Maximum in density of electrolyte solutions: Learning about ion–water interactions and testing the Madrid-2019 force field EP

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ABSTRACT

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 these solutions. We also performed molecular dynamics simulations to estimate the TMD at 1 and 2 m with the Madrid-2019 force field, which uses the TIP4P/2005 water model and scaled charges for the ions, finding an excellent agreement between experiment and simulation. All the salts studied in this work shift the TMD of the solution to lower temperatures and flatten the density vs temperature curves (when compared to pure water) with increasing salt concentration. The shift in the TMD depends strongly on the nature of the electrolyte. In order to explore this dependence, we have evaluated the contribution of each ion to the shift in the TMD concluding that Na^+, Ca^{2+}, and SO_4^{2-} seem to induce the largest changes among the studied ions. The volume of the system has been analyzed for salts with the same anion and different cations. These curves provide insight into the effect of different ions upon the structure of water. We claim that the TMD of electrolyte solutions entails interesting physics regarding ion–water and water–water interactions and should, therefore, 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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I. INTRODUCTION

Generally, when a liquid is cooled at constant pressure its density increases. However, this is not the case for some tetrahedrally coordinated liquids, such as water. For water, the density increases when cooling it down to 4 °C (at room pressure), but below this temperature the density decreases.[1] Thus, water presents a maximum in density when cooled at constant pressure, and the temperature at which it occurs is denoted as the temperature of the maximum in density (TMD).

It is known that the maximum in density of water is related to the relative positions of the molecules (i.e., to the overall structure of water).[2] What happens to the TMD when one adds a solute

to water? In general, it is found that the maximum occurs at lower temperatures,[3,4] except for the case of some diluted alcohols.[5–7] It is tempting to assume that electrolytes destroy the tetrahedral order of water so that, when added to water, they provoke a decrease in the TMD. In addition, it is conceivable that certain ions could be more efficient than others in disturbing this tetrahedral order. Since electrolytes fully dissociate into cations and anions in water solutions, it could be expected (at low concentrations) that the impact on the TMD has a contribution arising from the cation and another one from the anion (evidently, at moderate and high concentrations, ion–ion interactions would also play a role in the description of the system). The problem of the TMD of electrolytes has a long history. Despretz[8,9] measured in 1839 the TMD for ionic solutions

experimentally (almost two centuries ago). He described the shift in the TMD, Δ, as

$$\Delta = TMD^{solution} - TMD^{H_2O} \tag{1}$$

and proposed what is called the Despretz law that states that

$$\Delta = K_m\, m, \tag{2}$$

where K_m is the Despretz constant (that adopts different values for different salts), TMD represents the temperature of the maximum in density, and m is the molality of the electrolyte solution (i.e., mols of salt per kilogram of water). Toward the end of the 19th century, Coppet determined the TMD of other salts,[10] followed by further measurements done by Wright in 1919.[11] Finally, all the results were gathered in the International Tables of Physical Chemistry data[3] in 1928. It should be stated that, in most of these studies, the value of the molality was rather small (typically less than 0.5 m). For higher concentrations, the value of the shift increases and experiments were difficult to carry out due to the spontaneous formation of ice before the TMD could be reached. After that, the interest in this matter has remained rather unnoticed for almost a century. Only relatively recently, Pokale and co-workers have revisited the problem but only for very diluted solutions.[12,13] We hereby put forward some reasons why this problem should be revisited and further investigated.

For the last 40 years, the interest regarding the properties of supercooled water has increased significantly.[14,15] The behavior of supercooled liquid water at low temperatures is anomalous in a number of properties, one of which is its maximum in density (arguably a quite important one). The molecular origin of this maximum in water is connected to an increase of the tetrahedral ordering of the liquid molecules when cooled and to the open low density structure generated when this ordering takes place[16] (not surprisingly, ice with perfect tetrahedral order is less dense than liquid water). Of the several theoretical scenarios, the one proposing the existence of a liquid–liquid critical point in water (in addition to the liquid–gas critical point)[17] stands out and is gaining increasing recognition by the scientific community.[18–23] In fact, this second critical point has been found in simulations for several water models.[24–26] The attention focused on the supercooled region of water has translated to electrolyte solutions as well. The study of the TMD of these solutions may provide key information aimed at understanding the origin of the aforementioned anomalous thermodynamic behavior of water, as adding salt not only decreases the freezing point but also makes homogeneous nucleation more difficult,[27] thus allowing us to study water solutions at much lower temperatures than possible for pure water.[28] In addition to that, it has been suggested by Gallo and co-workers that adding electrolytes to water may facilitate the experimental approach to finding the liquid–liquid critical point of the solution, as its critical parameters would be more accessible than those of pure water.[29]

Adding a salt to water also modifies other properties of the solution, such as the ice freezing point temperature[30] or even the structure of water.[31] However, there are some conceptual differences between the shift in the TMD and the shift in the freezing temperature, the latter having a sound theoretical basis. When a solute is added to a solvent, the chemical potential of the solvent decreases

and lower temperatures are needed to bring it into equilibrium with the solid. Thus, a simple ideal solution model can describe this phenomenon, leading to the celebrated van't Hoff equation, which states that for a 1 m electrolyte solution, the freezing temperature decreases 1.9 K times the number of ions formed by the dissociation of the electrolyte (i.e., two ions per molecule of NaCl and three ions per molecule of $MgCl_2$). The value of the proportionality constant is related to the melting temperature and melting enthalpy of pure water. Of course, deviations from ideal behavior modify somewhat this prediction, but overall, the freezing point depression can be described by this "universal" equation up to 1 m (with a typical error of one degree) so that any 1:1 electrolyte solution at this concentration freezes at about $-4\,^{\circ}$C. Note that only properties of water (both in the solid and in the liquid phase) enter in the description of the freezing point depression when described as a colligative property. At high concentrations, the van't Hoff law does not hold as deviations from ideal behavior modify significantly the freezing point depression. Note that the properties of the solid phase of water do not enter at all in the description of the TMD, which must then be regarded as a "one-phase" property (in contrast to the freezing point depression). Furthermore, since the Despretz constant is significantly different for each salt even at low concentrations, the TMD is not a colligative property.

There is yet another good reason to study the TMD of electrolytes in the 21st century, after experiments seemingly concluded in 1928. With the revolution of computer simulations, in the mid-20th century, two main techniques were proposed to study the behavior of condensed matter: Monte Carlo[46] (MC) and Molecular Dynamics[47] (MD). It took some time until electrolyte solutions simulations could be accomplished. The first simulations of ionic systems date from the mid-1970s[48–52] (soon after the first pioneering MD simulation of water by Rahman and Stillinger[53]). It was immediately clear that a good force field was needed to be able to reproduce the properties of these solutions. Therefore, in order to study the TMD of solutions, it is indispensable to use a model of water that predicts this property accurately. Has the TMD been taken into account when developing models for pure water? This is illustrated in Fig. 1 and Table I, where the TMD of several realistic water models
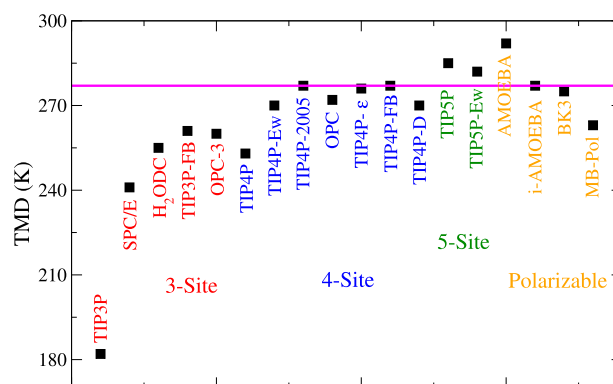

FIG. 1. TMD for several water models. The solid line is the experimental TMD of water. The different water models are grouped by their geometry. In each group, the water models are shown in chronological order.

TABLE I. TMDs for different water models, as reported in the literature.

