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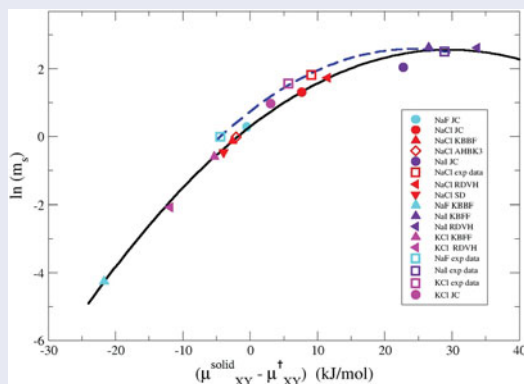
Estimating the solubility of 1:1 electrolyte aqueous solutions: the chemical potential difference rule

A.L. Benavides^a, M.A. Portillo^b, J.L.F. Abascal^b and C. Vega^b

^aDivisión de Ciencias e Ingenierías, Universidad de Guanajuato, Guanajuato, Mexico; ^bDepartamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain

ABSTRACT

A simple empirical rule to estimate the solubility of force fields of 1:1 aqueous electrolyte solutions at ambient conditions is proposed. The empirical prescription states that the logarithm of the solubility can be described by a second-order polynomial of the chemical potential difference of the salt in the solid and the salt in the standard state in solution. The rule will be denoted as the chemical potential difference rule. It is shown that the recipe is able to provide reasonable values of the solubility of 1:1 aqueous electrolytes (having the NaCl structure in the solid phase) for a number of different force fields for which the solubility has been computed in a rigorous way. This clearly indicates that reproducing only the experimental values of the free energy of hydration of ions at infinite dilution (which yield the standard state chemical potential of the salt in water) is not enough to foresee the experimental values of the solubility. The difference between the chemical potential of the salt in the solid phase and in the standard state seems to be the variable that controls the value of the solubility. This finding should be taken into account in the future when developing force fields for 1:1 electrolytes in water aimed at reproducing the experimental solubilities.



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1. Introduction

Computer simulations play an important role in providing a molecular understanding of fluids. Nowadays they are applied to a variety of systems, including simple and molecular liquids, polymers, colloids, biomolecular systems and liquid mixtures. Since the results obtained from computer simulation depend on the quality of the force field used to describe the interactions between molecules, the research of realistic intermolecular potentials is an active area of research. Liquid water is one of the systems that has been studied more often by computer simulations and it is not surprising that a number of potentials have

been proposed for this important molecule [1]. However, concerning its mixtures there is still room for building improved force fields. Systems, as for example CuCl and AgCl are important components of hydrothermal fluids and AgCl also plays a crucial role as a reference electrode in electrochemistry [2,3]. Seawater is also an important water solution. Most of Earth's surface is covered by seawater. It is mainly composed by pure water (around 96.5%) plus a number of elements and ionic species. However, if one wants a quick and approximated description of seawater one can say that it is a 0.55 molal solution of NaCl in water (where molality describes the number of

moles of salt per kilogram of water). The properties of seawater play a crucial role in determining the climate on Earth. It is also true that desalination will become (as anticipated by Johann Fischer) a crucial theme of research in the future [4]. Besides, probably reflecting that life started on the seas, the cells contain, besides water, a significant amount of NaCl (with a concentration around 0.1 molal). It means that proteins and many other biological molecules act in a medium that contains not only water but also certain amounts of salt. The two examples of NaCl aqueous solutions illustrate the importance of having an accurate description of them for life on Earth. Thus, computer simulations of aqueous salt solutions are and will be an important area of research and accurate force fields are required for them [5–28].

