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Continuous medium approach to approximate the high concentrated aqueous electrolyte with different type of electrochemical structure

Marion Maffre, Xuanze Wang, Jie Deng, Siraprapha Deebansok, Yachao Zhu, Frédéric Favier, Daniel Bélanger, Olivier Fontaine

Abstract

Superconcentrated aqueous electrolytes have recently emerged as a new class of electrolytes, called water-in-salt electrolytes. They are distinguished, in both weight and volume, by a quantity of salt greater than water. Currently, these electrolytes are attracting major interest, particularly for application in aqueous rechargeable batteries. These electrolytes have only a small amount of free water due to an ultrahigh salt concentration. Consequently, the electrochemical stability window of water is wider than the predicted thermodynamic value of 1.23 V. Hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) have been shown to be shifted to more negative and positive potentials, respectively. The decrease in free water population is recognized as being involved in the increase in the electrochemical stability window of water. Here, we study the quantitative contribution of the decrease in the free water molecule concentration to the permittivity of the solution and of the activity of water to the OER and HER overpotentials when the salt concentration increases. We compare our model with that of Kornyshev and get three types of electrolyte structures: diluted, gradient of water contents, and aggregation. The theoretical calculation of the redox potentials of the OER and HER is compared with the experimentally determined electrochemical properties of aqueous LiTFSI electrolytes.

Introduction

Solvent-in-salt electrolytes are concentrated electrolytes in which the amount of salt, in mass and volume, is smaller than that of the solvent. The solvent may be non-aqueous^{1–4} or aqueous.^{5–7} In contrast to their non-aqueous counterparts, concentrated aqueous electrolytes called “water-in-salt” electrolytes (*WISEs*) are particularly attractive. This is mainly because water is inflammable^{1,2} that these electrolytes are opening a new direction to the production of safer electrochemical energy storage devices.^{6,8}

The increase in salt concentration raises the electrochemical stability window of water to $\sim 3\text{--}4$ V,⁹ while it is thermodynamically limited to 1.23 V.¹⁰ This is due to the greater overpotentials of both hydrogen [*HER*, Eq. (1)] and oxygen evolution reactions [*OER*, Eq. (2)] in such superconcentrated electrolytes,



This extension of the electrochemical stability window of water in concentrated aqueous electrolytes can be explained by two phenomena: first, by the decrease in the quantity of free water in the solution as the salt concentration increases,¹¹ and second, by the modification of the electrode/electrolyte interface at extreme negative and positive potentials in *WISEs*.^{5,9,12–16} At the negative electrode, the *HER* potential shift is attributed to the formation of a solid–electrolyte

interphase (*SEI*),¹⁻³ while the shift of the *OER* potential at the positive electrode is correlated with a particular structure of the electrochemical double layer.^{4,5}

For a diluted aqueous solution composed of lithium bis(trifluoromethylsulfonyl)imide (LiTFSI), called salt-in-water electrolyte (*SIWE*), it is known that cations have a complete solvation shell, i.e., the amount of water molecules in the solution is sufficient to dissociate and solvate the ions.^{4,5,15,17} However, this is no longer the case for *WISEs*; the lithium ions are under-hydrated.^{5,15,17,18} This leads to three important changes in the solution. The first one is the decrease in the solvated radius of ions, and thus the distance between ions. The second is the decrease in water activity (especially free water molecules). For diluted electrolytes, the activity of the solvent is considered to correspond to an infinite dilution factor and is equal to one.¹⁹⁻²¹ However, this is not the case for concentrated electrolytes since the solvent is no longer in sufficient excess. Maki *et al.*²² studied the dependence between the water activity and the molar fraction of salt in aqueous CaCl₂, MnCl₂, and ZnCl₂ solutions. They have shown that an increase in salt concentration leads to a decrease in the activity coefficient of water. The third corresponds to the change in solution permittivity. The permittivity of electrolyte solutions is lower than that of the pure solvent.²³

Moreover, the Nernst equation for the *HER* and *OER* depends on the water activity,

[Eqs. (3) and (4), respectively], at pH = 7,¹¹

$$E_{HER} = E_{H_2/H_2O}^0 - \frac{R \cdot T}{2 \cdot F} \ln \left(\frac{(a_{H_2}) \cdot (a_{OH^-})^2}{(a_{H_2O})^2} \right), \quad (3)$$

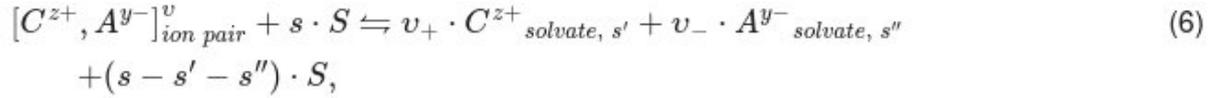
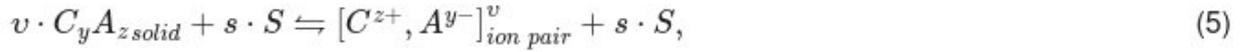
$$E_{OER} = E_{O_2/H_2O}^0 + \frac{R \cdot T}{4 \cdot F} \ln \left(\frac{(a_{O_2}) \cdot (a_{H^+})^4}{(a_{H_2O})^2} \right), \quad (4)$$

where E_{H_2/H_2O}^0 and E_{O_2/H_2O}^0 are the standard potentials of the *OER* and *HER* [V vs standard hydrogen electrode (SHE)], respectively, R is the perfect gas constant (8.314 J K⁻¹ mol⁻¹), T is the temperature (K), F is Faraday's constant (9.648 × 10⁴ C mol⁻¹), and a_i is the activity of species i . Thus, as the Nernst potential is independent of water activity for diluted electrolytes, it becomes dependent on water activity for concentrated electrolytes. However, the water activity is difficult to determine.

In this study, we will study the effect of salt concentration on the distance between the ions, the activity coefficient of water, and the permittivity of the solution. The dependence of hydrated radius of ions and salt concentration will be calculated using the Stokes–Einstein equation. The water activity will be determined by the *Gibbs–Duhem*²⁴ relation and *Debye–Hückel*²⁵ theory. The effect of salt concentration on electrolyte permittivity will be quantified by approximating the permittivity as a function of water permittivity. Finally, these parameters will enable us to predict the potential of *OER* and *HER* by the Nernst equation. For this purpose, aqueous electrolytic solutions based on LiTFSI will be studied.²⁶ It will be shown that salt concentration impacts the distance between the ions, the solution permittivity, the water activity, and the *OER* and *HER* potentials. For that, we introduce a model of a dielectric medium with an effective permittivity, shown as ϵ_{eff} , and different water permittivities, ϵ_{water} .

