2)	0.9531(2)
	0.03	0.9945(2)	0.9867(2)	0.9679(2)
0.5	0	0.8931(2)	0.8838(2)	0.8644(2)
	0.005	0.8995(2)	0.8904(2)	0.8710(2)
	0.01	0.9061(2)	0.8966(2)	0.8778(2)
	0.015	0.9127(2)	0.9036(2)	0.8838(2)
0.75	0	0.8427(2)	0.8337(2)	0.8141(2)
	0.004	0.8484(2)	0.8391(2)	0.8196(2)
	0.008	0.8533(2)	0.8436(2)	0.8246(2)
	0.12	0.8584(2)	0.8489(2)	0.8299(2)
1	0	0.7974(2)	0.7880(1)	0.7687(1)
	0.002	0.8002(2)	0.7910(2)	0.7717(1)
	0.004	0.8029(1)	0.7938(1)	0.7743(1)
	0.006	0.8056(2)	0.7963(2)	0.7770(1)

Table 4: Molecular simulation data for the density of solutions of CsCl in mixtures of water and methanol at 1 bar. For the density, the uncertainty of the last digit is given in parentheses.

		ρ / g cm^{-3}		
χ_{MeOH} / mol mol^{-1}	x_{Cs^+} / mol mol^{-1}	T / K		
		288.15	298.15	318.15
0	0.02	1.1262(2)	1.1212(2)	1.1086(2)
	0.04	1.2437(2)	1.2379(2)	1.2245(2)
	0.06	1.3549(2)	1.3487(2)	1.3353(2)
0.25	0.02	1.0493(2)	1.0404(2)	1.0226(2)
	0.04	1.1470(2)	1.1378(3)	1.1194(2)
	0.06	1.2420(2)	1.2331(3)	1.2143(2)
0.5	0.01	0.9358(2)	0.9256(2)	0.9061(2)
	0.02	0.9772(2)	0.9678(2)	0.9479(2)
	0.03	1.0182(3)	1.0100(2)	0.9900(2)
0.75	0.004	0.8576(2)	0.8486(2)	0.8287(2)
	0.008	0.8720(2)	0.8627(2)	0.8432(2)
	0.012	0.8869(2)	0.8775(2)	0.8578(2)
1	0.002	0.8041(2)	0.7943(1)	0.7751(1)
	0.004	0.8105(1)	0.8012(1)	0.7818(1)
	0.006	0.8175(1)	0.8079(1)	0.7886(1)

4.1. Salt-free Solvent Mixture

Studying a ternary electrolyte solution first requires an adequate description of the salt-free solvent mixture. The volumetric behavior of the salt-free solvent mixture water-methanol is discussed here based on the molar excess volume v^{E}

$$v^{\mathrm{E}}(T, \chi_{\mathrm{MeOH}}) = v(T, \chi_{\mathrm{MeOH}}) - \chi_{\mathrm{MeOH}} v_{\mathrm{MeOH}}^{\mathrm{pure}}(T) - (1 - \chi_{\mathrm{MeOH}}) v_{\mathrm{W}}^{\mathrm{pure}}(T), \quad (6)$$

where v is the molar volume of the mixture, v_i^{pure} are the pure component molar volumes, and the methanol mole fraction is χ_{MeOH} in our notation. Results for the molar excess volume of the mixture water + methanol at 298.15 K are shown in Fig. 1.

The experimental results from the present work are compared to a correlation of experimental data of Coquelet et al. [41]. Excellent agreement is observed. The deviations are below about ± 0.01 cm^3 mol^{-1}. Furthermore, molecular simulation results from the present work are shown. They were obtained using $\eta_{\mathrm{W-MeOH}} = 0.993$. That parameter was fit to reproduce the minimum of v^{E}, which is found for equimolar composition both experimentally and