Model	TMD (K)
Expt.	277[32]
TIP3P	182[33]
SPC/E	241[33]
H₂ODC	255[34]
TIP3P-FB	261[35]
OPC-3	260[34]
TIP4P	253[33]
TIP4P-Ew	274[36]
TIP4P-2005	277 (this work)
OPC	272[37]
TIP4P-ϵ	276[38]
TIP4P-FB	277[35]
TIP4P-D	270[39]
TIP5P	285[40]
TIP5P-EW	282[41]
AMOEBA	292[42]
i-AMOEBA	277[43]
BK3	275[44]
MB-Pol	263[45]

is presented.[32–45] In addition, Kiss and Baranyai published a relevant work about the TMD of water models.[54] The trend is clear: models proposed in the 1970s, 1980s, and 1990s did not reproduce the experimental value of the TMD of water. It should be pointed out that, until the mid-1990s (with the notable exception of the pioneering work of Rahman and Stillinger[55]), this property was rarely determined in computer simulations due to its high computational cost.[56,57] However, its determination is straightforward with current computational resources, and, in recent years, it has gained relevance among the community, being nowadays often used as a target property. Models with a TMD within three degrees of the experimental value are the polarizable models BK3[44] and i-AMOEBA[43] and the non-polarizable models TIP4P-Ew,[36] TIP4P/2005,[58] TIP4P-FB,[35] and TIP4P-ϵ[38] (TIP5P[59] does not reproduce exactly the TMD of water when Coulombic interactions are treated with Ewald sums, which is now the standard approach).

What about the force fields for ions? Typically, the density and the Gibbs free energy of hydration have been used as target properties, whereas the TMD has not been considered as a target property when designing force fields for electrolytes. It is our impression that this approach should be reconsidered, as this property is certainly related to the impact of the ions on the structure of water. We have recently proposed a force field based on the TIP4P/2005[58] water model for electrolyte solutions, which has been denoted as Madrid-2019[60] (as a follow-up name from its archetype, which was only parameterized for NaCl[61]). After the success of both models, we have further extended this methodology to more ions, to which we have named, for consistency, the Madrid-2019-Extended model.[62] The Madrid and subsequent electrolyte models have yet another peculiarity: the charge attributed to the ions is not an integer number (in electron units), but rather they have been assigned a 0.85 e charge for 1:1 electrolytes. This approach is denoted as charge scaling or electronic continuum correction (ECC), and it can be regarded as a "cheap" way of introducing some polarization in an implicit way. The theoretical basis for that was proposed by Leontyev and Stuchebrukhov[63–68] and has been further developed by Jungwirth and co-workers,[69–73] by Kann and Skinner,[74] and by several other groups,[75–82] including ourselves.[61,62,83] These models have been shown to provide a better description of numerous properties of salt solutions[84–89] than unit charge models.

In this work, we shall perform experiments to determine the TMD of several electrolyte solutions. For certain salts, we shall use large samples and for others we shall adopt the methodology of Hare and Sorensen,[90] which has been proven useful to determine the properties of supercooled water (by measuring small samples to avoid nucleation). MD simulations with the Madrid-2019 force field will also be performed for the same purpose. The key question of this work is as follows: Can a current force field describe the experimental values of the TMD of electrolyte solutions? Our goal is to put the TMD back on the table for groups developing force fields for ions, since it contains information on how the electrolytes affect the structure of water. This property could also be regarded as a test property to discuss whether or not the use of scaled charges improves the electrolyte force-field. In addition, we shall provide some hints on the effect of individual ions on the TMD of the solution, and from there on, we will try to ascribe these changes, albeit in a rough and simplistic manner (since the elucidation of the structure of water in the vicinity of electrolytes is out of the scope of this work), to the rearrangement of the water molecules around the ions.

II. EXPERIMENTAL PROCEDURE

Solutions were prepared by weighing in an Mettler AE-240 balance using MilliQ water. Uncertainty in molality was estimated in 0.004 mol kg⁻¹. Two different procedures have been used for making the density measurements against temperature. Both are based on the visual determination of the position of the solution/air interface—the meniscus—in capillary glass tubes. The experimental methodology for the samples with a TMD around or higher than 261 K (i.e., temperatures above $-12\,^{\circ}$C as LiCl, NaCl, KCl, and MgCl₂) was as follows: they were introduced in a 60 ml glass threaded flask and closed with a glass stopper soldered to a capillary tube with an internal diameter of 0.66 mm. The flask was sealed with a Viton O-ring and tightly closed with a threaded cap. To avoid water vaporization in the capillary, its end was also sealed with a silicone tube and a plastic stopper. The flask and capillary were submerged in a methanol reservoir, whose temperature is controlled with a Lauda RP845 thermostat. In an experiment, a temperature program was applied, and the meniscus position was recorded with a Promon U750 digital camera. Therefore, a set of data pairs (temperature, position) was obtained for each experiment. The knowledge of the reference density ρ_0 at one reference temperature T_0 allows the conversion of the meniscus position into density data. Therefore, ρ_0 was measured using a DMA 5000 vibrating tube densimeter. This instrument was calibrated using MilliQ water and octane as reference fluids, their densities being obtained from the literature.[91,92] The density ρ is obtained at the desired temperature using

$$\rho = \rho_0 \frac{V_{f,0} + S_0 L_0}{V_{f,0}(1 + 3\alpha(T - T_0)) + S_0(1 + 2\alpha(T - T_0))L(1 + \alpha(T - T_0))},$$
(3)

where $V_{f,0}$, S_0, and L_0 are the flask volume, the capillary cross section area, and meniscus position at the reference temperature, respectively, and α is the glass linear thermal expansivity. $V_{f,0}$, S_0, and α were determined by performing calibration experiments with pure water. Therefore, from L, i.e., the meniscus position, the density of the sample at the temperature T is readily obtained using Eq. (3).

With this procedure, we observed that the samples can be kept in the metastable liquid state only down to around $-12\,°C$. One of the key factors for liquid supercooling is the sample volume: the smaller the volume, the less probable the liquid–solid transition becomes. Therefore, for the other salt aqueous solutions (Li_2SO_4, Na_2SO_4, $MgSO_4$, and $CaCl_2$), which are expected to have TMDs below $-12\,°C$, we have used another method (following Hare and Sorensen[90]) with smaller volumes. The sample was injected into a thin capillary tube (internal diameter 0.3 mm) of around 100 mm long; its total volume is $\sim 7\,\mu l$, 10 000 times smaller than that needed for the first method. The capillary was not totally filled; around 10 mm of air was left in order to observe the meniscus. The capillary was flame sealed, marked with a file to have a reference point for measuring the meniscus position, and introduced in a methanol bath, also controlled with the Lauda thermostat. A stereomicroscope was used for determining the position of the meniscus in the capillary. As in the first method, a temperature program was applied and the meniscus and reference positions were recorded also using the digital camera, which was coupled to the microscope. The density is calculated from Eq. (3), but making $V_{f,0} = 0$, since there is no flask,

$$\rho = \rho_0 \frac{L_0}{L(1 + 2\alpha(T - T_0))(1 + \alpha(T - T_0))}. \tag{4}$$

Therefore, the only needed calibration constant is the glass linear thermal expansivity, also obtained from experiments performed with pure water. With this method, we observed that solutions can be supercooled down to around $-21\,°C$. Due to this limiting temperature, the only solution for which the density maximum could be determined at 2 m is that of LiCl (the TMD is shifted to lower temperatures with increasing concentration). The uncertainty with both methods is estimated to be $5 \cdot 10^{-4}$ g cm^{-3}. However, it must be pointed out that repeatability of the first one is much better,

TABLE II. Source, purity, measured density, and literature[93] density at 25 °C, ρ, ρ_{lit} for the studied salts in aqueous solution at molality m = 1 mol kg^{-1} (2 m concentration is also included for LiCl).

Salt	Source	Purity (%)	ρ (g cm^{-3})	ρ_{lit} (g cm^{-3})
LiCl	Alfa Aesar	99.3	1.019 71	1.019 40
LiCl (2 m)	Alfa Aesar	99.3	1.041 41	1.040 56
NaCl	Carlo Erba	99.4	1.036 04	1.036 15
MgCl$_2$	PanReac	99.8	1.070 17	1.070 09
KCl	Sigma-Aldrich	99.8	1.041 04	1.041 42
CaCl$_2$	Sigma-Aldrich	99.4	1.082 32	1.081 49
Li$_2$SO$_4$	Alfa Aesar	99.5	1.083 71	1.083 51
Na$_2$SO$_4$	Sigma-Aldrich	99.5	1.112 58	1.112 92
MgSO$_4$	Sigma-Aldrich	99.8	1.109 87	1.110 27

$5 \cdot 10^{-6}$ vs $2 \cdot 10^{-4}$ g cm^{-3}. This makes it significantly more precise for TMD determination, which has been estimated in 0.3 K for the former and in 1.5 K for the latter. Table II gives the density at 25 °C compared with literature,[93] as well as the source and purity of the studied salts. Density matches with literature within some unities in the fourth decimal figure, which is the usual agreement found for this magnitude.