DETERMINING THE DISTANCE BETWEEN CATIONS OF DIFFERENT CONCENTRATIONS

An electrolytic solution is obtained when a salt dissociates into ions in the presence of a solvent.²⁷ The process of dissociation of a given salt C_yA_z into cations C^{z+} and anions A^{y-} in a solvent S proceeds in the following two steps:



where v denotes the stoichiometric coefficient, $C_yA_z \text{ solid}$ denotes the salt, s denotes the stoichiometric coefficient of free solvent molecules, S denotes the solvent, $[C^{z+}, A^{y-}]_{ion \text{ pair}}^v$ denotes the ion pairs from the salt, v_+ denotes the stoichiometric coefficient from the solvated cations, $C^{z+}_{\text{solvate}, s'}$ denotes the solvated cation, v_- denotes the stoichiometric coefficient from the solvated anions, $A^{y-}_{\text{solvate}, s''}$ denotes the solvated anion, s' denotes the stoichiometric coefficient of molecules of solvent that solvates the cations, and s'' denotes the stoichiometric coefficient of molecules of solvent that solvates the anions. In a solution, the cationic charge is stabilized either by the solvent molecules or by the anions. In Eqs. (5) and (6), a parameter s is introduced as the number of solvent molecules, and two different cases can be considered for this parameter.

A very large s corresponds to a very low salt concentration, for example, 0.001 mol of salt in 10 l of solvent. In the present case, the solvent used is water and an electrolyte with a very large s is called salt-in-water electrolyte (*SIWE*) system, which is a common solution system. In this case, the salt amount (s) in the water is almost negligible, and the permittivity of the solution can be regarded as equal to that of water ($\epsilon_{eff} = \epsilon_{water}$). At the same time, due to the existence of a large number of water molecules, the cations are fully solvated. In opposition, a very small s corresponds to a very high concentration. For aqueous electrolytes, a large amount of salt in a small amount of water corresponds to water-in-salt electrolyte (*WISE*), which is a highly concentrated or superconcentrated solution system.²⁸ In this case, there are an excess of both cations and anions relative to free water molecules. The ion–ion and ion–solvent interactions are then modified, and aggregation must occur between cations and anions, resulting in gelation and stabilization of the system as demonstrated in a study by *Schlumpberger* and *Bazant*.²⁹ An effective permittivity in the solution should be considered as ϵ_{eff} , so the permittivity of the solution must be very different to that of pure water.

The first step of salt dissociation in a solvent corresponds to the formation of ion pairs from the salt [Eq. (5)], while the second describes the dissociation of the ion pairs and then the solvation of the ions by the solvent molecules [Eq. (6)]. All these reactions lead to the formation of an electrolytic solution, composed of ions and solvent molecules. If the equilibrium of the second step is displaced to the right [Eq. (6)], then the electrolyte is called a strong electrolyte, and all ions in the solution are dissociated. Otherwise, for intermediate cases, a weak electrolyte is obtained.³⁰ According to Eqs. (5) and (6), an electrolyte solution is composed of ions in the presence of more or less important quantity of solvent (coefficient s). Moreover, there are two distinct populations of solvent molecules. The first one corresponds to solvent molecules that are solvating cations (coefficient s') and anions (coefficient s''). The second is about free solvent molecules (coefficient $s - s' - s''$) with limited (if any) interactions with salt ions [Eq. (6)]. As such, the latter population corresponds to water molecules not solvating ions. Classically, in a dilute electrolyte [Fig. 1(e)], the solvent is considered in excess; thus, the s coefficient is considered infinite [Eq. (5)] as the number of molecules solvating the ions is negligible compared to the

number of free solvent molecules ($s - s' - s''$) $\rightarrow \infty$. If this coefficient decreases and its value approaches the stoichiometry of A^{V-} and C^{Z+} , then a concentrated electrolyte is obtained. To determine the effect of increased salt concentration on both water populations, it is possible to compare the number of moles of free and non-free water in the *SIWE* and *WISE*.

