A Trio of Revelations: Weakly Solvating Modulation in Aqueous Electrolytes for Zinc Metal Batteries

Zhenrui Wu[a] and Jian Liu*[a]

The emerging concept of weakly solvating electrolytes in multivalent ion aqueous batteries has garnered attention due to their enhanced kinetic performance at a low cost. This article aims to dissect the concept of "weakly solvating electrolyte" into three revelations, i.e., ion solvation, hydrogen bonding strength, and ionic interactions. It is revealed that a weakly interacting solvent must satisfy the requirements of having a so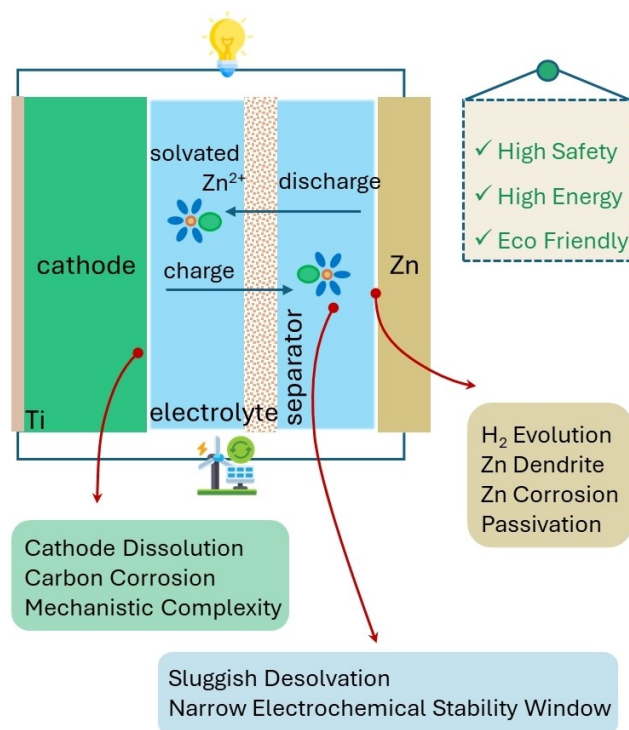lvation strength weaker than water molecules, as well as disrupting rather than strengthening hydrogen bonding within them. Moreover, electrolyte chemistry requires balancing multiple factors, and one weakly interacting solvent can exhibit varying effects with different anions of zinc salts. This study offers quantitative descriptors to the concept of weak solvation, particularly for aqueous electrolytes, and provides insights for future electrolyte advancements for multivalent ion batteries.

Introduction

Aqueous Zn metal batteries (AZMBs) have gained attention due to the high safety characteristics and high volumetric capacity of Zn metal (5848 Wh L^{-1}).[1–3] However, the strong interaction between Zn^{2+} and H$_2$O in the solvation sheaths causes sluggish desolvation kinetics, leading to inhomogeneous Zn deposition (Scheme 1).[4,5] Moreover, H$_2$ evolution becomes a conspicuous parasitic reaction in AZMBs due to the similar potentials of H$_2$O/H$_2$ and Zn^{2+}/Zn redox pairs and the fast proton transfer in the hydrogen bonding (HB) network of H$_2$O.[6,7] The attraction from Zn^{2+} to O of solvating H$_2$O, elongating the OH bond,[8] also lowers the Gibbs free energy of OH dissociation.[9]

Weakly solvating electrolyte (WSE) has emerged as a promising solution to de-strengthen Zn^{2+}-H$_2$O interaction, reduce the Zn^{2+} desolvation barrier, and mitigate H$_2$O-related parasitic reactions.[10] A secondary solvent with decent H$_2$O miscibility and relatively weak solvating power to Zn^{2+}, is called a weakly interacting solvent (WIS),[11] such as acetonitrile (AN).[10] By introducing a WIS,[10–13] recent studies have modulated the Zn^{2+} solvation structure with an increased number of anions and fewer solvating H$_2$O molecules.

Nevertheless, a lack of fundamental understanding about the modulating scheme towards WSE widely exists. Herein, we suggest sets of solvent descriptors to guide the rational WIS selection, clarify overlapped concepts in battery electrolyte research, and conclude a trio of revelations about the weak

Scheme 1. Schematics and challenges of zinc metal batteries.

solvation in aqueous electrolytes. Finally, we provide insights for future electrolyte chemistry and high-function aqueous battery development.