III. SIMULATION DETAILS

All simulations have been performed in a system containing 555 water molecules[58] and the corresponding number of ions for concentrations 1 and 2 m. This choice of the number of water molecules is convenient since for a 1:1 electrolyte solution, an 1 m concentration is achieved by adding ten cations and ten anions of such electrolyte.

Molecular dynamics simulations were carried out in the NpT ensemble (at $p = 1$ bar) using the GROMACS 4.6.7 package.[94] Although 1 bar is not identical to room pressure, the impact of this very small difference of pressures on the densities and TMD is negligible. To maintain the temperature and pressure, the Nosé–Hoover thermostat[95,96] and an isotropic Parrinello–Rahman barostat[97] have been used, respectively, with a relaxation time of 2 ps. The equations of motion were integrated with the leap frog algorithm[98] with a time step of 2 fs. In our simulations, both the Lennard-Jones (LJ) and the electrostatic interactions have been truncated at 10 Å and long range corrections to the LJ potential for pressure and energy were included. To account for long-range electrostatic forces, the smooth PME method was used.[99] For the chloride solutions, we have implemented the LINCS algorithm to constrain the water geometry.[100,101] However, for sulfate solutions, we have chosen the SHAKE algorithm[102] (both for the sulfate group and for the water molecules) since it has been proved to be more efficient in this case.

To locate the position of the TMD, we first launched some short simulations at regular intervals of 15–20 K along the room pressure isobar to get a rough estimate of the position of the maximum. Then, more points were calculated with longer simulation times until the deviation of consecutive simulations for the same point was of the order of the statistical error. This required longer simulation times at the lowest temperatures due to the fact that relaxation times for these state points are slower. For each selected temperature, the simulations were run between 100 and 300 ns for 1 m solutions and up to 500 ns for 2 m solutions and low temperatures. The total simulation time for this work is around 45 μs. Finally, the densities obtained at different temperatures (typically we considered nine to twelve different temperatures for each concentration) were fitted to a cubic polynomial whose derivative gives the value of the TMD in its intersection with 0. The estimated error in the TMD is 1 K for 1 m solutions, 2 K for 2 m chloride solutions, and 4 K for 2 m sulfate solutions.

IV. RESULTS

The experimental and simulated density for the 1 m chloride solutions along the room pressure isobar are presented in Fig. 2. The maximum density and the temperature at which it occurs
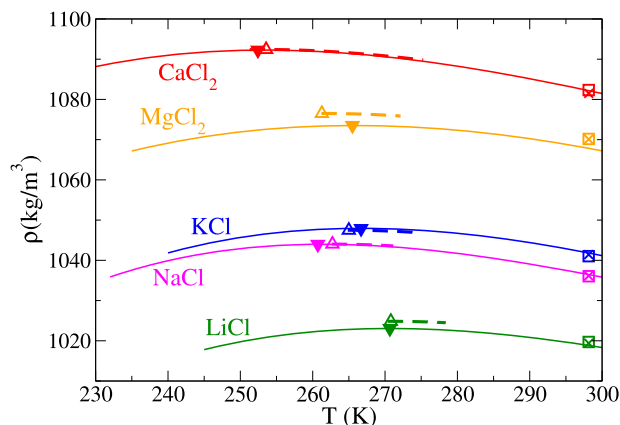
FIG. 2. Density for various chloride solutions at 1 m as a function of temperature at room pressure. Solid lines: simulations for the Madrid-2019 model. Dashed lines: experiment. TMD: empty up triangles (experimental results from this work) and filled down triangles (simulations). Density at room temperature from experiments: crosses (results from Ref. 93) and empty squares (results from this work).

TABLE III. Temperature of maximum density (TMD) and the density at the maximum for chloride solutions at 1 m and room pressure (2 m results for LiCl are also presented). Er% is the percentage deviation of the simulated from experimental results. The asterisk (*) for MgCl$_2$ indicates that a small extrapolation (0.1 K) was needed to estimate the location of the maximum in the experimental results. The experimental solubilities (in molality) at 25 °C for these salts are as follows: LiCl = 19.95, NaCl = 6.15, KCl = 4.81, MgCl$_2$ = 5.81, and CaCl$_2$ = 7.3.[104]

Salt	TMD (K)			ρ_{max} (kg m^{-3})		
	Expt.	Madrid-2019	Er%	Expt.	Madrid-2019	Er%
LiCl	270.8	270.7	0.04	1024.8	1023.1	0.17
LiCl (2 m)	264.8	265.0	0.08	1046.5	1045.6	0.1
NaCl	262.7	260.7	0.76	1044.0	1044.0	0.01
KCl	265.0	266.7	0.64	1047.5	1047.9	0.04
MgCl$_2$	261.3*	265.5	1.6	1076.5*	1073.5	0.28
CaCl$_2$	253.6	252.4	0.47	1092.4	1092.2	0.02

(TMD) are given in Table III (where results for the 2 m LiCl solution have also been included). It was necessary to extrapolate the experimental results of the magnesium chloride by a small amount (around 0.1 K) to estimate the location of the maximum. The reader may wonder why this extrapolation was needed. The answer is simple. When performing experiments for the magnesium chloride solution, the sample froze upon cooling before the TMD was reached. The lowest temperature at which we performed experiments for each salt solution is visible in Fig. 2, and it was either a temperature below the TMD (so that further experiments were not required) or a temperature at which we could not avoid the freezing of the sample.

In Fig. 2, it can be seen that the experimental results of this work at room temperature match those of Laliberté. It is also noticeable the good agreement between the experimental and simulation results. For some salts (i.e., CaCl$_2$, KCl, and NaCl), the simulated densities are hardly distinguishable from the experimental ones,

whereas for LiCl and MgCl$_2$ solutions, the simulated densities lay slightly below the experimental ones. However, for these two salts, there is a roughly constant offset between the two lines (the simulated and experimental density curves) along the studied range of temperatures (i.e., they have the same shape). Thus, the model captures extraordinary well the change in the density of the solution with temperature. It should be emphasized that although the Madrid-2019 force field was certainly designed to reproduce the experimental densities at 298 K, there was not guarantee that it would be able to still reproduce the density at 50 K below its parameterization temperature (although it is known that it does for pure water[103]).

In Table III, the TMD and the density at the maximum of the chloride solutions predicted by the Madrid-2019 force field are compared to their corresponding experimental values. Er% stands for the percent deviation between experiments and simulations, which is typically very small (even for the case of the 2 m LiCl solution). For the maximum in density, the deviation is lower than 0.25%. Concerning the TMD, the Err% is typically below 0.8%, with the exception of MgCl$_2$ for which it is twice as large. This amounts to a typical deviation of about 1–2 K for all the considered chloride solutions, except for MgCl$_2$, for which the deviation is around 4 K (the model performs slightly worse for this salt). It must be pointed out that these deviations are not systematic, as for certain salts the simulated TMD and maximum density are higher than those from experiments and for other salts it is the other way around. Note that the shift in the TMD induced by a 1 m solution of chlorides is 6 (LiCl), 12 (KCl), 14 (NaCl), 16 (MgCl$_2$), and 24 (CaCl$_2$) degrees. The expected change in the freezing point (for a 1 m solution) is of ~4 K for a 1:1 electrolyte and 6 K for a 1:2 electrolyte. Therefore, the addition of electrolytes has a much larger effect on the TMD than on the freezing point and each salt has a different fingerprint in the TMD.