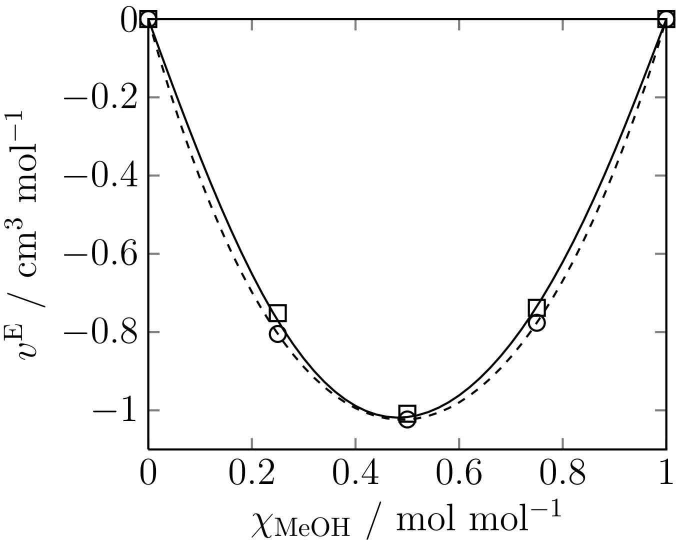

Figure 1: Molar excess volume of mixtures of water and methanol at 298.15 K. (□) experimental data, this work, (○) molecular simulation data, this work, (−) correlation of experimental data by Coquelet et al. [41], (−−) correlation of the present molecular simulation data.

in the simulations. The deviation of $\eta_{\mathrm{W-MeOH}}$ from 1 is only small. Using $\eta_{\mathrm{W-MeOH}} = 1$, the minimum of v^{E} is about 15% above the experimental result. Using the adjusted value of $\eta_{\mathrm{W-MeOH}}$, the dependence of v^{E} on χ_{MeOH} is predicted well by the simulation.

The density of the salt-free solvent mixture is the basis for the correlation used here for describing the density of the ternary electrolyte solutions. As Coquelet et al. [41], we employ a Redlich-Kister type correlation, which in our notation writes as

$$v^{\mathrm{E}}(T, \chi_{\mathrm{MeOH}}) = (1 - \chi_{\mathrm{MeOH}})\chi_{\mathrm{MeOH}} \sum_k A_k(T)(1 - 2\chi_{\mathrm{MeOH}})^k, \;\; k = 0, 1, \dots \,, \tag{7}$$

where the A_k are fit parameters. We also use Eq. (7) here for correlating the molecular simulation data. The Redlich-Kister coefficients A_k for describing the molar excess volume of mixtures of water and methanol for all temperatures studied here are presented in Appendix B, cf. Table B.1. Two parameter sets are reported. The first one describes the experimental data. It is adopted from Coquelet et al. [41], but also describes the present experimental results within their uncertainty. The second one is obtained from a fit to the present simulation data for the system water + methanol. The densities of pure water and pure methanol, which are needed in addition to the Redlich-Kister fit to calculate the density of the mixture, are taken from Tables 1 and 3.

4.2. Electrolyte Solutions

Fig. 2 shows the measured and simulated densities of solutions of NaCl and of CsCl in mixtures of water and methanol at 298.15 K.