How to develop a good force field for an ionic solution (say NaCl in water)? Certainly, first-principles calculations can be used to obtain the intermolecular forces for ionic solutions [29,30]. However, this route is very expensive and more often an effective approximated force field is proposed and a set of target properties are selected to find the potential parameter values able to reproduce as closely as possible the set of selected properties. Until recently, the typical set of target properties for ionic solutions included the hydration free energy of the salt at infinite dilution [31–33], the radial distribution functions (rdf) and the density of the solution because these magnitudes are available from experimental work. As usual, one is selecting properties involving the size of the molecules (rdf, density) and properties involving the energy of the interactions (the hydration free energy). In our previous studies with water we have shown that phase equilibria in general, and in particular the fluid–solid equilibria can be very useful when developing force fields. In the case of salt solutions, an interesting property is the solubility limit (or more simply, the solubility) defined as the maximum amount of salt that water can dissolve before salt precipitation occurs. The solubility could indeed be a target property to develop force fields but a procedure to determine it in computer simulations is needed. The first paper dealing with the problem of the solubility of an ionic salt (KF) in water by simulation was done by Ferrario *et al.* [34], followed by the work of Sanz and Vega [35] for NaCl. After these works several efforts have been performed to calculate the solubility by simulation of other ionic aqueous solutions [36]. The solubility of several models of NaCl in water has been computed by different groups using the chemical potential route [24,37–40]. The chemical potential route requires the knowledge of the chemical potential of the salt in the solid phase and the chemical potential of the salt in solution at different concentrations since at equilibrium the chemical potential in both phases should be equal. Two models of NaCl that have received

considerable attention are those proposed by Joung and Cheatham (JC) [41] and by Smith–Dang (SD) [42]. Both are based on the SPC/E water model [43]. For these two models, the results of the solubility (at room temperature and pressure) recently reported by three research groups are in mutual agreement [39,40,44–46]. This is important since it has clarified previous discrepancies found in the literature for the solubility of the JC and SD models using different methodologies. However, there are still some important open challenges concerning the evaluation of the solubility by numerical simulations for ionic solutions [36]. For instance, polarisable and non-polarisable models are still far from reproducing the experimental solubility of the NaCl aqueous solution using the chemical potential route [5,47]. Another issue is that the solubility obtained from direct coexistence simulations [24–27,48] was apparently different from that calculated via the chemical potential route. This issue has been solved recently [49] though it is fair to say that some further theoretical work is needed to understand completely the impact of charged interfaces on phase equilibria of finite size systems [50]. In any case, the solubilities obtained from direct coexistence in the recent work [49] are at least in very good agreement with those evaluated through the chemical potential route. However, long runs (lasting microseconds) and large systems (containing several thousand particles) are needed for the direct coexistence technique. Therefore, this way of determining solubilities becomes also very expensive from a computational point of view. We can conclude that the calculation of the solubility is computationally expensive regardless of whether one is using the chemical potential or the direct coexistence route. Note that efficient techniques to obtain phase equilibria as the NpT+test particle method [51] proposed by Lofti, Vrabec and Fischer or the Gibbs ensemble developed by Panagiotopoulos [52] cannot be employed in principle to determine the solubility of an electrolyte in water.

When developing force fields it is often the case that several models must be tested before arriving to the ‘optimised’ model. For this reason, it may be difficult and expensive to develop force fields aimed at reproducing the experimental values of the solubility. With this last difficulty in mind, it is interesting to try to find simple rules to help in the design of force field models for ionic solutions. Is there any way to have an approximate idea of the solubility of a model without these expensive calculations? If one is looking for an alternative method to determine the solubility which is both fast and rigorous then the answer (at present) is no. However, the answer could be different if we look for a simple and efficient recipe to estimate the solubility in an *approximated* way. Rules