It might be tempting to attribute the success of the Madrid-2019 model in reproducing the TMD as a merit mainly of the water model, leaving the electrolyte force field out of the picture. To discourage this idea, we have studied the TMD for NaCl and KCl solutions at 1 m using the TIP4P/2005 model for water combined with different electrolyte models (with unitary charges): the recently developed model by Yagasaki et al.[105] (designed to reproduce the experimental value of the solubility of these two salts) and the celebrated Joung and Cheatham (JC) model, originally proposed for TIP3P, TIP4P-Ew, and SPC/E water models, employing Lorentz–Berthelot rules to adapt it to the TIP4P/2005 model (this model was proposed in previous work and it yields reasonable results for many properties of the salt solution[61]). As shown in Fig. 3, the agreement with experiment for the two models with integer charges is not so good. The density at 298 K is somewhat overestimated in the two force fields that use integer charges for the ions. In fact, since the density at room temperature was not used as a target property, this is not surprising. What is even more relevant is that the shift in the TMD of these two models is somewhat larger (by about five degrees) than that found both in experiments and with the Madrid-2019 model. The shift of the unitary models are of about 20 K for NaCl and 16 K for KCl, whereas the experimental shifts are 14 and 12, respectively. This suggests that the structural changes induced by integer charged ions are too large, which was already anticipated by Benavides et al.[61] in a previous
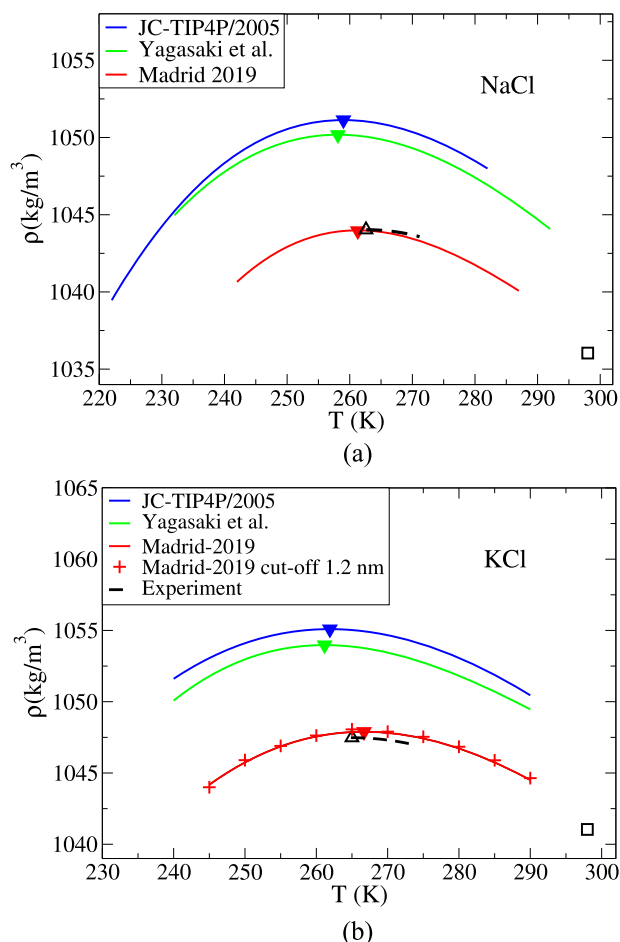
FIG. 3. Density for (a) NaCl and (b) KCl solutions at 1 m and room pressure as a function of temperature for different electrolyte models evaluated in this work: Madrid-2019,[60] Joung-Cheatham-TIP4P/2005,[61] and the force field developed by Yagasaki et al.[105] The solid lines are the fit to the simulated densities and the filled down triangles represent their TMD values. Our experimental measurements (dashed lines for densities and empty up triangles for TMD) are also shown. The open square stands for the experimental density at room temperature as determined in this work. The plus symbols are simulations with the Madrid-2019 using a cutoff of 12 Å. Long range correction to the LJ part of the potential were included for both values of the cutoff (i.e., 10 Å and 12 Å).

study. In Fig. 3(b), we have included a simulation of KCl with the Madrid-2019 model using a cutoff of 12 Å, which yields a TMD of 266.6 K to be compared with the value 266.7 K determined using the cutoff established in Sec. III (i.e., 10 Å). This proves that the TMD reported in this work is not significantly affected by the cutoff value.

Let us now present the results for the sulfate solutions (Fig. 4 and Table IV). It can be noticed that some experimental results are missing. In particular, the low solubility of potassium and calcium sulfates, which is below 1 m at room temperature, caused the precipitation of the salt. However, we were able to determine the TMD for these two salts from computer simulations. Why it is possible to determine the TMD for certain salts in simulations whereas it is not
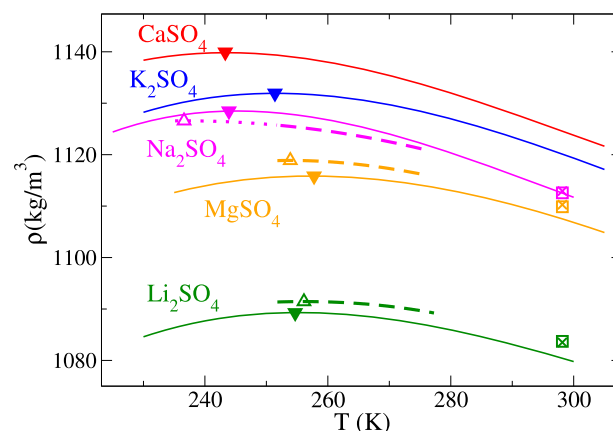

FIG. 4. Density for various sulfate solutions at 1 m as a function of temperature at room pressure. Solid lines: simulations for the Madrid-2019 model. Dashed lines: experiment. Dotted lines: extrapolation from experimental results. TMD: empty up triangles (experiment) and filled down triangles (simulations). Density at room temperature from experiments: crosses (results from Ref. 93) and empty squares (results from this work).

possible to do it in experiments? The answer is that the probability of a first order phase transition (via nucleation) is much lower in simulations than in experiments. The time for homogeneous nucleation decreases as the inverse of the volume[107] so that when having small systems as those used in simulations (nanometric dimensions), one can often enter the "metastable room." In addition, simulations are free of impurities thus avoiding heterogeneous nucleation, which is often the main cause of nucleation in experiments. Two types of phase transitions can occur in experiments: freezing of water and precipitation of the salt. Freezing of water is not expected to take place in simulations for two reasons. (1) (Thermodynamic consideration) The melting temperature of the TIP4P/2005 model of water is 250 K (so for an electrolyte solution using this model it is even lower). (2) (Kinetic consideration) The formation of ice in simulation is extremely unlikely due to the extremely small size of the system. With respect to precipitation, it should be pointed out that the solubility of the force field for the salts of this work is unknown

TABLE IV. Temperature of maximum density (TMD) and the density at the maximum for sulfate solutions at 1 m and room pressure. Er% is the percentage deviation of the simulated from the experimental results. The asterisks (*) in the experimental results of Na$_2$SO$_4$ indicate that the experimental results have been extrapolated ~15 K so that the estimate should be taken with care. The experimental solubilities (in molality) at 25 °C for these salts are as follows: Li$_2$SO$_4$ = 3.12, Na$_2$SO$_4$ = 1.96, K$_2$SO$_4$ = 0.69, MgSO$_4$ = 3.07, and CaSO$_4$ = 0.02.[104,106]

	TMD (K)			ρ_{max} (kg m^{-3})		
Salt	Expt.	Madrid-2019	Er%	Expt.	Madrid-2019	Er%
Li$_2$SO$_4$	256.1	254.9	0.55	1091.4	1089.3	0.20
Na$_2$SO$_4$	237*	243.4	2.9	1126.6*	1128.5	0.17
K$_2$SO$_4$	Insoluble	251.4		Insoluble	1131.9	
MgSO$_4$	253.9	257.8	1.5	1118.9	1115.8	0.27
CaSO$_4$	Insoluble	243.8		Insoluble	1139.9	

(except for NaCl where it has been shown to be in reasonable agreement with experiment[61,105]). Therefore, we have no reason to believe that the solubility of the salts described by the Madrid-2019 is much lower than the experimental ones. In fact, no signs of aggregation nor precipitation were observed neither at room temperature at the experimental solubility limit nor at the much lower temperatures considered in this work. Note that spontaneous precipitation is not expected in brute force simulations unless the solubility limit is significantly overcome.[108,109] Due to all these facts, we were able to determine the TMD at 1 m and 2 m for all the salts considered in this work, and ice formation or precipitation has not been an issue. To study electrolyte solutions experimentally at lower temperatures, it would be necessary to further reduce the size of the sample using microemulsions to confine water to drops of (1–10) μm of diameter.[110] This technique was used by Mishima and co-workers, who managed to reach temperatures beyond the limit of homogeneous nucleation of pure water.[111,112] Angell and co-workers adopted the same approach for studying the homogeneous nucleation rates of the ice formation in electrolyte solutions.[113,114]

As shown in Fig. 4 and Table IV, most of the findings already discussed for the chloride salts also hold for the sulfates. The deviations between simulation and experiment for the density at the maximum are of about 0.25% or less, and the error for the TMD is typically smaller than 4 K. The worst agreement is obtained for Na_2SO_4, but it must be noted that the experimental data were extrapolated by 15 K to obtain a rough estimate of the TMD. It is interesting to notice that the relative deviation between experiments and simulations for the TMD and ρ_{max} of the magnesium salts (the chloride and the sulfate) are very similar. This seems to indicate that, for these two salts, small deviations from experiment arise mainly from the parameterization of the cation.