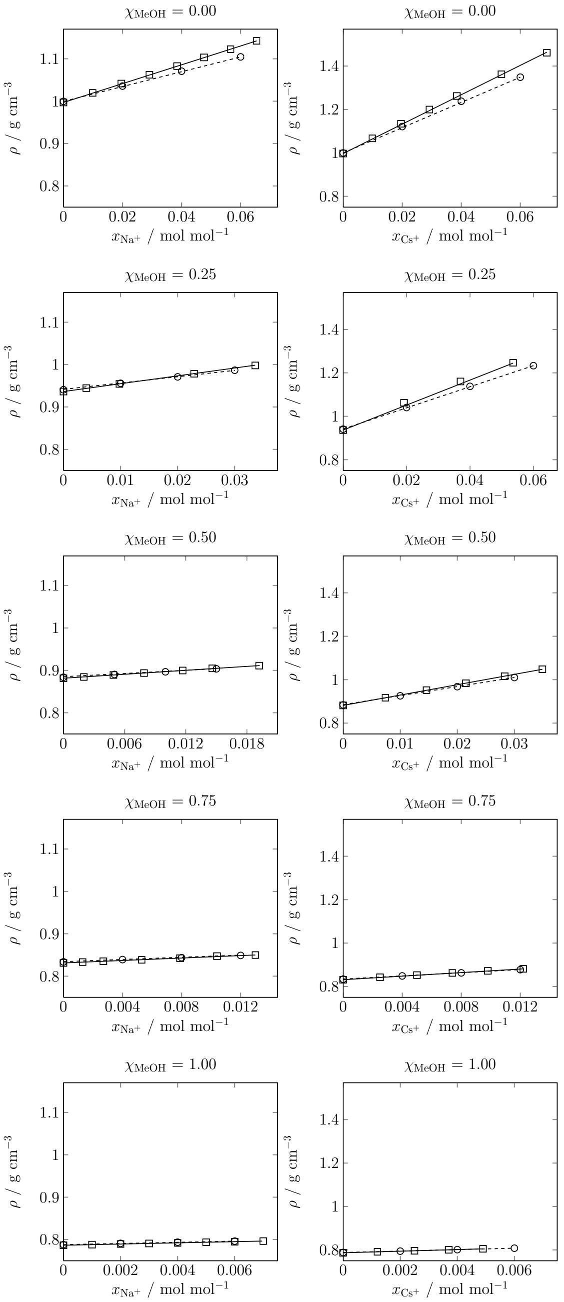

Figure 2: Densities of solutions of NaCl (left column) and CsCl (right column) in mixtures of water and methanol over the cation mole fraction at 298.15 K. Results from the present work: (□) experiment, (○) molecular simulation, (−) correlation of experimental data, (−−) correlation of molecular simulation data.

For both salts in pure water ($\chi_{\mathrm{MeOH}} = 0$), the increase in the density upon addition of the salt is slightly underpredicted by the models. The salt models used here are not individual models but taken from an ion model set for all alkali halides, so that compromises regarding the performance for some salts had to be made [32]. However, the higher the methanol content in the mixture, the better the agreement between experiment and simulation. This is a remarkable finding since in the development of the ion models, only data on aqueous solutions were used. The influence of adding methanol is predicted surprisingly well by the models.

In previous work of our group [36, 42], it was found that both for aqueous and methanolic solutions of alkali halide salts, the density of the solution is an almost perfectly linear function of the ion mole fraction. That finding was based on results for $x_{\mathrm{C}^+} \leq 0.05$ mol mol^{-1}. The present results, both from experiment and from molecular simulation, show that the linearity holds also up to the solubility limit for the studied salts. Additionally, the linear relation is also found to hold for mixed solvents. Thus, for the ternary electrolyte solutions, we employ the correlation

$$\rho(T, \chi_{\mathrm{MeOH}}, x_{\mathrm{C}^+}) = \rho_{solv}(T, \chi_{\mathrm{MeOH}}) + b_{salt}(T, \chi_{\mathrm{MeOH}})\ x_{\mathrm{C}^+} \tag{8}$$

$$\text{with} \qquad b_{salt} = \left(\frac{\partial \rho}{\partial x_{\mathrm{C}^+}}\right)_{T, \chi_{\mathrm{MeOH}}}, \tag{9}$$

where ρ_{solv} is the density of the salt-free solvent mixture, which is obtained as described in the previous section. The slope of the density b_{salt} was fit to the data for each individual solvent composition.

In Fig. 3, the slope of the density b_{salt} determined from experimental and molecular simulation data is shown for 288.15, 298.15 and 318.15 K.