to estimate phase transitions are not new in computer simulations. For instance, the Hansen–Verlet freezing criterion [53], the excess entropy freezing rule [54] or the Lindemann melting prescription [55] are often invoked in computer simulation studies. In a previous work, some of us proposed two empirical rules that can give a rough estimation for the NaCl aqueous solution solubility at 298 K and $p = 1$ bar. One of them is based on the number of ionic pairs as a function of molality (which can be easily obtained from simple NpT or NVT simulations). The other rule requires the calculation of the NaCl solid chemical potential and the standard chemical potential of the salt in solution. As mentioned above, the NaCl solid chemical potential is also required for the estimation of the solubility using the chemical potential route, so its calculation cannot be avoided with this rule. The NaCl solid chemical potential can be obtained, for instance, with well-established methodologies such as the Einstein crystal [56] or the Einstein molecule techniques [57–60]. The evaluation of the infinite dilution chemical potential can be performed through any of the chemical potential route methods but using a narrower interval of concentrations than in a normal solubility calculation. These two empirical rules worked well for three models of NaCl aqueous solution at ambient conditions (see Figures 10 and 11 in Ref. [46]). The aim of this work is to explore whether these two prescriptions also apply to other 1:1 electrolytes at ambient conditions.

2. Results

Mester and Panagiotopoulos [45] have evaluated the solubility of different force fields for 1:1 salts (in particular, NaCl, NaI, NaF and KCl) in SPC/E water using the chemical potential route. Therefore, their results allow to test the two empirical rules. They considered the model of Weerasinghe *et al.* [61] for Na^+ and Cl^- and the models of Gee *et al.* [62] for K^+ and F^- , both models referred to as KBFF, the model of Reiser *et al.* [9] (RVDH) and the Joung and Cheatham model [41] (JC). The parameters of these models are given in Tables I and II as Supplementary material of Ref. [45]. Some relevant data for these models will be used in this work and are shown in Table 1. We shall now test the two recently proposed empirical rules for the evaluation of the solubility.

2.1. The ionic pairs rule

The ionic pairs rule of NaCl in aqueous solution says that an approximated value of the solubility, at $T = 298$ K and $p = 1$ bar, may be obtained as the concentration at which the number of ionic pairs is close to 0.075. The ionic pair

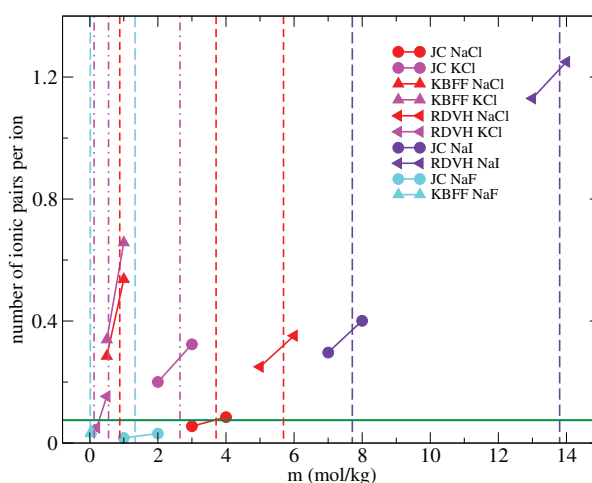


Figure 1. Number of ionic pairs per ion versus molality for several models of NaCl, KCl, NaI and NaF aqueous solutions. The horizontal line corresponds to the 0.075 number of ionic pairs per ion and the solubilities of the models [45] are shown as vertical dashed lines.

formation occurs when a cation and an anion are in direct contact in the solution at a given concentration. It can be calculated from the cation–anion radial distribution function obtained in NpT or NVT simulations by integrating it up to the first minimum [10,66]. See also Equations (12) and (13) in Benavides *et al.*'s [46] work. Our calculations for the ionic pairs per ion of several models for NaCl, KCl, NaI and NaF aqueous solutions are presented in Figure 1. The simulations were performed using Gromacs with 555 molecules of water and different number of ions to mimic the nominal salt concentration. All details are similar to those of our recent work [46]. Simulations typically lasted 20 ns, with a time step of 2 fs, with a Nosé–Hoover thermostat and a Rahman–Parrinello barostat using in both cases a relaxation time of 2 ps. The Lennard–Jones (LJ) and the Coulomb real space contributions were truncated at 9 Å, and the Particle Mesh Ewald (PME) technique was used to deal with the electrostatic interactions. Long range corrections to the LJ part of the potential were also added.