In Fig. 5, we compare the results of this work with the available experimental data from the literature. Although it may be surprising, the best compilation of experimental measurements for the TMD of

electrolytes comes from the International Tables of 1928.[3] To the best of our knowledge, this problem has rarely been revisited. Good agreement is found (see Fig. 5) both for the experimental and simulation results of this work when compared to those from 1928.[3] A linear extrapolation of the experimental results has been done up to 2 m, finding that these values fall quite close to the results obtained in this work from computer simulations of the Madrid-2019 and for the only experimental result we were able to calculate (i.e., LiCl). To the best of our knowledge, the experimental TMD of these electrolyte solutions at 2 m has never been reported. This suggests that the linear dependence predicted by Despretz is still valid for all the salts presented in Fig. 5, the deviations being relatively small, at least for concentrations up to 2 m.

Since the Despretz constant K_m relates the molality of the solution to the shift in TMD (Δ), it would be useful express our results in such way. To evaluate Δ for the Madrid-2019 force field, the value of the TMD of pure water (TIP4P/2005) is needed. In the original paper proposing the model, the value 278 K was estimated[58] using MC simulations, and four years later, we calculated a TMD of 277 K using MD.[115] Other authors have reported 276 K[38] and 275 K.[39] Due to these discrepancies, we have recalculated the TMD of the TIP4P/2005 model for the system size employed throughout this work, namely, 555 water molecules, obtaining a TMD of 277.3 K (see Fig. 6).

The shift in the TMD of the solutions with respect to pure water is summarized in Table V. For salts with monovalent cations, Δ appears to be proportional to the concentration of the electrolytes for concentrations up to 2 m (although for sulfates certain moderate deviations of the linear behavior are observed). However, for salts with divalent cations (for instance, $MgCl_2$ and $MgSO_4$), deviations from linear behavior are observed between 1 and 2 m. We were not able to determine by computer simulations the TMD at 2 m of calcium salts ($CaCl_2$ and $CaSO_4$). The results obtained for these solutions are displayed in Fig. 7. Below 205 K, extremely long runs would be needed to equilibrate the sample (due to the hampering in diffusion by the high salt concentration and the low temperature). Archer and Carter showed that high concentrated electrolyte solutions
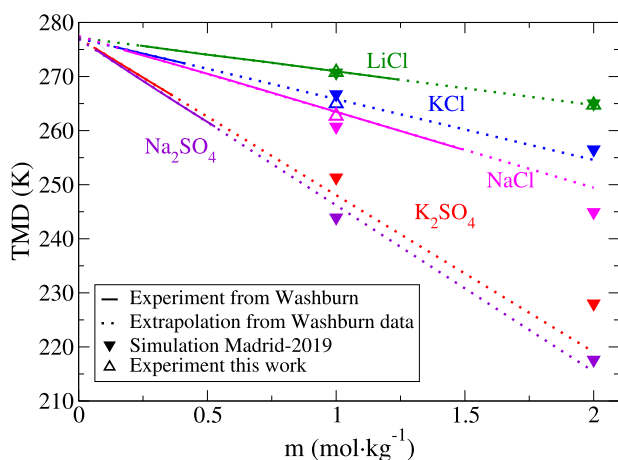
FIG. 5. TMD for various solutions as a function of concentration (in molality) obtained in this work and from experiments. Solid lines are the results from experiments of Ref. 3, and dashed lines are the extrapolation of these results. Filled down triangles are the simulation results for TMDs obtained in this work using Madrid-2019 force field. Empty up triangles are the experimental results of this work.
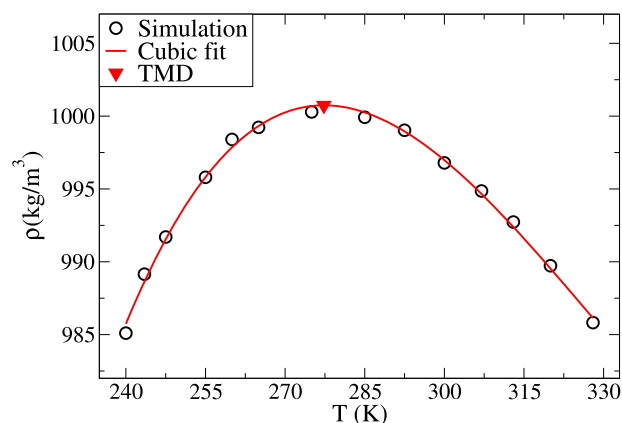
FIG. 6. Density of TIP4P/2005 pure water as a function of temperature at $p = 1$ bar as obtained from the simulations of this work. The TMD of the model is located at 277.3 K.

TABLE V. Shift in the TMD, Δ (in degrees), with respect to pure water for the solutions and concentrations studied in this work. The experimental TMD of pure water is 277.1 K and for the TIP4P/2005 is 277.3 K. The asterisk (*) indicates that the value for Na_2SO_4 was estimated by extrapolating about 15 K our experimental results.

| Salt | Cl⁻ | | | SO₄²⁻ | | |
| | Madrid-2019 | | Expt. | Madrid-2019 | | Expt. |
	1 m	2 m	1 m	1 m	2 m	1 m
Li^+	− 6.6	−12.3	− 6.3	−22.4	−49.5	−21.0
Na^+	−16.6	−32.4	−14.4	−33.9	−59.7	−40.1*
K^+	−10.6	−20.8	−12.1	−25.9	−49.0	Insoluble
Mg^{2+}	−11.8	−32.1	−15.8	−19.6	−48.8	−23.2
Ca^{2+}	−24.9	<−72	−23.5	−33.5	< −77	Insoluble

TABLE VI. Individual Despretz coefficients ($K_m^{\pm}$) for the ions considered in this work [see Eq. (5) for the definition of $K_m^{\pm}$]. The coefficients were obtained from the regression of the experimental results (although similar values would had been obtained from the analysis of the simulation results).

Ion	$K_m^{\pm}$
Li^+	−3.0
Na^+	−11.6
K^+	−8.8
Mg^{2+}	−8.3
Ca^{2+}	−17.6
Cl^-	−3.2
SO_4^{2-}	−15.8

suppress the anomalies present in pure water when studying the minimum in the heat capacity of NaCl solutions.[116] We believe that the density anomaly is also suppressed in the case of of the $CaSO_4$ 2 m solution, as the density appears to follow the linear behavior expected from a conventional liquid down to 200 K. For $CaCl_2$, we were not able to simulate below 205 K, as the diffusion was hindered. We, therefore, conclude from Fig. 7 that the value of the TMD for these salts (in case there is still a maximum in density) lies below 205 K.