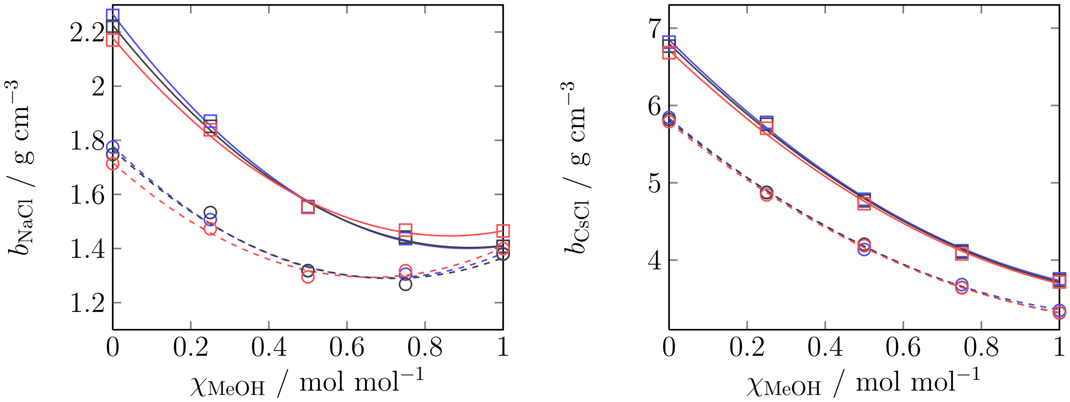

Figure 3: Slope of the density b_{salt}, cf. Eq. (9), of NaCl solutions (left) and CsCl solutions (right) over the composition of the salt-free solvent mixture water + methanol. Colors indicate the isotherms 288.15 K (blue), 298.15 K (gray) and 318.15 K (red). As the temperature influence is small, the results overlap. Results from the present work: (□) experiment, (○) molecular simulation, (—) correlation of experimental data, (– –) correlation of molecular simulation data.

The experimental data of the NaCl solutions reveal a surprising behavior: For aqueous solutions, the slope of the density decreases with increasing temperature. This trend is reversed for methanolic solutions. Furthermore, at approximately equimolar composition of the salt-free solvent mixture, the slope of the density is independent of the temperature. This behavior is also predicted by the molecular simulations. The experimental results show that b_{NaCl} does not decline linearly with increasing χ_{MeOH}. The trend is predicted well by the molecular simulations. In the simulations, a shallow minimum is found for all temperatures, which is present in the experimental data only for the higher temperatures.

The experimental data of the CsCl solutions show a more steady decline of the slope of the density when adding methanol to the solution. Comparing NaCl and CsCl in pure methanol, the temperature dependence is reversed: b_{NaCl} decreases with increasing temperature, while b_{CsCl} increases with increasing temperature. Consequently, for CsCl solutions the isotherms of the slope of the density do not intersect. In general, the temperature dependence of b_{CsCl} is weaker than the temperature dependence of b_{NaCl}. All this is predicted well by the molecular models.

To establish a correlation, b_{salt} is described by a polynomial of second degree:

$$b_{salt}(T, \chi_{\mathrm{MeOH}}) = b_{2,salt}(T)\chi_{\mathrm{MeOH}}^2 + b_{1,salt}(T)\chi_{\mathrm{MeOH}} + b_{0,salt}(T) \tag{10}$$

The fit parameters $b_{k,salt}$ were determined individually for each isotherm for both the experimental and the simulation data and are given in Appendix B, cf. Table B.2.

Together with the pure component molar volumes of water and methanol, Eqs. (7), (8) and (10) fully determine the density in the ternary system water-methanol-salt. From that correlation, it is possible to deduce any volumetric property of interest. In the following, we focus on the partial molar volume of the salt at infinite dilution v_{salt}^{∞} in the mixed solvent with composition χ_{MeOH}. It can be shown that, from the correlation developed here, this quantity can be obtained as

$$v_{salt}^{\infty}(T, \chi_{\mathrm{MeOH}}) = \frac{-b_{salt}(T, \chi_{\mathrm{MeOH}})\ M_{solv} + M_{salt}\ \rho_{solv}(T, \chi_{\mathrm{MeOH}})}{\rho_{solv}(T, \chi_{\mathrm{MeOH}})^2} \tag{11}$$

$$M_{solv} = \chi_{\mathrm{MeOH}} M_{\mathrm{MeOH}} + (1 - \chi_{\mathrm{MeOH}}) M_{\mathrm{W}}, \tag{12}$$

where M_i is the molar mass of component i.

The results for the partial molar volume of both salts at infinite dilution as determined from experiments and predicted by the simulations are shown in Fig. 4.