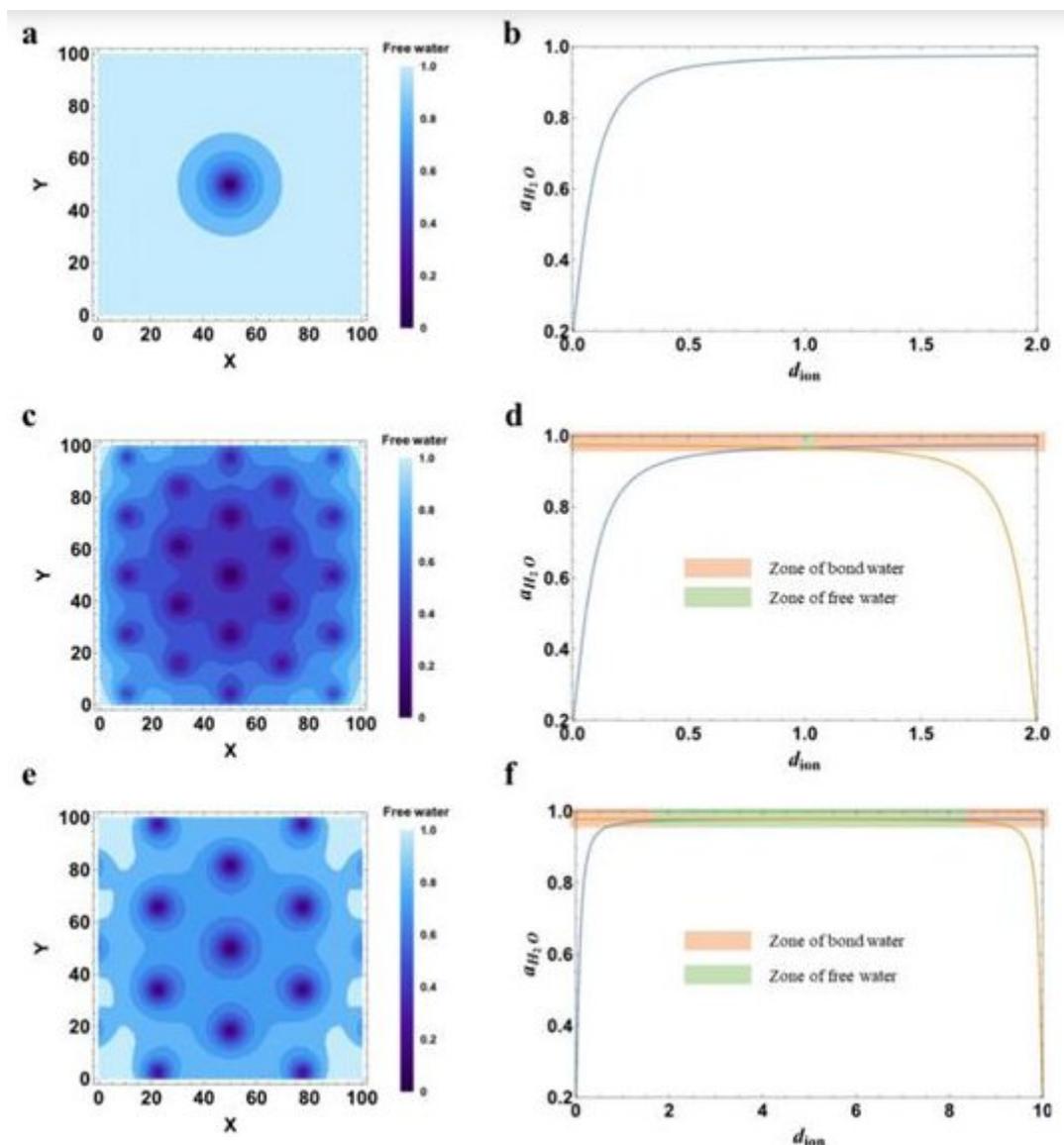


Fig. 1. 1D and 2D plots showing the water activity in the solution, and in the 1D plot, the orange part shows solvating water and the green part shows free water. (a), (c), and (e) 2D plots of one single cation as standard, molality of 20m, and molality of 0.3m, respectively. (b), (d), and (f) 1D plots of one single cation as standard, molality of 20m, and molality of 0.3m, respectively.

In this work, only water molecules forming the first primary solvation shell of ion are included in the non-free water population. It is established that cations are preferentially solvated by water molecules.^{31,32} Moreover, due to the fact that TFSI⁻ anions are bulky and have a delocalized charge, their solvation can be neglected.³³⁻³⁶ Molecular dynamics and x-ray diffraction studies predict that Li⁺ ions are solvated by four water molecules.^{5,37,38} Accordingly, four water molecules have been assumed to solvate each molecule of LiTFSI. [Figure 2](#) illustrates the effect of LiTFSI molality on the molar percentage of free water in the solution ([supplementary material](#), Sec. S2). The free water molar percentage decreases as the LiTFSI molality increases. An electrolyte

solution based on LiTFSI is considered as *SIWE* for molalities between 0 and 5 mol.^{5,39} The molality, m , corresponds to the number of *moles* of salt per kg of solvent. For LiTFSI concentration greater than $5m$, the number of solvent molecules decreases sharply and becomes less than the number of moles of salt. The solution is then assimilated to a *WISE*. The maximum molality is 21 mol (i.e., 21 mol LiTFSI per 1 kg water) at room temperature (25 °C).⁴⁰ *SIWE* solutions are predominantly composed of free water molecules (% > 50). This is not the case for *WISEs*; the percentage of free water becomes negative when the LiTFSI molality is greater than or equal to $15m$ LiTFSI (shown in Fig. S1). The solution contains no free water molecules, and the ions are not totally solvated. The number of water molecules per lithium ion becomes less than 4. This leads to an important modification of the solvation shell of Li^+ (shown in Fig. S2).

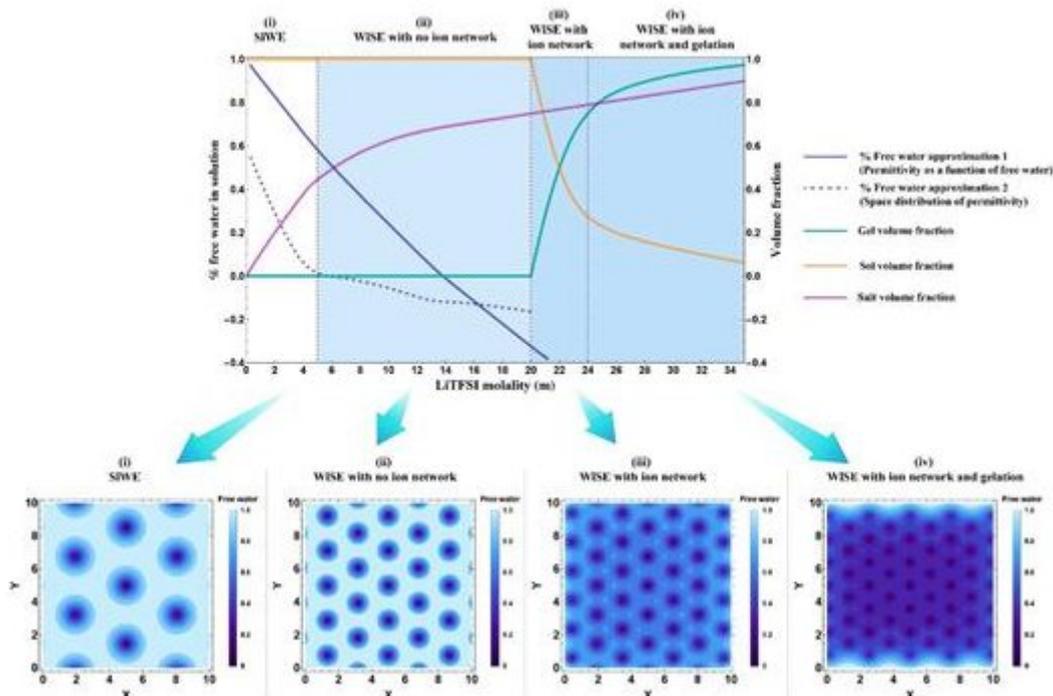


Fig. 2. Percentage of free water in the solution, and volume fractions for gel, sol, and total salt after aggregation and gelation in the solution, according to the molality. Each section corresponds to a 2D contour plot at different concentrations to show the state of ions in the solution.

One way to show the change in the ion solvation shell with salt concentration is to determine the solvated radius of ions as determined using the Stokes–Einstein equation [Eq. (S3)].^{41,42} The values of the lithium-ion diffusion coefficients and the viscosity of the solutions used to calculate the ion radius are included in Table S3. The effect of LiTFSI concentration on the solvated radius R_{Li^+} , R_{TFSI^-} , and d_{ion} is shown in Fig. S3. The solvated radius of TFSI⁻ ions is determined to verify the hypothesis of neglecting the TFSI⁻ solvation [Fig. S3(a)].