What Makes a Solvent "Weak"? – Solvating Power and Polarity Descriptors

The conceptualization of WIS could be traced back to studies using a "diluent," such as fluorinated ethers, to ameliorate the high viscosity (η) and poor ion transport issues of the highly concentrated electrolytes.[14–17] Therein, the selection of a

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diluent followed some empirical rules that the diluent itself does not dissolve the salt but is miscible with the primary solvent.[18] To achieve the former rule, one metric – a small dielectric constant (the relative permittivity, ε_r), i.e., the inadequate ability of the solvent to shield the ionic bonding and dissociate the salt – was advised.[19] Transplanting this concept to aqueous electrolytes, any solvent with solvating power weaker than the primary solvent, H_2O, is a WIS,[10] unless it is weak enough, called an "anti-solvent," such as fluorinated alkyls, to cause salt precipitation.

Solvating power is equivalent to "polarity" by pragmatical definitions.[20,21] It is not determinable by a single physical quantity.[22] Owing to the strong polarity of H_2O, finding a WIS for an aqueous electrolyte is viable through two empirical descriptors: ε_r, describing a solvent's salt-dissociating capability, and Gutmann's donor number (D_N),[23] describing the Lewis's basicity[24] of a solvent coordinating with Zn^{2+}.[25] More specifically, ε_r and D_N smaller than H_2O ($\varepsilon_r = 80.4$, $D_N = 18.0$ kcal mol^{-1}), indicate the weak solvating power of a WIS (such as 1,4-dioxane)[26] and its absence in Zn^{2+}'s primary solvation sheath.[26] In addition to ε_r and D_N, Gutmann's acceptor number (A_N) is added to indicate a solvent's solvating power to the anion. Following these criteria, solvents are classified into five categories: strongly interacting solvent (SIS), co-solvent, WIS, latent solvent, and anti-solvent.[27]

As summarized in Figure 1, an SIS is indicated by high D_N and decent ε_r, such as phosphate esters (trimethyl phosphate,[28] triethyl phosphate,[29] tributyl phosphate),[30] amides (dimethylformamide,[28] dimethylacetamide,[31] tetramethylurea),[32] some alcohols (1,2-propanediol, tert-butanol), and others with electron-donating functional groups (dimethyl sulfoxide,[33] N-methyl-2-pyrrolidone),[34] An SIS, surpassing H_2O in solvating Zn^{2+}, is readily incorporated into the primary Zn^{2+} solvation sheath, thereby popping out solvating H_2O and reducing H_2O-related side reactions. A comparable D_N to H_2O is the characteristic of a "co-solvent," including alcohols (MeOH,[35] EtOH,[36] PrOH,[35] iPrOH,[37] ethylene glycol (EG),[38,39] glycerol)[40] and ethers (tetrahydrofuran,[41] 1,3-dioxolane,[42] monoglyme,[43] diglyme),[11,44] who enters Zn^{2+} solvation sheath simultaneously with H_2O.

In contrast, low D_N and decent ε_r highlight a WIS, including carbonate esters (ethylene carbonate (EC),[45] propylene carbonate (PC),[46] diethyl carbonate),[47] carboxylate esters (methyl acetate),[48] nitriles (AN,[10] propionitrile,[49] adiponitrile),[50] some ethers (tetraglyme,[51] 1,4-dioxane),[52] and sulfolane (SL).[53] These solvents, with mediocre solvating power, would facilitate the inclusion of anions, such as triflate (OTf$^-$), in Zn^{2+}'s solvation sheath. This would promote the formation of contact ion pairs (CIPs) even in a dilute electrolyte, leading to a facile Zn^{2+} desolvation that reassures Zn^{2+} flux and favors homogeneous Zn deposition. Some ketones (acetone,[12] butanone)[13] and esters (ethyl formate, dimethyl carbonate,[54] γ-butyrolactone)[55] have D_N values falling between OTf$^-$ and H_2O, so they are less effective in facilitating CIPs. In addition, low D_N and high A_N configure a "latent" solvent, primarily fluoroalcohols (2, 2, 2-trifluoroethanol,[56] hexafluoroisopropanol (HFIP)),[27] that solvates the anion rather than Zn^{2+}, which is of interest for enhancing Zn^{2+} mobility.[57]

Low D_N and low A_N (often low ε_r) configure an anti-solvent, such as fluorinated ethers,[16] that solvate neither the cation nor the anion, solely playing the role of diluting viscous (organic) electrolytes. It might be worth discussing that WIS in WSEs is not the same as the diluent in highly concentrated electrolytes: a diluent aims to retain the "high-concentration salt-solvent clusters" characteristic while reducing η and enhancing overall conductivity. While, introducing a weak solvent, which does not participate in Zn^{2+} solvation due to its weak solvating power, helps form an anion-reinforced solvation structure, more CIPs and less H_2O in the solvation sheath, exhibiting high conductivity and low η of a WSE.