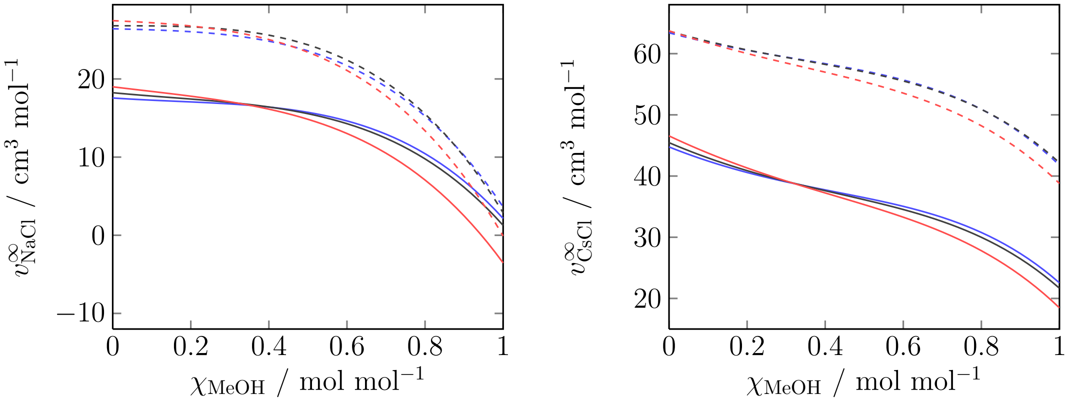

Figure 4: Partial molar volume of the salt at infinite dilution v^{∞}_{salt}, cf. Eq. (11), of NaCl solutions (left) and CsCl solutions (right) over the composition of the salt-free solvent mixture water + methanol. Colors indicate the isotherms 288.15 K (blue), 298.15 K (gray) and 318.15 K (red). Results from the present work: (–) correlation of experimental data, (– –) correlation of molecular simulation data.

Both for NaCl and CsCl, the partial molar volume of the salt is distinctly lower in methanol than in water. This indicates that the ions have a strong ordering effect especially on methanol. For NaCl solutions, $v^{\infty}_{\mathrm{NaCl}}$ depends only weakly on χ_{MeOH} for χ_{MeOH} below about 0.5 mol mol^{-1}, while for larger χ_{MeOH} an important decrease of $v^{\infty}_{\mathrm{NaCl}}$ is observed. For CsCl solutions, the decrease of $v^{\infty}_{\mathrm{CsCl}}$ is more steady.

The temperature dependence of v^{∞}_{salt} is weak both for NaCl and CsCl. While $v^{\infty}_{\mathrm{NaCl}}$ increases slightly with increasing temperature in water, it decreases with increasing temperature in methanol. The same is true for $v^{\infty}_{\mathrm{CsCl}}$. For both salts, there is a solvent composition for which the temperature dependence vanishes. For high temperatures, the partial molar volume of NaCl in methanol is negative. This is remarkable since despite addition of salt, the volume of the solution decreases. In contrast, the partial molar volume of CsCl in methanol is positive. Comparing both salts and considering that they comprise the same anion shows that especially Na^+ ions have a strong influence on the structure of methanol.

The experimental findings discussed above are correctly predicted by the molecular simulations. However, there are some quantitative differences which are of the order of 10 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$ for both salts. Fig. 4 clearly shows that they are induced by the models of the systems salt + pure solvent, while the effects of the mixed solvents are well predicted. Taking into account that the salt models were taken from an ion model set and not adjusted individually and the fact that adjustments of the ion models were only made using experimental data for the solvent water, the predictions are of remarkable quality.

To point out the different behavior of the salts in the two pure solvents water and methanol more clearly, the temperature dependence of v^{∞}_{salt} in both pure solvents is shown in Fig. 5.