An interesting idea would be to analyze whether the Despretz law can be described using a group contribution method, that is, assuming that each ion contributes by a certain amount to a given macroscopic property so that

$$\Delta = (\nu_+ \, K_m^+ + \nu_- \, K_m^-)m = K_m \, m, \qquad (5)$$

where ν_+ and ν_- account for the stoichiometry coefficients of the cation and anion, respectively (for instance, $\nu_+ = 2$ and $\nu_- = 1$ for the Na_2SO_4 salt). This is a reasonable approach only at diluted concentrations, where ion–ion interactions play a minor role. Whenever properties of the salts are described by individual contributions of

the ions it is necessary to assign an arbitrary value to the contribution of one of the ions. Since LiCl is the salt with the smallest shift in the TMD (i.e., 6.3 K), we assign to the chloride anion contribution half of the total shift of LiCl (i.e., 3.2). Once the chloride contribution is set, the contributions of the rest of the individual ions were determined to reproduce as accurately as possible the experimental results. The best fit to the experimental results was obtained with the parameters provided in Table VI. The predictions of the shift in TMD via the group contribution method are given in Table VII. It is clear that the group contribution method is able to describe the experimental results quite well both for the chloride and for the sulfate salts in 1 m solutions. The ions with the smallest contribution are Li^+ and Cl^- followed by Mg^{2+}, K^+, Na^+, being SO_4^{2-} and Ca^{2+} the ones provoking the largest shifts. This group contribution to the TMD has been described in a recent review[13] although the individual values obtained in this work differ from those previously reported.[13] Note, though, that what really matters is the prediction for a certain salt since the individual values depend on the choice of an arbitrary value to a certain reference ion. If one assumes that the contribution of anions and cations to Δ is both negative, it seems reasonable to consider the salt with the smallest value of Δ (i.e., LiCl) and to assign to each of the ions half of the total value of Δ of this salt.
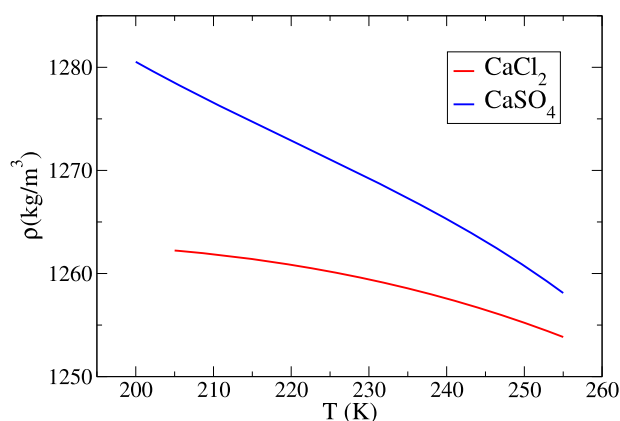

FIG. 7. Density for 2 m solutions at 1 bar as a function of temperature with the Madrid-2019 model. The density of $CaCl_2$ has been shifted +80 kg/m³ for visual clarity.

TABLE VII. Shift in the TMD of different salt solutions at a 1 m concentration measured experimentally and calculated from the individual contribution of each ion. The asterisk (*) indicates that the value has been estimated from extrapolation of the experimental results. Since for two salts the experimental values are not available (due to their low solubilities), in those cases, the group contribution estimation is compared to the results obtained from simulations using the Madrid-2019 model.

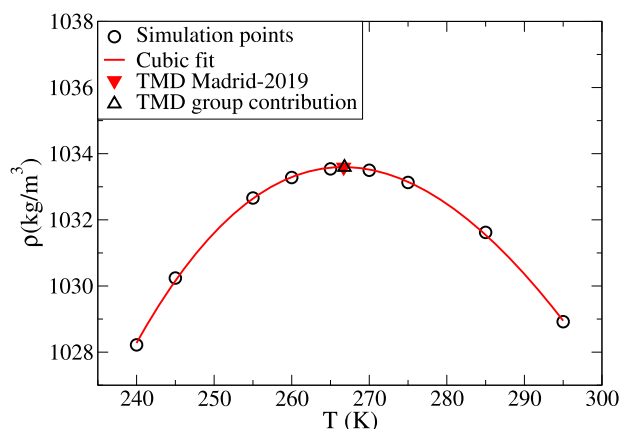| Salt	Group contribution shift (K)	Expt. shift (K)
LiCl	−6.2	−6.3
NaCl	−14.8	−14.4
KCl	−12.0	−12.1
$MgCl_2$	−14.7	−15.8
$CaCl_2$	−24.0	−23.5
Li_2SO_4	−21.8	−21.0
Na_2SO_4	−39.0	−40.1*
K_2SO_4	−33.4	−25.9(sim)
$MgSO_4$	−24.1	−23.2
$CaSO_4$	−33.4	−33.5(sim)

FIG. 8. Density (as a function of the temperature) of an aqueous solution containing two salts NaCl + LiCl for a concentration of 0.5 m for each individual salt and at 1 bar. Results were obtained from computer simulations using the Madrid-2019 force field. The value of TMD obtained from simulations was 266.7 K.

An interesting application of the group contribution method is that presumably it could help to predict the TMD of a multicomponent mixture of electrolytes (at least at low concentrations where crossed interactions between individual ions are not important). The idea is to use the Despretz law and to assume that the individual contributions ($K_m^{\pm}$) are additive. To test this idea, we have determined the TMD (by using computer simulations) of a binary mixture of LiCl (0.5 m) and NaCl (0.5 m) in water. Simulation results are presented in Fig. 8 and the value for Δ is −10.6 K. According to the ion contributions (see Table VI), in such a mixture, the Na$^+$ ion contributes −5.8 K, Li$^+$, −1.5 K and Cl$^-$ −3.2 K, yielding a total shift (Δ) of −10.5 K. Thus, it seems that it is possible to obtain a reasonable estimate of the TMD of multicomponent mixtures of electrolytes using the Despretz law for each individual ion (at least for a 1 m solution).

So far, we have presented the density of the solution in units of mass per unit of volume, which is a convenient magnitude in experiments. The fact that density rises more when adding a salt with a higher molecular weight to the solution does not provide a straightforward interpretation of how the salt affects the volume of the solution. In order to compare the expansion of the system in the presence of different electrolytes, we must somehow void the effect of mass. For this purpose, we could either represent the number density (number of particles per unit of volume) or simply plot the volume of the system for solutions with the same number of particles. We will hereby adopt the latter approach, since we only have two different number of particles for solutions with the same concentration, namely, those with stoichiometry 1:1 (575 particles for a 1 m solution) and those with stoichiometry 2:1 or 1:2 with (585 particles for a 1 m solution). These volumes are displayed in Fig. 9. If one bears in mind that different ions have different sizes, it is to be expected that the volume of the solution will be larger for the bigger ions. The estimation of the size of the ions by itself represents a challenge, which will be later addressed. However, as a first approximation, we can take the ionic radii (obtained from the distance between the ions in the crystal). The order of the cations by size is

Li$^+$ < Na$^+$ < K$^+$ for monovalent and Mg^{2+} < Ca^{2+} for divalent ones. Thus, intuitively one would expect that the volume of the system with the same number of cations (and with the same number and type of anions) would increase with the radii of the cations. However, the volume of CaCl$_2$ solution is smaller than that of the MgCl$_2$ solution and the LiCl solution has a larger volume than the NaCl solution (the same holds for the sulfate solutions). Intuition does not work to estimate the volume of a salt with a 1 m concentration. How is that possible? The volume of a solution has two contributions: the volume occupied by the ions and the volume occupied by water (from a thermodynamic point of view, the total volume is a sum of the partial volumes of each component and it is clear that the partial volume of water must be strongly affected by the type of ion dissolved in water). This points to the fact that water is somewhat more expanded in a magnesium solution (when compared to calcium solution) and the same is true for a lithium solution (when compared to a sodium solution). Thus, the volumes of water in lithium and magnesium solutions are larger than expected. Both of these cations (Li$^+$ and Mg^{2+}) have the highest charge density in their series (concerning monovalent and divalent cations). That points to a stronger electrostatic contribution in their interaction with water. In fact, magnesium is known to form an hexacoordinated complex in water.[117] This tight constraint of the water molecules in the first shell is also found around Li$^+$ cations (although in this case the lithium cation is tetracoordinated with water) and this fact has been linked to the unusual long residence times of water in the first hydration shell of both these cations.[118,119] Therefore, the structuring of water in the neighborhood of Li$^+$ and Mg^{2+} must be related to the unexpected expansion of water in these solutions.