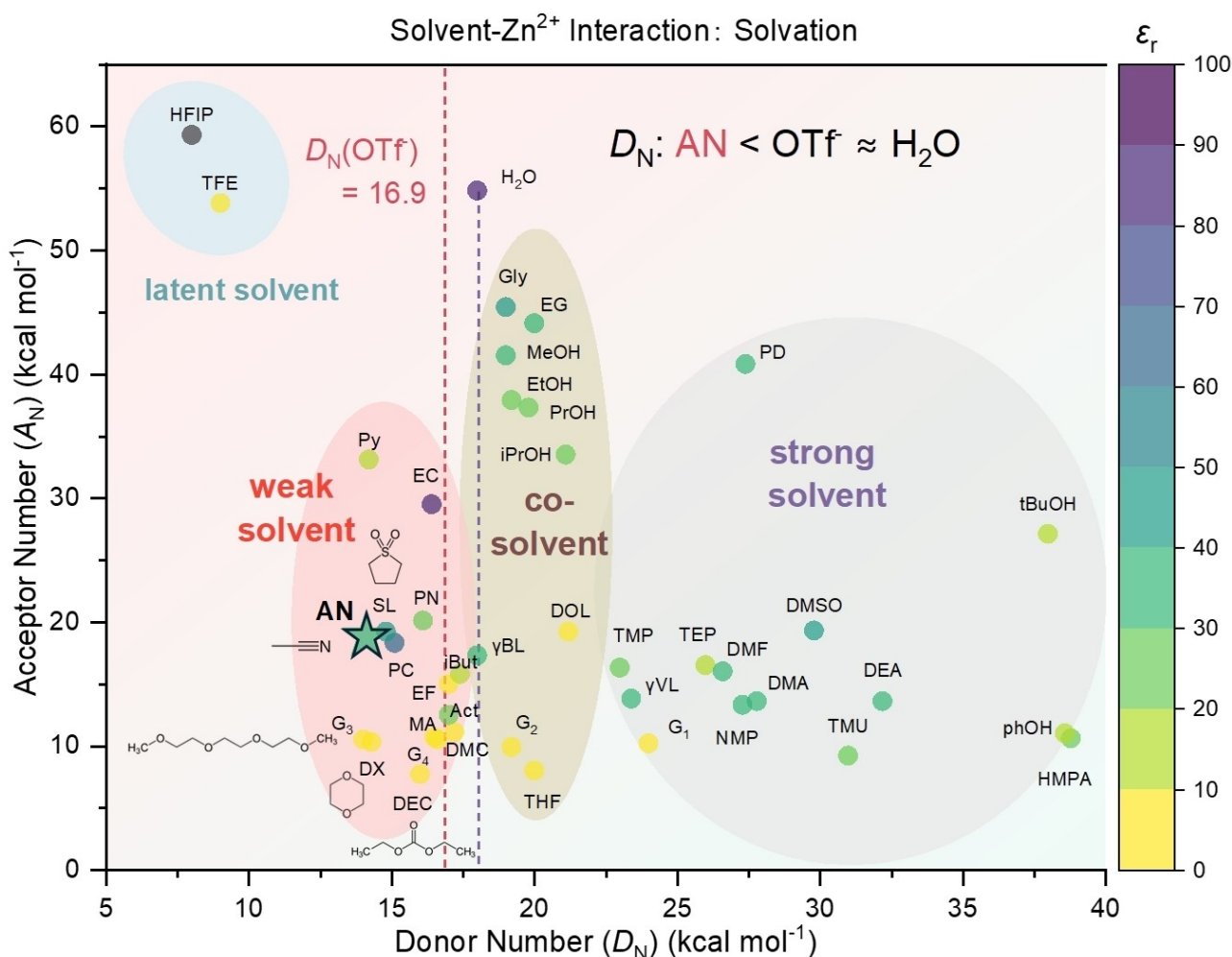**Should a Weak Solvent be Protic? – Finding the Right Solvent for Aqueous Electrolytes**

Aqueous electrolytes have high polarity and HB characteristics. The latter, which drastically affects the electrolyte's η, electrochemical stability, and thermal stability, has been overlooked. We suggest using E^N_T, β, and α (HB acidity, KAT's parameter),[58–60] to denote the solvent's H_2O miscibility, hydro-