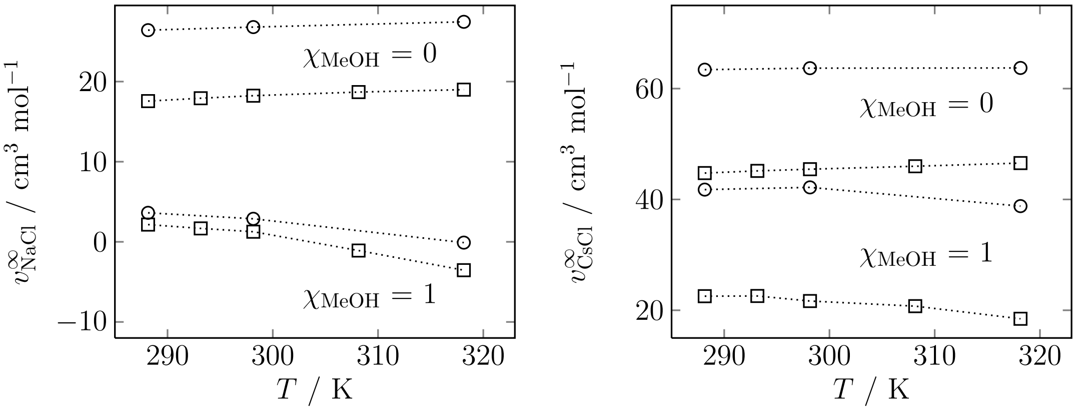

Figure 5: Partial molar volume of the salt at infinite dilution v^{∞}_{salt}, cf. Eq. (11), of NaCl solutions (left) and CsCl solutions (right) over the temperature. The two sets of data in each plot correspond to pure water as the solvent ($\chi_{\mathrm{MeOH}} = 0$, top) and pure methanol as the solvent ($\chi_{\mathrm{MeOH}} = 1$, bottom). Results from the present work: (□) experiment, (○) molecular simulation. Dotted lines are guides to the eye.

As already known from Fig. 4, for both salts v^{∞}_{salt} increases with increasing temperature in an aqueous solution, while it decreases with increasing temperature in a methanolic solution. This feature and also the quantitative incline / decline is predicted well by the molecular simulations. It is instructive to interpret this behavior in the light of Kirkwood-Buff theory [43–45]. The present results indicate that for both salts in water, the total correlation of the ions with the solvent molecules is lowered with increasing temperature. In contrast, for both salts in methanol the total correlation of the ions with the solvent molecules is enhanced with increasing temperature. A rigorous assessment of this relation might be carried out using additional simulations. However, that study is beyond the scope of the present work as large system sizes are needed to avoid finite size effects [46] and Kirkwood-Buff integrals usually show poor convergence [47], which is especially cumbersome for the infinite dilution case studied here.

4.3. Comparison of Experimental Data from the Literature and the Present Work

For both systems studied in the present work, density data have been reported before.

There are four sets of data for NaCl in solutions of water and methanol: Takenaka et al. [1] studied the system in great detail, covering the same concentration and temperature ranges as the present work. Khimenko [4] and Werblan [5] studied only the isotherms 293.15 K and 298.15 K, respectively, and their works also cover only parts of the concentration range. For these two sets of data, the numbers were taken here from the Dortmund Data Bank [48] because the original sources could not be retrieved. The fourth data set on NaCl solutions is that of Guetachew et al. [6], who report densities at 298.15 K. Unfortunately, it is difficult to compare their data to any of the other sets because their measurements were not carried out at constant compositions of the salt-free solvent mixture. That data set is therefore omitted in the following discussion.

For solutions of CsCl in mixtures of water and methanol, densities have so far only been reported by Werblan [5]. Also that data set was taken from the Dortmund Data Bank because the original source could not be retrieved. In Fig. 6, the experimental data from the literature are compared to the correlation of experimental data developed in the present work. Since different salt-free solvent compositions were studied in the literature, this comparison is carried out based on the slope of the density $b_{salt}(\chi_{\mathrm{MeOH}})$ at 298.15 K. To this end, the literature data were correlated using the same linear relationship as for the data of the present work, cf. Eq. (8). The linear trend was confirmed from inspection of the data of Takenaka et al. [1] and of Khimenko [4], while the data of Werblan [5] showed considerable scatter.