For each salt two concentrations were selected, one slightly below and another one slightly above the reported solubilities. The solubilities calculated by Mester and Panagiotopoulos and the experimental ones are shown in Table 1. Solubility values are shown as vertical dashed lines in the Figure 1. Since, for some of the solutions, Panagiotopoulos and co-workers do not give the solubility value but rather an open interval (see Table 1), we decided to use the limit value of these intervals: for the KBFF model of NaI we used the $m_s = 14$, for the RDVH model of NaF we used $m_s = 0.011$ and for the JC model of NaF we used $m_s = 1.33$. Thus, the number of ionic pairs at the solubility limit corresponds (approximately) to the

Table 1. Some simulation properties for KBFF, RDVH and JC models of NaCl, NaI, NaF and KCl aqueous solutions at $T = 298.15$ K and $p = 1$ bar as obtained by Mester and Panagiotopoulos [45]. The Henry's law standard state chemical potentials experimental data, μ^\dagger , are taken from Wagman *et al.* [63] The experimental solid chemical potentials, μ^{solid} , are taken from the NIST-JANAF thermochemical tables [64], and the experimental solubilities, m_s , from the CRC Handbook of Chemistry and Physics [65].

Salt	Property	KBFF	RDVH	JC	Experiment
NaCl	μ^{solid} (kJ/mol)	-407.521(2)	-384.910(2)	-384.060(2)	-384.024
	$\mu^\dagger_{\text{NaCl}}$ (kJ/mol)	-404.9(2)	-396.4(2)	-391.7(2)	-393.133
	m_s (mol/kg)	0.88(2)	5.69(7)	3.71(4)	6.15
NaI	μ^{solid} (kJ/mol)	-304.773(2)	-315.078(2)	-288.182(2)	-284.572
	μ^\dagger_{NaI} (kJ/mol)	-331.3(2)	-348.8(2)	-310.9(2)	-313.47
	m_s (mol/kg)	>14	13.8(2)	7.71(6)	12.28
NaF	μ^{solid} (kJ/mol)	-505.412(2)	-530.221(2)	-539.779(2)	-545.081
	μ^\dagger_{NaF} (kJ/mol)	-483.7(2)	-496.4(2)	-539.3(2)	-540.68
	m_s (mol/kg)	0.0142(4)	<0.011	>1.33	0.99
KCl	μ^{solid} (kJ/mol)	-419.023(2)	-401.306(2)	-406.943(2)	-408.761
	μ^\dagger_{KCl} (kJ/mol)	-413.7(2)	-389.4(2)	-410.0(2)	-414.49
	m_s (mol/kg)	0.55(1)	0.126(3)	2.65(5)	4.77

intermediate value between these two concentrations. This procedure was used to have a certain idea of the statistical error in the number of ionic pairs (by having two concentrations) and also to analyse the slope of the increase of the number of ionic pairs with concentration in the vicinity of the solubility limit.

As it can be seen this rule is not a general one for 1:1 electrolyte models since the concentrations at which the formation of ionic pairs is around 0.075 are not close to the reported solubilities, except for some models of NaCl. Thus, our recently proposed rule does not hold in general and should not be used. However it seems that, at least, we can state one conclusion after analysing the results of Figure 1. For all models with moderate solubility (i.e. lower than 10 m), the number of ionic pairs at the solubility limit is lower than 0.5 (50%). Note that the particular case of the high solubility of NaI could be explained by the disparate sizes of the cation and anion which translate in a small value of μ_{XY}^{solid} even in a halite crystal structure (the ions with opposite charge to that of a given one are at almost similar distances than those with like-charges). Thus if the number of ionic pairs found in a computer simulation of a 1:1 electrolyte is 0.5 or higher, it is most likely that the considered solution is supersaturated, i.e. at a concentration above the solubility limit. Quite often, in simulations of biological molecules in water containing small amount of 1:1 salts, it has been reported that the ions were forming dimers even at low concentrations. In retrospective this seems to be a clear indication that the salt was supersaturated (with respect to the solubility limit of the considered model). One should remind that a 1 m solution of NaCl in water can be supersaturated even though the experimental solubility of NaCl in water found is 6.1 m because the solubility of the

model is not necessarily identical to the experimental one. Besides, since most of the force fields tend to provide low values of the solubility, this seems to be a rather general problem [39].