In order to further analyze the volumes found in this work (Fig. 9), we have come up with a simple idea (admittedly far from any sophistication) which is to determine the "free volume available for water" in each solution. The free volume is hereby defined as

$$V_{free} = V - N_{cations}\ V_{cations} - N_{anions}\ V_{anions}. \qquad (6)$$

The free volume can be conceived as the volume available to water once the volume occupied by the ions is subtracted. Therefore, the free volume removes from the physical picture the fact that two salts may have different number of ions of different size, hence, focusing on the volume available to water. The ions are assumed to be spherical and their volumes are evaluated as $4/3\pi R^3$. In order to define the radii of ions in solution (which is not a trivial task), we shall use the formalism proposed by Schmid et al.,[120] which was quite useful in our previous work[84] to estimate the correction to the Gibbs free energy of hydration with a Born-like type formula. This prescription uses the distances d_{ion-O_w} (which is the first peak of the ion-O_w correlation function, being the O_w the water oxygen) and subtracts the volume contribution of the water molecule, which varies depending on whether it interacts with anions or cations. Admittedly, the assigned value to the size to the water molecule has a certain arbitrary character. Values of the radii of the ions obtained following this procedure are presented in Table VIII.

The results for the free volume are displayed in Fig. 10. Once the size of the ions is taken into account, the smallest volume occupied by water is found for the CaCl$_2$ solution and the largest being that of the LiCl solution. The same holds for the sulfates: the CaSO$_4$ solution has the smallest free volume and the Li$_2$SO$_4$ is the one
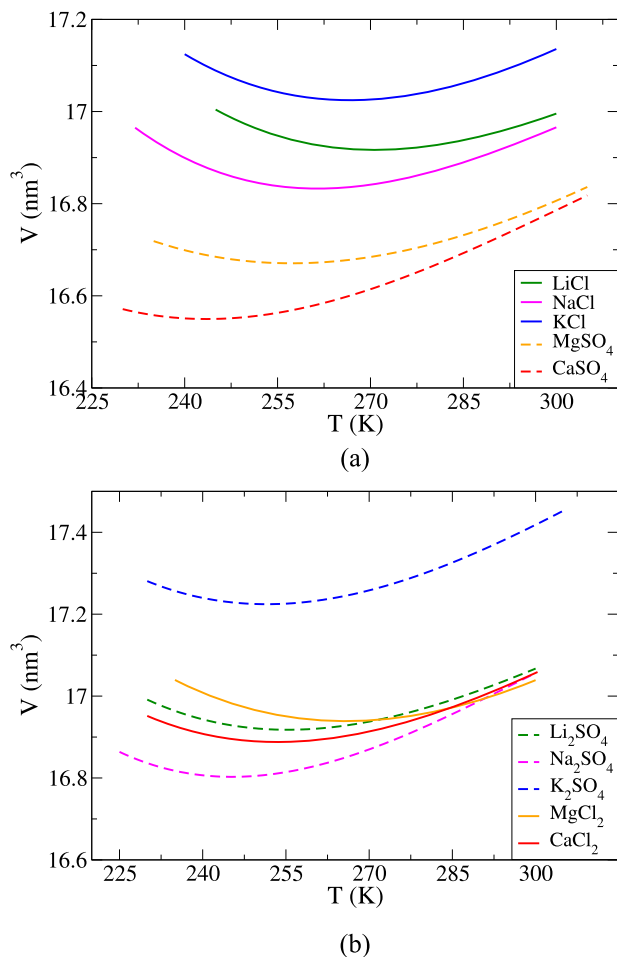
FIG. 9. Volume of solutions of (a) 1:1 electrolytes and (b) 2:1 and 1:2 at a concentration of 1 m using a system that contains 555 water molecules and the corresponding number of ions to obtain an 1 m solution.

TABLE VIII. Distance of the first peak d_{ion-O_w} (in Å) of the ion–water radial distribution function at 298 K (and, in parentheses, at 260 K). The radii of the cations and the anions are estimated using the prescription suggested by Schmid et al.[120] (i.e., subtracting 0.63 Å to cations and 1.40 Å to anions to the distance of the corresponding peak of the radial distribution function to account for the size of the water molecule). Note that the sulfate group has been considered as spherical and we have used the distance S-O_w as the $d_{anion-O_w}$. As can be seen, the radii of the ions estimated in this way are rather independent of the temperature in the temperature window of our simulations.

Salt	$d_{cation-O_w}$	R_{cation}	$d_{anion-O_w}$	R_{anion}
LiCl	1.84(1.84)	1.21	3.03(3.04)	1.63
NaCl	2.33(2.34)	1.70	3.03(3.04)	1.65
KCl	2.73(2.70)	2.10	3.03(3.04)	1.63
MgCl$_2$	1.92(1.92)	1.29	3.03(3.04)	1.63
CaCl$_2$	2.38(2.40)	1.75	3.03(3.04)	1.63
Li$_2$SO$_4$	1.84(1.84)	1.21	3.75(3.77)	2.35
Na$_2$SO$_4$	2.33(2.34)	1.70	3.75(3.76)	2.35
K$_2$SO$_4$	2.73(2.70)	2.10	3.75(3.75)	2.35
MgSO$_4$	1.92(1.92)	1.29	3.75(3.76)	2.35
CaSO$_4$	2.38(2.40)	1.75	3.75(3.76)	2.35

Finally, in the simulations (for which we have both free volumes and TMD at 1 m for all the salts), a correlation between the free volume of the solutions and the shift in TMD may be established. For the chloride solutions, the system with the largest free volume (LiCl) presents the smallest shift in TMD, whereas the biggest shift is found for the system with the smallest free volume (CaCl$_2$). The rest of the chloride salts (NaCl, KCl and MgCl$_2$) have similar shifts in the TMD and similar free volumes. For the sulfates, we also observe a correlation between the free volume and the shift in the TMD: the smaller the free volume, the larger the shift in the TMD (when comparing salts with the same stoichiometry). Thus, for sulfates with monovalent cations, the TMD shift increases in the order Li$^+$ < K$^+$ < Na$^+$, which is the order in which the free volume decreases and for divalent cations the shifts increases as Mg^{2+} < Ca^{2+}, which is also the reverse order of the free volume. We conclude that there is a certain correlation between the free volumes and the magnitude of the shift in the TMD.

Finally, it is useful to analyze the behavior of the thermal expansion coefficient α_p defined as

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p. \quad (7)$$

Obviously at the TMD, the thermal expansion coefficient (α_p) vanishes. This magnitude provides information regarding the local curvature of the density profile along the isobar. When α_p changes slowly, it means that the density profile is very flat over a wide range of temperatures. The results of α_p for the chloride solutions at 1 m are presented in Fig. 11.