For the pure solvents water and methanol, the results from experiments from previous work of our group [36, 42] are also included in Fig. 6. They are in very good agreement with the correlation developed in the present work. For solutions of NaCl in mixtures of water and methanol, the agreement between the data of Takenaka et al. [1] and the correlation to experimental data obtained in the present work is excellent. The data of Khimenko [4],

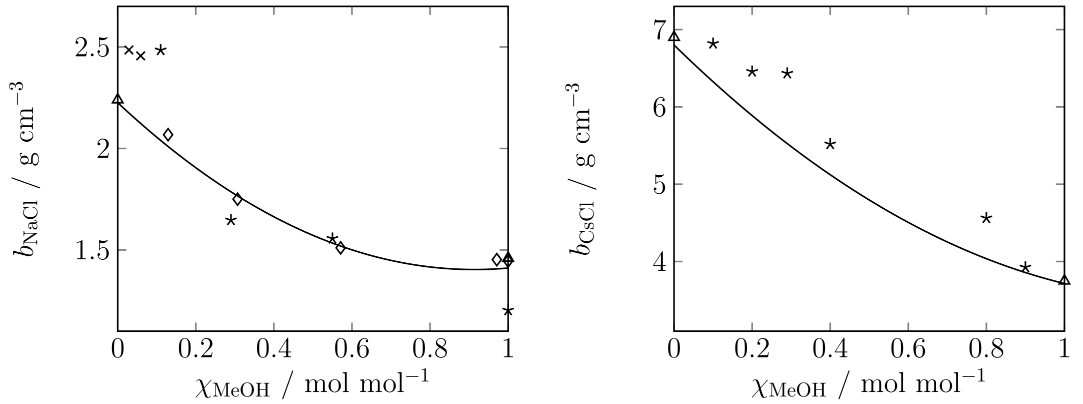

Figure 6: Slope of the density b_{salt}, cf. Eq. (9), of NaCl solutions (left) and CsCl solutions (right) over the composition of the salt-free solvent mixture water + methanol. All displayed data are at 298.15 K except for the results of Khimenko [4], which are at 293.15 K. The lines represent the correlation of experimental data from the present work. Symbols denote experimental data from the literature: (◇) Takenaka et al. [1], (×) Khimenko [4], (⋆) Werblan [5], (△) Reiser et al. [36, 42]. For solutions of NaCl and CsCl in pure water, the results of Reiser et al. [42] were interpolated between 293.15 and 303.15 K.

which were reported only for high water concentrations, deviate considerably from both our data and those of Takenaka et al. [1]. The same holds for most of the data of Werblan [5], which scatter very strongly.

5. Conclusions

Densities of solutions of NaCl and CsCl in mixtures of water and methanol were studied by experiment and molecular simulation. For the NaCl solutions, the experimental data from the present work are found to be in very good agreement to those reported by Takenaka et al. [1]. For the CsCl solutions, up to now only the unreliable data of Werblan [5] were available. The employed molecular models for the ions were taken from a set of models for all alkali and halide ions, for which the parameters were obtained by a fit to density data of dilute aqueous solutions only. The ion models are combined with established solvent models using the Lorentz-Berthelot combining rules. The models show excellent predictions for the dependence of the electrolyte solution density on the composition of the salt-free solvent mixture. Also the temperature dependence is predicted correctly. Some quantitative differences are found, which stem, however, from deviations in the models of the electrolytes in the pure solvents, for which no individual adjustments were carried out. Altogether, taking into account that the employed molecular models are very simple, the results are very encouraging.

Both salts are found to behave differently in the two pure solvents water and methanol. The present results indicate that the effect of ions on methanol is even more pronounced than their effect on water. This is especially true for the Na^+ ion. The good agreement between simulations and experiments shows that the employed models give a realistic picture of the solution behavior. Therefore, subsequent molecular simulations should be carried out in future work, as they can provide additional insight into the solution behavior on the molecular level.

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Appendix A. Simulation Details

In the present work, MD simulations were carried out with the molecular simulation program *ms*2 [49]. Equilibration and production took 100,000 and 2,000,000 time steps of length 1.2 fs, respectively. The equations of motion were integrated with a gear predictor-corrector scheme of fifth order. The simulations were run with a total of 1000 particles in the NpT ensemble, employing the velocity scaling thermostat and Andersen's barostat. All interactions were evaluated explicitly up to the cutoff radius of 15 Å. The usual LJ long-range corrections to the virial and the energy were included. Electrostatic long-range interactions were calculated using Ewald summation, where the real and reciprocal space cutoff were 15 Å. Statistical simulation uncertainties were estimated with the block average method by Flyvbjerg and Petersen [50].