2.2. The chemical potential difference rule

The chemical potential of a 1:1 electrolyte XY (X=cation, Y=anion) in water can be expressed in terms of the activity coefficient as

$$\mu_{XY} = \mu_{XY}^\dagger + 2RT \ln m + 2RT \ln \gamma(m). \quad (1)$$

where μ_{XY}^\dagger is the Henry's law (infinite dilution) standard chemical potential of the salt, m is the molality of the salt in solution (i.e. the number of moles of salt per kilogram of water) and $\gamma(m)$ is the mean ionic coefficient (in the molality scale) which is a measure of the deviation of the salt chemical potential from the ideal solution. Note that the activity coefficient γ depends on the salt concentration. The solubility, m_s , can be computed in a rigorous way by equating the chemical potential of the salt in the solid phase, μ_{XY}^{solid} , to that of the salt in the solution:

$$\mu_{XY}^{\text{solid}} = \mu_{XY}^\dagger + 2RT \ln m_s + 2RT \ln \gamma(m_s) \quad (2)$$

It is clear that, to properly determine the solubility, one needs to know the value of μ_{XY}^{solid} , μ_{XY}^\dagger and γ . For the computation of μ_{XY}^{solid} , it is necessary to perform calculations for the pure solid while for the determination of μ_{XY}^\dagger one requires to perform calculations of the salt in water at infinite dilution. It is interesting to point out that the standard chemical potential is related to the excess chemical potential of the salt at infinite dilution (the connection between

these two magnitudes was described by Sanz and Vega [35]). However, the evaluation of γ relies on the determination of the chemical potential of the salt in solution at several concentrations and that makes the calculations somewhat expensive. For this reason we tried recently to estimate (in a approximate way) the solubility using only μ_{XY}^{solid} and μ_{XY}^{\dagger} . Based on the results obtained for some force fields of NaCl in water, we suggested the following rule (with the chemical potentials given in kJ/mol):

$$\begin{aligned} m_s &= 1.552 + 0.275 (\mu_{\text{NaCl}}^{\text{solid}} - \mu_{\text{NaCl}}^{\dagger}) \\ &= 1.552 + 0.275 \Delta\mu, \end{aligned} \quad (3)$$

where we have defined $\Delta\mu$ as

$$\Delta\mu = (\mu_{XY}^{\text{solid}} - \mu_{XY}^{\dagger}) \quad (4)$$

In particular, we showed [46] that this prescription was able to provide reasonable values for the solubility of the following force fields of NaCl in water: JC/SPC/E [41], SD/SPC/E [42], JC-SPC/E-ion/TIP4P/2005 [46], JC/TIP4Pew [40], AH/BK3 [5,47,67,68], KBI-SPC/E [45,62,69] and SD-BMHTF-SPC/E [40,70–73]. This rule was designed to predict the solubility of models with values of $\Delta\mu$ between -3 and 8 kJ/mol. In fact, within this range of values, the rule works very well. However, for some of the models considered by Mester and Panagiotopoulos [45], $\Delta\mu$ can be as low as -20 kJ/mol and as high as 30 kJ/mol. Therefore, it would be desirable to have an extended version of the rule able to cover a wider range of $\Delta\mu$ values. Here, we investigate an alternative empirical recipe that it is able to reproduce reasonably well all the simulation results for the solubility of 1:1 electrolytes.