Two interesting facts can be observed in the behavior of α_p. First, there is a kind of invariant-like point. For a temperature of 290 K, the value of α_p is ~20 ×10^{-5} K for all chloride salts. Second, when adding salt to water, not only is the TMD shifted but also the density vs temperature curve flattens. For the electrolyte solutions, it takes a wider range of temperatures (as compared to pure
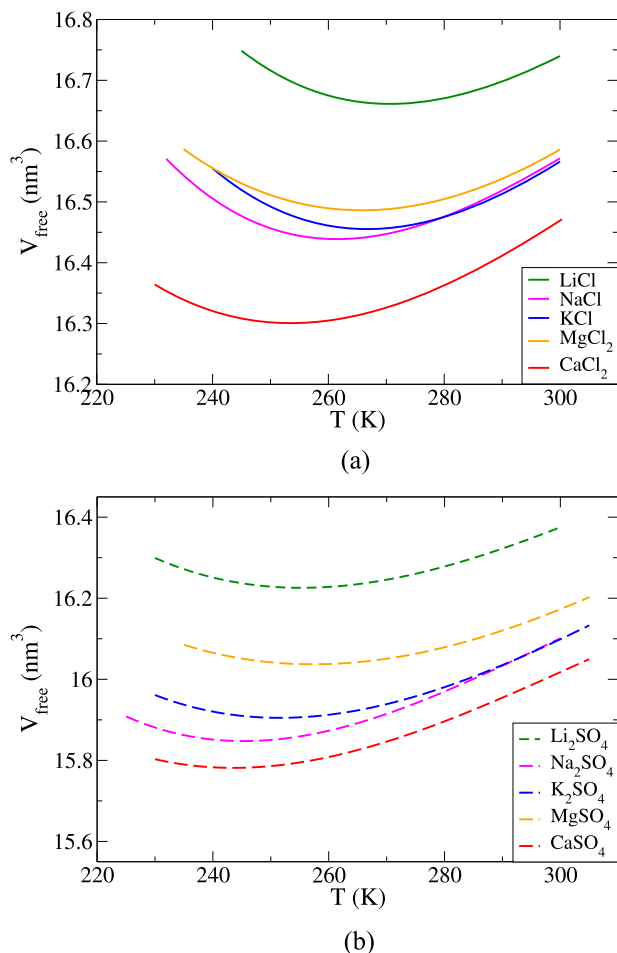
in which water is more expanded. In an oversimplification of the matter, the most expanded water can be regarded as the most tetrahedrically ordered (after all, ice is less dense than water and occupies more volume), and so it could be stated that in calcium solutions, water molecules are more disordered than for the other solutions, whereas for lithium solutions, water is more ordered. For potassium and sodium chloride solutions whose free volumes are rather similar to each other, the differences in the total volumes of the solutions (Fig. 9) can be reasonably well explained by the different sizes of the ions. Note that in Fig. 10, there is a crossing between the free volumes of NaCl and KCl at high temperatures, being the order as follows: KCl < NaCl < LiCl. This is consistent with a previous study of Nguyen et al.,[121] which showed that at room temperature for a 4 m solution, the packing of the water molecules around the monovalent ions followed the inverse order (that is K$^+$ > Na$^+$ > Li$^+$). They attributed this to the higher rigidity of the water molecules in the Li$^+$ solvation shells due to electrostatic forces, which lead to increasing voids in the surroundings of the cation.

FIG. 10. Free volume available to water in the (a) chloride and (b) sulfate solutions at 1 m concentration and room pressure. The free volume was evaluated from simulations for a system that contains 555 water molecules and the corresponding number of ions to obtain an 1 m concentration.

FIG. 11. Thermal expansivity coefficient, α_p, for pure water and chloride solutions at 1 m and room pressure as obtained from computer simulations of the Madrid-2019 force field.

FIG. 12. Relative densities (with respect to their values at the TMD, ρ_{max}) for 1 m and 2 m solutions of NaCl as obtained from computer simulations of the Madrid-2019 force field. Relative temperatures (with respect to the TMD) are represented in the x axis.

water) to reach the "invariant" point starting from the temperature at which $\alpha_p = 0$. Generally, the lower the TMD, the wider the interval required to reach a certain positive value of α_p. For sulfates (results not shown), we reached similar conclusions and the flattening of the density vs temperature curve is even more pronounced than for chlorides. Thus, as a rule of thumb, the lower the TMD, the flatter the density profile becomes. This rule also holds when comparing two concentrations of the same salt. In Fig. 12, we can see how the density profile of the 2 m solution of NaCl changes more slowly with temperature than that of the 1 m solution. In addition, for the 1 m solution, the density decrease is more pronounced at temperatures below the TMD than at temperatures above it. It is clear that the density vs temperature curve of electrolyte solutions is always flatter than that of pure water, making the determination of the TMD somewhat more difficult.
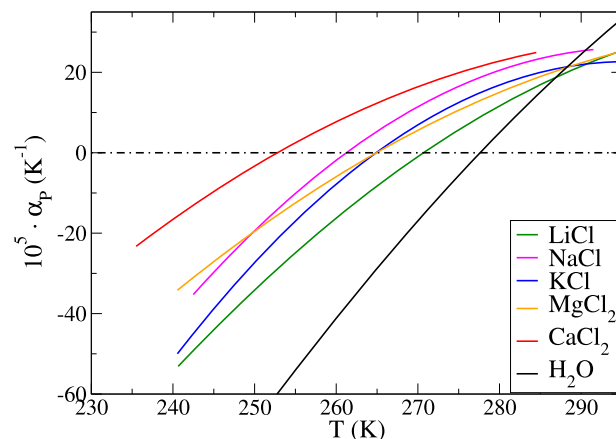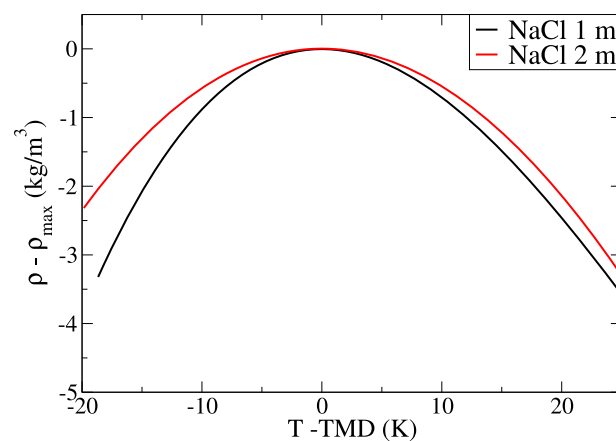
V. CONCLUSIONS

In this paper, we revisit the problem of the TMD (temperature of maximum density) for electrolyte solutions, a topic somewhat forgotten after intense research activity during the period of 1840–1930. We experimentally measured the maximum in density for several ionic solutions, including chlorides and sulfates at a concentration of 1 m. By using macroscopic samples, we were able to determine experimentally the TMD for temperatures down to 261 K. By using the method of Hare and Sorensen, we were able to reach temperatures of around 250 K and determine the maximum in density. We also estimated the TMD from computer simulations using the Madrid-2019 force field, which was able to reproduce the experimental results quite well not only for the location of the TMD but also for the density at the maximum.

For monovalent ions, we found that the shift in the TMD is approximately linear for concentrations up to 2 m (consistent with the Despretz law). However, for divalent cations, important deviations from linearity are observed for concentrations higher than 1 m. We also found that not all ions are equally efficient in shifting the TMD. For monovalent cations, the magnitude of the shift in the TMD follows the order $Li^+ < K^+ < Na^+$, and for divalent cations, the magnitude of the shift in the TMD follows the order $Mg^{2+} < Ca^{2+}$. Regarding the anions, the chloride ion produces a smaller shift in the TMD than the sulfate group. The "champions" in the capacity of shifting the TMD of water are Na_2SO_4 and $CaSO_4$, leading to shifts of about 35 K even for a 1 m solution. Calcium sulfate is insoluble in water so this prediction could not be corroborated experimentally, although considering the overall good performance of the force field, it seems reliable.

We address the possibility of describing the displacement of the TMD of a salt as a sum of the contribution of its individual ions. By assigning an arbitrary (but reasonable) value to the chloride anion, we were able to determine the contribution of each individual ion. The ordering found for the cations was $Li^+ < Mg^{2+} \simeq K^+ < Na^+ < Ca^{2+}$ and for the anions $Cl^- < SO_4^{2-}$.

Finally, in an attempt to understand the physics of the system, we represented the volume of the system as a function of temperature for all the electrolytes considered in this work. When the volume (instead of the density) is plotted, the effect due to the different atomic masses of the ions is avoided. We observed that lithium solutions had larger volumes than sodium solutions. Similarly, the volume of magnesium solutions was larger than that of calcium solutions. This counterintuitive finding reflects somewhat the distinct ordering of water molecules in the vicinity of the studied ions. For a 1 m solution, the number of molecules of water per ion is about 28 for 1:1 electrolytes and ~18 for 1:2 or 2:1 electrolytes. Typically, there are 4–7 molecules of water in the first hydration shell and 17–25 in the second one. This means that there is barely unperturbed water in the solution (i.e., each ion can be surrounded at most by two water layers without finding another ion). 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 hope that this work motivates further research on this topic, both in the experimental side and the simulation side. The TMD can certainly be useful to develop new force fields for electrolytes and to provide a molecular understanding of how their presence affects the structure of water.

DEDICATION

We would like to dedicate this paper to the memory of C. Austen Angell. He has been a source of inspiration for younger researchers, with constant curiosity up until the very end, always providing good advice and leading the research concerning the behavior of supercooled water and solutions.

SUPPLEMENTARY MATERIAL

In the supplementary material, we have collected the numerical results for densities obtained in this work via experiment and simulations.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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