Figure S3(a) reveals that the increase in LiTFSI molality leads to a decrease in the solvated radius of the Li^+ and TFSI⁻ ions. The solvated radius of the lithium ions decreases from 0.202 to 0.082 nm when the molality increases from 0.3 to 21 m LiTFSI, H₂O. The non-solvated radius of Li^+ (R_{Li^+}) is 0.077 ± 0.01 nm, according to studies by Nguyen *et al.*,³² Salomon,⁴³ and others.^{44,45} This observation is in accordance with the literature; at high concentrations, less solvent molecules per mole of salt are available.^{46–48} Thus, if at low concentrations, there is a significant difference between the solvated and unsolvated radii of lithium ions, this difference becomes negligible at high concentrations and confirms the incomplete solvation of lithium ions (Fig. S3). For *SIWEs*, the solvated radius only slightly decreases. The increase in salt concentration leads to a decrease

in the amount of free water. Nevertheless, the solution has enough water molecules to solvate the ions in the solution (Fig. S3). Then, for *WISEs*, the solvated radius decreases more strongly. As the salt concentration increases, the free water molecules disappear, and the solvation shell of the ions becomes incomplete.

Furthermore, Fig. S3(a) shows that both solvated radii of TFSI⁻ lithium ions are similar, independent of the salt concentration. This result is surprising considering that the unsolvated radius of the TFSI⁻ anions is 0.450 nm according to a study by Salomon⁴³ and 0.326 nm according to a study by Nguyen *et al.*^{32,49} Thus, beyond the fact that R_{Li^+} and R_{TFSI^-} are in the same order, R_{TFSI^-} is smaller than the unsolvated radius of TFSI⁻ anions. These observations support the approximation that only the lithium ions are solvated in the solution. In a study by Chidiac *et al.*,⁵⁰ the TFSI⁻ presents two dimensions of 0.608 and 0.461 nm. Nevertheless, the R_{TFSI^-} obtained is smaller than the different proposed unsolvated radius of TFSI⁻ anions. We will assume that only the lithium cation is solvated due to its size and charge density, compared to those of the TFSI⁻ anions.⁵¹ The radius of TFSI⁻ ions is assimilated to a constant value of 0.376 nm (corresponding to the average of the non-solvated radii from the studies by Salomon⁴³ and Nguyen *et al.*^{32,49}).

In general, the Stokes–Einstein equation is a poor guide for small molecule diffusion, as discussed in a study by Evans *et al.*,^{52,53} but in this paper, the result obtained from the Stokes–Einstein equation is mathematically correct. Figure S3 demonstrates an incomplete solvation of ions at very high concentrations. As free water decreases, the degree of solvation decreases. Assuming that free water can completely disappear at a certain moment, then in theory, solvation will also disappear completely at this time, and the ions at this time are almost non-solvated, and their radius is naturally similar to the theoretical radius value of the non-solvated ion.

In a *WISE* solution, the number of water molecules is not sufficient to efficiently screen the electrostatic field created by the lithium ions. Consequently, the TFSI⁻ anions enter the solvation shell of lithium ions and the distance between cations and anions decreases.⁵ To confirm this point, the minimum distance between two ions of opposite charges, d_{ion} (corresponding to the distance between the solvated radius of Li⁺ and unsolvated radius of TFSI⁻), was determined, Fig. S3(b). As expected, d_{ion} decreases when the LiTFSI molality increases, Fig. S3(b). This is due to the fact that R_{Li^+} decreases [Fig. S3(a)] and confirms that, for highly concentrated *WISEs*, the amount of water molecules is not sufficient to fully solvate the ions in the solution.⁵ The study of the solvation shell of lithium ions, by molecular dynamics, carried out in a study by Li *et al.*,¹⁸ highlighted that the increase in salt concentration has two effects. The first is that the missing water molecules are replaced by the oxygen atoms of the TFSI⁻ anions, in the solvation shell. Since TFSI⁻ anions are hydrophobic, the probability of finding a water molecule around these anions is low. Thus, the greater the number of oxygen atoms of the TFSI⁻ anions involved in the first lithium coordination shell, the lower the number of water molecules in the solvation shell. Therefore, there is a competition between water molecules and oxygen atoms of TFSI⁻ anions to participate in the first solvation/coordination shell of Li⁺. The second corresponds to the formation of lithium–lithium dimers at short distances. Generally, this cation–cation interaction is very unlikely due to the strong repulsion between ions of the same charge (more especially for Li⁺, which have a very high electronic density). Nevertheless, it is made possible in a *WISE* solution by the dehydration of the Li⁺ cations.⁵

APPROXIMATION 1: EXPRESSION OF EFFECTIVE PERMITTIVITY AS A FUNCTION OF FREE WATER PERCENTAGE

Permittivity is a critical parameter of an electrolyte. In this section, the permittivity is evaluated by taking into account the effect of: (i) the solution concentration [Eqs. (7) and (8)], (ii) the percentage of free water [Eq. (9)], and (iii) Kornyshev’s model [Eq. (10)]. For all of these calculations, the

objective is to establish an expression of ϵ_{eff} that could assess the variation of dielectric properties of water in *WISEs*.

In a diluted solution, the solvent is considered as a continuous medium of uniform permittivity equal to that of the pure solvent due to the fact that ions are totally dissociated in the case of a strong electrolyte.^{54,55} Therefore, the permittivity of such aqueous LiTFSI solutions is equivalent to that of pure water ($\epsilon_{H_2O} = 78.46 \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$ at 25 °C).^{43,56,57} Nevertheless, this approximation is not appropriate in *WISEs* because of the drastic decrease in the amount of water with increasing salt concentration [Fig. S3(b)]. Hasted *et al.*²³ showed that the permittivity of electrolyte solutions is lower than that of a pure solvent, for two reasons. The first is that the structure of the solvent in the immediate vicinity of the ions is disturbed. The second is that ions of finite size have no directional contribution to the permittivity of the solution. Different empirical formulas have been proposed to take into account the evolution of the dielectric constant of solvent.^{56,58–60} Fawcett and Tikanen^{56,59} proposed that ion pairing induced by a salt concentration increase leads to a decrease in the solution permittivity. For this reason, they have proposed a relation between the effective solution permittivity and the salt concentration,

$$\epsilon_{eff} = \epsilon_0 - A \cdot C_{sol} + B \cdot C_{sol}^{3/2}, \quad (7)$$

where ϵ_{eff} is the effective solution permittivity ($\text{C}^2 \text{ N}^{-1} \text{ m}^{-2}$), ϵ_0 is the permittivity of the pure solvent ($\text{C}^2 \text{ N}^{-1} \text{ m}^{-2}$), C_{sol} is the solution concentration (mol l^{-1}), A is the dielectric decrement of the electrolyte (l mol^{-1}), and B is a parameter describing the curvature of this dependence ($\text{l}^{3/2} \text{ mol}^{-3/2}$).