In Figure 2, the natural logarithm of the solubility of different XY salts solution models is presented as a function of the difference of chemical potentials, $(\mu_{XY}^{\text{solid}} - \mu_{XY}^{\dagger})$. Almost all the solubilities can be correlated in a unique curve (dark continuous line). Thus, although our initial rule stating that the solubility is a linear function of the difference between the chemical potential of the solid and that of the standard state does not work, the generalised version presented in Figure 2 is able to describe the results quite well. A justification of this curve can be obtained from the expression of equal chemical potential of the salt in the solid and in solution (Equation (2)). Then for electrolytes 1:1 we may write

$$\ln m_s = \frac{1}{2RT} (\mu_{XY}^{\text{solid}} - \mu_{XY}^{\dagger}) - \ln \gamma(m_s) \quad (5)$$

It is shown in Figure 2 that simulation results for $\ln(m_s)$ can be described quite well by a second-order polynomial of $(\mu_{XY}^{\text{solid}} - \mu_{XY}^{\dagger})$. This implies that $\ln \gamma(m_s)$ can be approximated by a second-order polynomial of $(\mu_{XY}^{\text{solid}} - \mu_{XY}^{\dagger})$. Let us discuss briefly the trends shown in Figure 2.

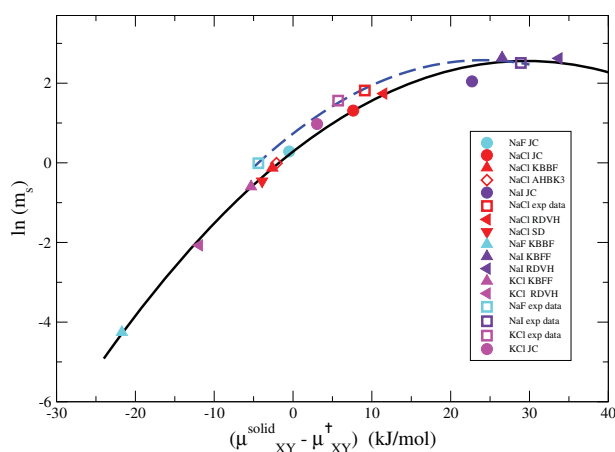


Figure 2. (Colour Online) Natural logarithm of the solubility m_s for different XY salts dissolved in water as a function of $(\mu_{XY}^{\text{solid}} - \mu_{XY}^{\dagger})$, the difference between the XY solid chemical potential, μ_{XY}^{solid} , and the XY standard dissolution chemical potential, μ_{XY}^{\dagger} . Symbols in red are for NaCl, indigo are for NaI, light blue for NaF and magenta for KCl aqueous solutions. Open squares with the corresponding colour represent the experimental data. We have included the results of Mester and Panagiotopoulos [45] for NaCl, NaI, NaF and KCl with the ions models of Weerasinghe *et al.* [61] for Na^+ and Cl^- and the models of Gee *et al.* [62] for K^+ and F^- , both labelled as KBFF, the model of Reiser *et al.* [9], labelled as RVDH and the Joung and Cheatham model [41] labelled as JC, all in SPC/E water [43]. Besides, the polarisable model AHBK3 [5,47,67,68] is shown for the NaCl aqueous solution. The blue discontinuous line represents an interpolation curve for the experimental data to guide the eye. The black continuous line is a polynomial fit using the data presented.

For salts with low or moderate solubility the activity coefficient is not too different from one and for this reason the solubility grows with $\Delta\mu$ (see Equation (5)). However, the solubility seems to reach a maximum value for very large values of $\Delta\mu$. The reason is the significant increase of the activity coefficient at high concentrations that according to Equation (5) contributes to reduce the solubility.

The take home message from Figure 2 is simple: developing force fields for salts in water aimed at describing only the standard state chemical potential does not seem to be a good idea. This has been the common procedure over the last three decades. What seems more efficient is to develop force fields which describe the difference between the chemical potential of the solid and the standard chemical potential.

