

Maximum in density of electrolyte solutions: learning about ion-water interactions and testing force-fields

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In this work we studied the effect of Li^+ , Na^+ , K^+ , Mg^{2+} and Ca^{2+} chlorides and sulfates on the temperature of maximum density (TMD) of aqueous solutions at room pressure. Experiments at 1 molal salt concentration were carried out to determine the TMD of the solutions. For density measurements below -15°C , the Sorensen methodology was adopted [1]. We also performed molecular dynamics simulations to estimate the TMD of these solutions at 1 m and 2 m with the Madrid-2019 force field [2], which uses the TIP4P/2005 water model [3] and scaled charges for the ions. Some of the results of this work are displayed in Fig. 1. Our experiments at room temperature are consistent with those from Laliberte [4] and the prediction of both the maximum in density and the TMD from simulations is in excellent agreement with our experimental results.

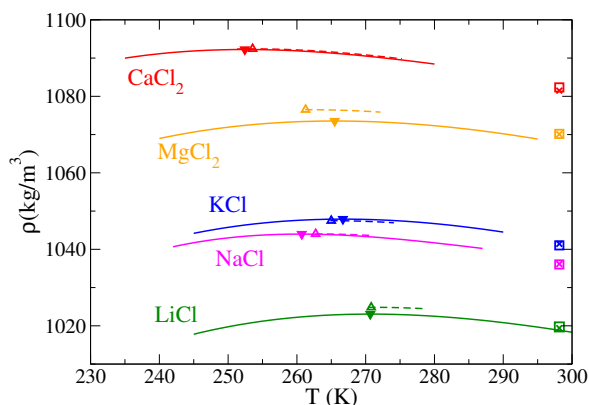


Fig. 1. Density for various chloride solutions at 1 m as a function of temperature at room pressure. Solid lines: simulations for the Madrid-2019 model. Dashed lines: experiment. Values of the TMD: empty up triangles (experimental results from this work), filled down triangles (simulations). Density at room temperature from experiments: crosses (results from Ref. [4]); empty squares (results from this work).

All the salts studied in this work shift the TMD of the solution to lower temperatures and flatten the density profile (when compared to pure water) with increasing salt

concentration. The shift in the TMD (Δ) depends strongly on the nature of the electrolyte. Despretz established a linear dependence of Δ with the salt concentration (in molality) as early as 1840 [5]. We hereby confirm that the Despretz law holds for all the salts considered here at least up to 1 m. In order to further explore this shift in the TMD, we have evaluated the contribution of each ion to Δ (from the experimental results), concluding that Na^+ , Ca^{2+} and SO_4^{2-} seem to induce the largest changes among the studied ions. We have proved that these group contributions are able to accurately predict the shift in TMD for 1 m mixtures.

Finally, the volume of the system has been analyzed for salts with the same anion and different cation. These curves provide an insight into the effect of different ions upon the structure of water. We conclude that for those ions with a strong coordinated first layer, namely Li^+ and Mg^{2+} (where water is not just coordinating the cation but forming a complex), the remaining water molecules accommodate in an expanded structure resulting from the configurations they adopt to enable hydrogen bonding with the “rigid” water molecules from the first solvation shell. We therefore claim that the TMD of electrolyte solutions entails interesting physics regarding ion-water and water-water interactions and should then be considered as a test property when developing force fields for electrolytes. This matter has been rather unnoticed for almost a century now and we believe it is time to revisit it.

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