For Shilov and Lyashchenko,⁶⁰ the solution permittivity is also a function of salt concentration. However, they have proposed another polynomial form to express the experimental static permittivity of solutions,

$$\epsilon_{eff} = \epsilon_0 + C \cdot C_{sol} + D \cdot C_{sol}^{3/2} + E \cdot C_{sol}^2 + F \cdot C_{sol}^{5/2}, \quad (8)$$

where C , D , E , and F are constants that depend on the solution (C : l mol^{-1} , D : $\text{l}^{3/2} \text{ mol}^{-3/2}$, E : $\text{l}^2 \text{ mol}^{-2}$, and F : $\text{l}^{5/2} \text{ mol}^{-5/2}$).

Here, we proposed to relate the effective solution permittivity to the free water molecules in the solution. A solution composed only of water has a permittivity of $78.46 \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$ at 25 °C.^{43,56,57} By considering only electrostatic interactions, this pure water solution can be assimilated to a solution containing 100% of free water molecules. Assuming that the permittivity of aqueous electrolytic solutions is a function of the concentration of free water in the *WISE*, the permittivity of the solutions can be determined [Eq. (9)],

$$\epsilon_{eff} = \epsilon_{H_2O} \cdot \%n_{H_2O_{free}}. \quad (9)$$

The above-mentioned equation is in accordance with the fact that in a diluted solution, the salt amount in the water is negligible and the permittivity of the solution is assimilated to the permittivity of water ($\epsilon_{eff} = \epsilon_{H_2O} \cdot \%n_{H_2O_{free}} = \epsilon_{H_2O} \cdot 100\%$).

Knowing that the number of free water molecules ($n_{H_2O_{free}}$) is proportional to the concentration of free water molecules ($C_{H_2O_{free}}$) (shown in Sec. S4 of the [supplementary material](#)), the effective solution permittivity (ϵ_{eff}) is a simple function of the concentration of free water molecules ($C_{H_2O_{free}}$). Thus, with our model, we simplify the complex polynomial functions [Eqs. (7) and (8)].

The effect of salt concentration on the solution permittivity, according to Eq. (9), is shown in Sec. S1 of the [supplementary material](#). Since LiTFSI solutions with a concentration higher than 15m are characterized by a zero free water content, the variation of permittivity is calculated for concentration lower than 15m. The transposition of molality into molarity is also presented in Sec. S1 of the [supplementary material](#).

Figure S1 shows that the permittivity of electrolytic solutions is lower than that of pure water (78.46 C² N⁻¹ m⁻² at 25 °C) and decreases as the salt molality increases. One explanation is that the solvent molecules used to solvate the ions no longer participate in the dipolar moment of the solution. The interaction between an ion and a solvent molecule leads to a change in the structure of the solvent molecule in the immediate vicinity of the ions. Due to this, this solvent molecule does not have an orientation contribution to the permittivity.⁵⁶ This leads to a decrease in the dielectric constant of the electrolyte solution.⁶¹ This phenomenon is more marked for highly concentrated electrolytes in which there are no more free water molecules in the solution. To determine the validity of this, the variation of the permittivity with the salt concentration has been fitted according to Eqs. (7) and (8). The results reveal that the evolution of permittivity is coherent with the work of Fawcett and Tikanen^{56,59} [Eq. (11)] and Shilov and Lyashchenko⁶⁰ [Eq. (12)]. This observation confirms the validity of the proposed model. The solution permittivity can be approximated to the free water molecule percentage.

APPROXIMATION 2: SPACE DISTRIBUTION OF EFFECTIVE PERMITTIVITY USING KORNYSHEV'S MODEL

Kornyshev proposed a formalism⁶² to describe the non-local screening of ions in structured polar liquids that mainly introduces the variation of solvent effective permittivity according to the distance between the ions,

$$\varepsilon_{eff} = \frac{\varepsilon}{1 + \left(\frac{\varepsilon}{\varepsilon_*} - 1\right) \cdot e^{-d'_{ion}}}, \quad (10)$$

where ε_* is the short wavelength permittivity, ε_{eff} is the effective permittivity, ε is the long wavelength permittivity, and d'_{ion} is the variable distance between two cations (nm or Å).⁵⁵ The plot of the effective permittivity as a function of the distance between cations is shown in the [supplementary material](#) (Fig. S6). In a solution, $\varepsilon_{eff}/\varepsilon = 1$ corresponds to the pure free water in the solution. In [Fig. 1](#), the one-dimensional plots showing the water activity in the solution with the distance between cations are obtained. In addition, the two-dimensional plots are the percentage of free water at the corresponding cations' distance.

In the *Debye–Hückel* theory, the solvent is usually considered in the system as a dielectric continuum with a fixed dielectric constant. However, for increasing concentrations of the solution, the presence of ions affects the physical properties of the medium and thus the permittivity, and a model of permittivity vs ion concentration was developed in the present study.

Based on Eq. (10), a relation between $\varepsilon_{eff}/\varepsilon$ and d'_{ion} can be obtained. So, [Fig. 1](#) introduces the two-dimensional plots of water activity in the solution, according to the solution molality and distance between two cations [Eqs. (11)–(14)]. [Figure 2](#) introduces this information in one-dimension under different reaction environments on a same plot.

[Figure 1\(a\)](#) describes the water activity under a standard condition, in two-dimensions (assuming only one cation in the solution), and [Fig. 1\(b\)](#) shows the value of the water activity under this condition. On the basis of [Figs. 1\(a\)](#), [1\(c\)](#), and [1\(e\)](#), respectively, introduce the change in water activity when the cations are close (high concentration) and far away (low concentration). At the

same time, [Figs. 1\(d\)](#) and [1\(f\)](#) depict the change in water activity when the cations are close and far, respectively.

From [Fig. 1](#), we can conclude that the closer the cation distance, the higher the concentration, the smaller the percentage of free water, and the smaller the water activity, and vice versa. This is explained in detail in the section titled “Water Activity Values Using Effective Permittivity,” including the calculation equations [Eqs. [\(11\)](#)–[\(14\)](#) and [Fig. 3](#)].