Appendix B. Correlation Parameters

Tables B.1 and B.2 contain the parameters of the empirical density correlation developed in the present work.

Table B.1: Parameters of the Redlich-Kister fits for the molar excess volume of mixtures of water and methanol, cf. Eq. (7).

	Experiment[a]						Simulation[b]		
T / K	A_0	A_1	A_2	A_3	A_4	A_5	A_0	A_1	A_2
288.15	−4.024	−0.319	0.113	0.382	0.621	0.291	−4.147	0.359	−0.387
293.15	−4.047	−0.314	0.125	0.462	0.475	−0.073	–	–	–
298.15	−4.069	−0.299	0.121	0.492	0.388	−0.283	−4.094	0.152	−0.492
308.15	−4.111	−0.219	0.082	0.378	0.328	−0.254	–	–	–
318.15	−4.146	−0.090	0.001	0.105	0.437	0.235	−4.020	0.139	−0.697

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[a] Taken from Coquelet et al. [41]

[b] No simulations were carried out for 293.15 K and 308.15 K

Table B.2: Parameters of the polynomial fits to the slope of the density, cf. Eq. (10).

	NaCl					
	Experiment			Simulation[a]		
T / K	$b_{2,\mathrm{NaCl}}$	$b_{1,\mathrm{NaCl}}$	$b_{0,\mathrm{NaCl}}$	$b_{2,\mathrm{NaCl}}$	$b_{1,\mathrm{NaCl}}$	$b_{0,\mathrm{NaCl}}$
288.15	1.0506	−1.9072	2.2658	0.9993	−1.3956	1.7788
293.15	1.0167	−1.8504	2.2444	–	–	–
298.15	0.9843	−1.7991	2.2255	0.9330	−1.3336	1.7662
308.15	0.9880	−1.7470	2.1975	–	–	–
318.15	0.9829	−1.6953	2.1778	0.9654	−1.2788	1.7172

	CsCl					
	Experiment			Simulation[a]		
T / K	$b_{2,\mathrm{CsCl}}$	$b_{1,\mathrm{CsCl}}$	$b_{0,\mathrm{CsCl}}$	$b_{2,\mathrm{CsCl}}$	$b_{1,\mathrm{CsCl}}$	$b_{0,\mathrm{CsCl}}$
288.15	1.9178	−5.0312	6.8499	1.6940	−4.1679	5.8345
293.15	1.8580	−4.9636	6.8225	–	–	–
298.15	1.8465	−4.9312	6.8002	1.5320	−4.0245	5.8094
308.15	1.7835	−4.8498	6.7596	–	–	–
318.15	1.7780	−4.8008	6.7170	1.5604	−4.0167	5.7797

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[a] No simulations were carried out for 293.15 K and 308.15 K

Nomenclature

Abbreviations

EOS	Equation of state
LJ	Lennard-Jones
MeOH	Methanol
MD	Molecular dynamics
W	Water

Symbols

b_{salt}	Slope of the density versus ion mole fraction
ϵ	LJ energy parameter
ε_0	Vacuum permittivity
n_i	Number of moles of component i
n_i^j	Number of sites of type j on molecule i
N	Number of molecules
η_{ij}	Binary interaction parameter
M_i	Molar mass of component i
q	Point charge
ρ	Mass density
r	Distance

σ	LJ size parameter
T	Temperature
$u(z)$	Uncertainty of the property z
U	Potential
v	Molar volume
v^{E}	Molar excess volume
v_i	Partial molar volume of component i
v_i^{pure}	Molar volume of pure component i
x_i	Mole fraction of component i
χ_{MeOH}	Methanol mole fraction in the salt-free solvent mixture

Subscripts and Superscripts

a, b, c, d	Site index
e	Electrostatic
i, j	Component / molecule index
k	Index for fit parameters
$salt$	Either NaCl or CsCl
$solv$	Solvent
∞	At infinite dilution

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