In Figure 2, we have also included the experimental results for three salts in water. The experimental data for these electrolyte solutions can also be correlated quite well by a polynomial expression. However, the curves showing the results of the models and those of the experiments are not identical since the latter ones are slightly shifted upwards. This strongly indicates that something is wrong with all of the models of ions in water. It is not

clear what is the origin of this failure. Probably the reason is similar to that found for all models when describing the diffusion coefficient of water in salt solutions [6,12]. One could of course argue that the failure is due to the fact that we are using in this work non-polarisable models for water (SPC/E) as well as for ions. This is certainly true. However, it is interesting to point out that the solubility of a polarisable force field of NaCl in water [68] is also well below the experimental value. Further work is needed to understand the origin of this deviation between the experimental and the simulation curves.

In any case, it is clear that we have found a simple prescription to estimate qualitatively the solubility of a 1:1 electrolyte at ambient conditions. The key quantity is the difference in chemical potential between the solid and the standard state of the solution. If one wants a large value of the solubility this difference must be large and positive. If one wants a low solubility the difference should be negative and with a large absolute value. This information provides a hint about how to modify the parameters of the force field. If the solubility of the model is low when compared to experiment, one may either increase the interaction energy between the ions and water (keeping the ion–ion potential parameters) or decrease the interaction energy between the ions (keeping the ion–water potential parameters). An analogous recipe would apply when the solubility is higher than the experimental value.

The main conclusion of this work is a correlation between $\ln m_s$ and $\Delta\mu$ found for 1:1 models of electrolytes. The correlation is given by the following expression:

$$\ln m_s = 0.28127 + 0.15403\Delta\mu - 0.0026054\Delta\mu^2, \quad (6)$$

where $\Delta\mu$ is given in kJ/mol. This recipe should be used for salts having the NaCl solid structure, also denoted as the halite structure, and it cannot be applied to CuCl, CsCl, or AgI as these salts crystallise in a different type of solid. Besides, its application is recommended in the region that was considered for the analysis: $0.01 m \leq m_s \leq 15 m$ and $-20 \text{ kJ/mol} \leq \Delta\mu \leq 30 \text{ kJ/mol}$.

Let us show a couple of examples to illustrate that it can be used to estimate solubilities for models not shown in Figure 2. For instance, for the NaCl model of Joung and Cheatham designed to be used along with the TIP4P-Ew model of water [74] this correlation estimates a solubility of 1.38 m (taking into account that $\Delta\mu = 0.28 \text{ kJ/mol}$ [37,40]) to be compared with the value obtained from rigorous calculations (1.43 m) [40]. For the JC-SPC/E ion-TIP4P/2005 model (described in our previous work [46]),

Equation (6) predicts a solubility of 2.8 m to be compared with the value obtained from free energy calculations, namely 3.5 m. The agreement, although not perfect, is still reasonable taking into account that the standard chemical potential was obtained from simulations using 270 molecules of water which is probably a small system size to determine the standard chemical potential accurately. In any case these two examples show that Equation (6) does not only provide a reasonable estimate for the solubility of 1:1 electrolytes in SPC/E water but also when other models of water are used. We hope that this simple expression can be used as a guide to those interested in developing force fields of ions in water aiming to reproduce the experimental solubilities.

For salts with very low solubility ($m_s < 0.001 m$, i.e. $\Delta\mu < -30 \text{ kJ/mol}$) the more reasonable choice is to assume that at high dilution $\gamma \simeq 1$ and then to estimate the solubility using the following expression:

$$\ln m_s = \frac{\Delta\mu}{2RT} \quad (7)$$

In fact this simple recipe describes correctly the solubility of highly insoluble salts as AgCl and AgBr (which crystallise in the NaCl structure) when the experimental values of $\Delta\mu$ for AgCl and AgBr are used.

Note finally that the availability of approximate values of the solubility limits may also be useful in future studies dealing with the kinetics of salt precipitation [75,76].

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Disclosure statement

No potential conflict of interest was reported by the authors.

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