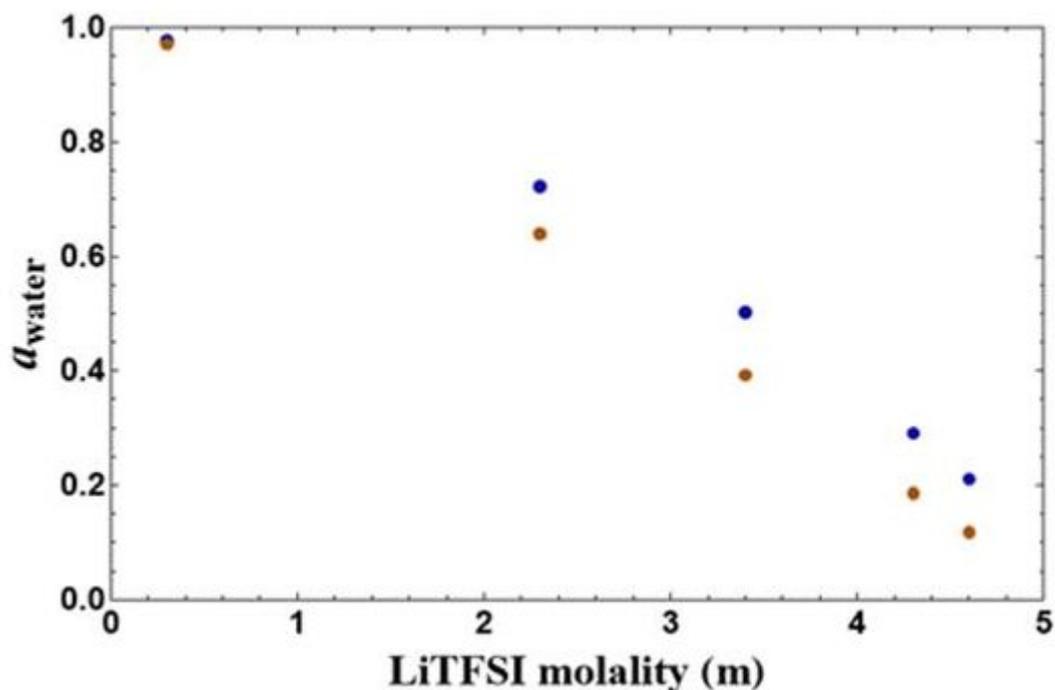


Fig. 3. Effect of LiTFSI concentration on water activity. The brown points show the water activity based on approximation 1: effective permittivity as a function of free water percentage, and the blue points show the water activity based on approximation 2: space distribution of effective permittivity.

In 2020, McEldrew *et al.* explored the theory of ion aggregation and gelation in superconcentrated electrolytes.⁶³ In concentrated electrolytes, such as ionic liquids and water-in-salt electrolytes, ion associations are more complex than simple ion pairs. When the degree of ion association reaches a certain critical value, an ion gel spontaneously forms. In simple terms, as the free water content decreases, the concentration of the solution must increase, reaching a certain threshold, and gelation will occur. In that paper, they used LiTFSI and NaOTF as study objects and found the critical concentration for this gelation, which is 0.17 mol fraction of salt. For LiTFSI, this mole fraction corresponds to a molality of 11.4m. [Figure 2](#) shows that the least free water in solution is between 7 and 12m (between mole fractions 0.12 and 0.18). It is slightly different from the conclusion obtained in a study by Kornyshev and Bazant, but it basically conforms to the critical interval. In general, it proves that the gelation of high-concentration electrolyte exists, and the difference range of the threshold is within an acceptable range. Therefore, it can be stated that the gelation and association start at 7m and finish at 12m. Before 7m, it is a pre-gel period. After 12m, is the post-gel period, and it reaches maximum when 12m. The similar results obtained by different models prove that the model in this paper is correct (although the gel points are not 100% identical). The correlation results obtained are also correct.

Three different situations are demonstrated for electrolytes: diluted [Fig. 2(i)], water distribution [Fig. 2(ii)], and aggregation [Figs. 2(iii) and 2(iv)]. When there is a lot of free water in the solution in comparison with the salt, the effective permittivity of the solution is basically equal to that of pure water. As the free water quantity decreases, the value of effective permittivity decreases until a minimum value is reached when the free water amount is minimum, thus for the highest concentration of salt, or when the solution begins to gellify. Our results are consistent with those of the study by McEldrew *et al.*⁶³ So, it is appropriate to correlate our model with that of the study by McEldrew *et al.*,⁶³ for establishing the relation between the solution concentration and gelation level. In Fig. 2, there is a lot of free water in zones (i) and (ii), more than 50% free water, which means that there is no gel in the solution. With the increase in molality, zones (iii) and (iv) show the information that the amount of free water drops, until there is no free water (0% of free water). So, the condition in zones (iii) and (iv) is gel. In zone (iii), the effective permittivity is equal to about 25% of free water, whereas in zone (iv), the effective permittivity is equal to about 0% of free water. So, the effective permittivity is highly different to pure water.

The permittivity of pure water is 81; according to the school and basic definition, this means that the ions in water have 81 times smaller attractions to each other at equal charges and distances than in air.

Thus, if the effective permittivity decreases by 50%, this means that water exerts a screening effect of 40 instead of 81, so the attraction charge of the ion is less screened. It is then conceivable that the weaker water influence increases the formation of ion pairs and gel states, as proposed by Bazant and Kornyshev.

WATER ACTIVITY VALUES USING EFFECTIVE PERMITTIVITY

In diluted electrolytes, the activity of the solvent is assimilated to an infinite dilution factor and is equal to one.^{19–21} However, it is not the case in *WISEs* as the solvent activity is less than one.^{22,64} We have theoretically determined the water activity by means of the developed *Gibbs–Duhem* relation,^{31,65}

$$a_{\text{H}_2\text{O}} = \exp\left(-\frac{2 \cdot m_{\text{LiTFSI}}}{m_{\text{H}_2\text{O}}} \cdot \left(1 + \frac{1}{\gamma_{\text{Li}^+} \gamma_{\text{TFSI}^-}}\right)\right), \quad (11)$$

where $a_{\text{H}_2\text{O}}$ is the water activity, m_{LiTFSI} is the LiTFSI molality (mol kg^{-1}), $m_{\text{H}_2\text{O}}$ is the water molality (mol kg^{-1}), γ_{Li^+} and γ_{TFSI^-} are the activity coefficients of Li^+ and TFSI^- , respectively. The demonstration is presented in Sec. S5 of the [supplementary material](#).

The activity coefficients of ions can be calculated using the *Debye–Hückel* theory,^{29,31,66}

$$\ln(\gamma_{\text{Li}^+} = \gamma_{\text{TFSI}^-}) = -\frac{A_{DH} \cdot C_{\text{LiTFSI}}^{1/2}}{1 + B_{DH} \cdot d_{ion} \cdot C_{\text{LiTFSI}}^{1/2}}, \quad (12)$$

where A_{DH} is one of the parameters of Debye–Hückel's theory [$\text{kg}^{1/2} \text{mol}^{-1/2}$, Eq. (13)], B_{DH} is the second parameters of Debye–Hückel's theory [$\text{kg}^{1/2} \text{nm}^{-1} \text{mol}^{-1/2}$, Eq. (14)], C_{LiTFSI} is the LiTFSI concentration (mol l^{-1}), and d_{ion} is the minimum distance between two ions (nm),

$$A_{DH} = \frac{N_a \cdot e_0^2 \cdot F}{8 \cdot \Pi} \left[\frac{2000}{(\varepsilon_{eff} \cdot \varepsilon_0 \cdot R \cdot T)^3} \right]^{1/2}, \quad (13)$$

$$B_{DH} = F \left[\frac{2000}{\varepsilon_{eff} \cdot \varepsilon_0 \cdot R \cdot T} \right]^{1/2}, \quad (14)$$

where N_a is the Avogadro number ($6.022\ 140\ 9 \times 10^{23}\ \text{mol}^{-1}$), e_0 is the fundamental charge ($1\ 602\ 177 \times 10^{-19}\ \text{C}$), F is Faraday's constant ($964\ 853 \times 10^4\ \text{C mol}^{-1}$), ϵ_0 is the permittivity of vacuum ($8\ 854\ 188 \times 10^{-12}\ \text{C}^2\ \text{N}^{-1}\ \text{m}^{-2}$), ϵ_{eff} is the effective solution permittivity, R is the perfect gas constant ($8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$), and T is the temperature (K). More details are given in Sec. S6 of the [supplementary material](#).

Water activity depends on activity coefficients of ions, which depend on the solution permittivity [Eqs. (11)–(13)]. To study the effect of permittivity on the solvent activity, water activity was calculated from *Kornyshev's* model [Eq. (10)]. For this purpose, the activity coefficients of Li^+ and TFSI^- [Eq. (12)] and the parameters of the *Debye–Hückel* theory [Eqs. (13) and (14)] were determined. The details are given in Sec. S6 of the [supplementary material](#). [Figure 3](#) shows the variation of water activities as a function of the LiTFSI molality.

[Figure 3](#) reveals that for both models [the classical *Debye–Hückel* theory, Eq. (9), and the extended one], the same trend is observed. The water activity decreases with an increase in salt molality. The decrease in water activity results from the fact that as the concentration of salt increases, the amount of water decreases. For 0.3m LiTFSI, H_2O , the water activity is close to 1, which indicates that this electrolyte is a highly diluted electrolyte. Yamada *et al.*⁶⁴ reported, experimentally, a water activity of 0.96 for 1.2m LiTFSI, H_2O at $30\ ^\circ\text{C}$. Referring to [Fig. 3](#), the water activity obtained theoretically is 0.87 (for both models). So, the theoretical activity, although of the same order of magnitude, is lower than the experimental value. One explanation is that the theoretical activity is obtained from experimental data at $25\ ^\circ\text{C}$.

Thus, when the concentration is smaller than 1m LiTFSI, H_2O , both models lead to similar activities. One explanation is the abundant presence of water molecules. For these molalities, approximating the permittivity of the solution to that of pure water is consistent and justified. This is not the case for higher molalities. The water activities according to the classical model of the *Debye–Hückel* theory are then slightly higher than those calculated with the extended version of the model. This can be attributed to the significant decrease in the amount of free water. Nevertheless, at very high molality (≥ 20), the values of the two models are again equivalent. This information suggests that the classical *Debye–Hückel* theory is suitable for both very dilute and very concentrated electrolytes.

By the way, if it is in an electrode system, the distribution of water near the cathode and anode is highly inhomogeneous, depending on the electrode potential and ion type. For example, in ionic liquids, the spatial distribution of water molecules will depend on the distribution of ions and electrostatic potentials in the electric double layer.⁶⁷ In addition, this may also affect whether the wide electrochemical window advantage of ionic liquids can be utilized in practical systems. Alternatively, in supercapacitors based on ionic liquid electrolytes, the hydrophobicity/hydrophilicity of ionic liquids and electrodes can have a strong influence on the distribution of ions and electroadsorbed water interfaces.⁶⁸ The use of hydrophilic ionic liquids helps keep water molecules away from negatively charged electrodes, even when large electrodes are polarized. However, in this paper, the electrode effect of the spatial distribution of water molecules is not integrated, and only the spatial distribution of water molecules in pure solutions, that is, the change from liquid to gel, is discussed.

THE CONSEQUENCES OF THE WATER ACTIVITY VARIATION ON *HER* AND *OER* REDOX POTENTIALS

The effect of salt concentration on the oxidation and reduction potentials of water can be quantified using the corresponding Nernst equations. It is possible to express *OER* and *HER*

potentials as a function of salt concentration, as demonstrated in Sec. S7 of the supplementary material,

$$E_{OER} = E_{O_2/H_2O}^{0'} + \frac{R \cdot T \cdot C_{LiTFSI}}{F \cdot C_{H_2O}} \cdot \left(1 + \frac{1}{\gamma_{Li^+} \cdot \gamma_{TFSI^-}}\right), \quad (15)$$

$$E_{HER} = E_{H_2/H_2O}^{0'} - \frac{2 \cdot R \cdot T \cdot C_{LiTFSI}}{F \cdot C_{H_2O}} \cdot \left(1 + \frac{1}{\gamma_{Li^+} \cdot \gamma_{TFSI^-}}\right), \quad (16)$$

where E_{OER} and E_{HER} are the redox potentials at equilibrium relative to the oxidation and reduction of water, respectively (V vs *SHE*), is the corresponding relative standard potential (V vs *SHE*), R is the perfect gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the temperature (K), F is Faraday's constant ($9.648 \times 10^4 \text{ C mol}^{-1}$), C_i is the concentration of the species i (mol l^{-1}), and γ_{Li^+} and γ_{TFSI^-} are the activity coefficients of Li^+ and $TFSI^-$, respectively.

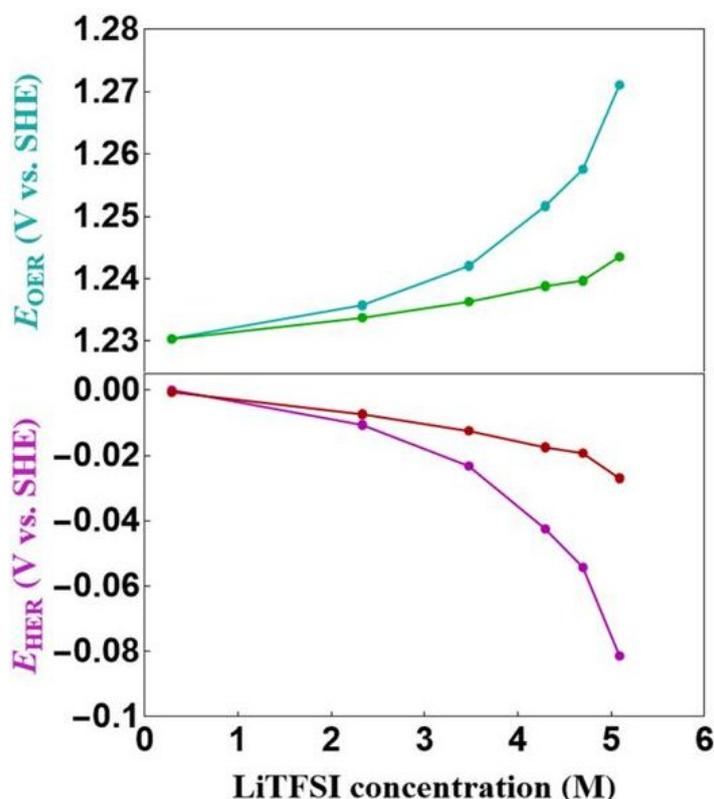


Fig.4. Effect of LiTFSI concentration on the *OER* and *HER* potentials, according to the Nernst equation dependent on the activity coefficients of Li^+ and $TFSI^-$, determined by the classical *Debye-Hückel* theory [Eqs. (15) and (16), respectively, at pH 0]. The cyan and purple data points are calculated with approximation 1: effective permittivity as a function of free water percentage. The green and brown data points are obtained with approximation 2: space distribution of effective permittivity.

Figure 4 shows the effect of LiTFSI concentration on the oxidation (*OER*) and reduction (*HER*) potentials of water at pH = 0 and at 25 °C. The standard potentials of the *OER* (O_2/H_2O) and *HER* (H_2/H_2O) are 1.23 and 0 V vs *SHE* at 25 °C, respectively.⁶⁹ The increase in salt concentration leads to a shift in the oxidation and reduction potentials of water to more positive and negative values, respectively. These shifts lead to an increase in the electrochemical stability of the water, delimited by the *OER* and *HER* potentials. More especially, an increase of 0.12 V is observed when the LiTFSI molality increases from 1 to 21m. This observation is in qualitative agreement with experimental results reported in the literature; increasing the LiTFSI concentration leads to

an extension of the electrochemical stability window of water, irrespective of the electrode material [gold,¹³ platinum,^{13,15,17} glassy carbon (GC),^{13,15} aluminum,^{5,7,14,17} and zinc¹⁷]. More especially, Coustan *et al.*¹³ studied the effect of LiTFSI concentration on the electrochemical stability of water by cyclic voltammetry. For this purpose, they have used various electrode materials, such as platinum (Pt), gold (Au), and glassy carbon (GC). They have observed an increase in the electrochemical stability window of water with salt concentration. An increase of 0.4 V for Pt, 0.5 V for Au, and 0.9 V for GC has been obtained when the molality increased from 1 to 21*m*. Thus, the increase in the electrochemical stability window for water obtained experimentally is larger than that determined here theoretically. One explanation is that only the contribution of the decrease in water activity is taken into account theoretically. The experimental measurements are not only influenced by the thermodynamics but also influenced by the kinetics of the electrochemical processes occurring at the electrodes. Hence, experimentally, *OER* and *HER* processes are more complex and include electrode reaction (e.g., oxidation), salt dissolution,¹⁵ and also precipitation of the LiTFSI salt.¹⁶

The proposed model can also be applied to the interface. According to Stern's model, the electrochemical double layer is composed of two zones. Closest to the electrode is a compact layer known as the Helmholtz layer. The characteristic populations in this zone are adsorbed ions and solvent molecules. Beyond this is a diffuse layer, known as the Gouy–Chapman layer. It is made up of solvated ions and solvent molecules.

The Helmholtz layer corresponds to a distribution of excess charge in the electrolyte that is homogeneous and symmetrical to that of the electrode material, over a distance x_H from the interface. This model predicts no change in the interface when the electrolyte salt concentration is increased. In contrast, the Gouy–Chapman model predicts a diffuse electrochemical double layer. The excess charge in the electrolyte is considered to be distributed over a certain area of space, whose characteristic thickness is the Debye length (l_D),

$$l_D = \frac{1}{zF} \sqrt{\frac{\varepsilon \cdot R \cdot T}{2 \cdot C}}, \quad (17)$$

where l_D is the Debye length (cm), z is the charge of the electrolyte, F is Faraday's constant ($9.648 \times 10^4 \text{ C mol}^{-1}$), ε is the permittivity of the medium (F cm^{-1}), R is the perfect gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the temperature (K), and C is the molar concentration of the electrolyte (mol l^{-1}). The length l_D depends on the concentration of the electrolyte. Thus, the length l_D depends on both the permittivity and electrolyte concentration

Thus, the increasing salt concentration has two effects on the electrochemical double layer. The first is that it is enriched in TFSI-anions. The second is that its thickness is modified. The Debye length is (i) proportional to the permittivity of the medium and (ii) inversely proportional to the salt concentration [Eq. (8)]. An increase in the salt concentration is accompanied by a decrease in the permittivity of the medium. This leads to a decrease in the Debye length. A more compact and denser double layer is formed. The direct consequence of this is that the *HER* and *OER* potentials are shifted toward more negative and positive values, respectively.

Conclusion

We have shown that in *SIWEs*, the majority population corresponds to free water molecules. Conversely, for *WISEs*, the amount of water relative to the salt is drastically reduced. The result for highly concentrated electrolytes ($>14m$ LiTFSI) is the absence of free water molecules and

incomplete solvation of ions. We have shown that the solvated ion radius decreases as well as the distance between ions of opposite charge. Moreover, we have determined the water activity, using the Gibbs–Duhem relation and the classical and an extended Debye–Hückel theory.^{31,65} We have made two observations for both models. First, in diluted aqueous electrolytes, the solvent activity is equal to one.^{19–21} Second, in *WISEs*, the water activity tends to zero. The direct consequence is that in a diluted electrolyte, the Nernst potential of *HER* and *OER* is independent of the concentration and activity of water, but this is not the case in a *WISE* solution. This has been confirmed by the shift of the *OER* and *HER* redox potentials to more positive and negative potentials, respectively, as the salt concentration increases. We have theoretically obtained a 0.12 V larger voltage window when the LiTFSI concentration increases from 1 to 21*m*. However, this increase is significantly lower than the values obtained experimentally. An increase of 0.4 V was obtained with a platinum electrode by Coustan *et al.*¹³ As a result, the decrease in water activity is not the major contribution responsible for the displacement of the *OER* and *HER* potentials.

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