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Figure 1. Metrics of solvating power in selecting a modulating solvent. The data table and references are provided in the supporting document (Table S1). The Gutmann donor numbers of two fluoroalcohols (i.e., TFE, HFIP) are estimated to be very small because of the strong electronegativity of the F atom.
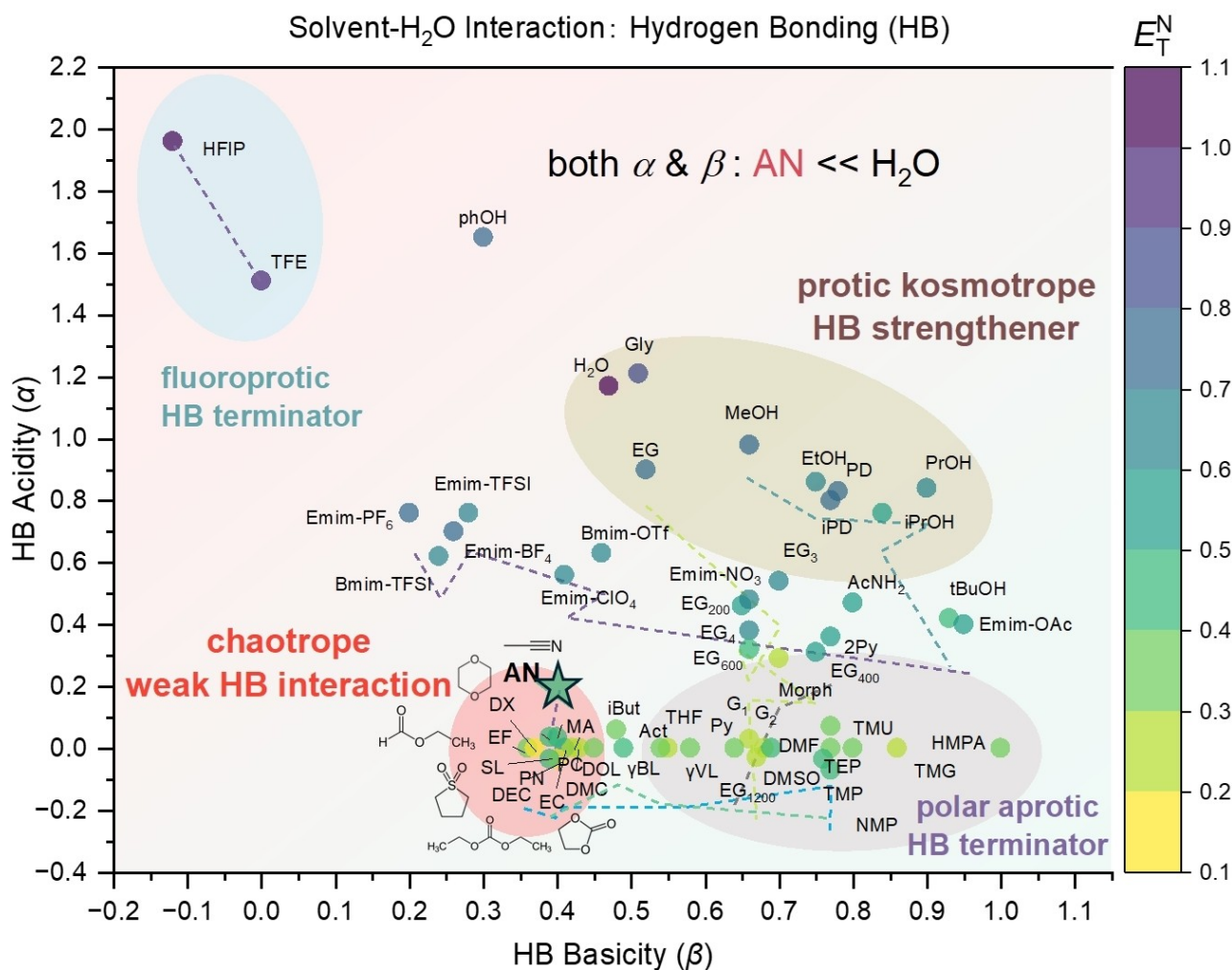
gen bonding acceptor (HBA) characteristic, and hydrogen bonding donor (HBD) characteristic, respectively. These three criteria serve as a parallel set of descriptors for solvent-H_2O interaction that classify the secondary solvent into protic kosmotrope, polar aprotic, fluoroprotic solvent, and aprotic chaotrope (Figure 2).

Protic solvents, primarily alcohols (MeOH,[35] EtOH,[36] PrOH,[35] iPrOH,[37] EG,[38,39] propanediol, glycerol,[61] polyethylene glycol (PEG)),[62] demonstrate "kosmotropic" characteristic, whose strong interaction with H_2O favors salt precipitation, known as "salt out." Their comparable β and α values to H_2O indicate dual-functioning roles of an HBD and an HBA. These molecular kosmotropes intertwine into the HB network and interrupt HB between H_2O, exhibiting anti-freezing potency of the electrolyte,[37] while still lengthening the OH, thus not circumventing the redox instability of H_2O.[63] These solvents containing hydrophilic functional groups are usually high in both D_N and A_N, overlapping with SIS in the light of solvating power, so they participate in solvating Zn^{2+} and the anion (ion-dipole interaction),[64] as well as strongly interact with H_2O to reinforce the HB network.[65] Big-molecule kosmotropes, such as

PEG with multidentate alcohol groups, are also called molecule-crowding agents or local aggregate (AGG) anchoring agent.[66]

Polar aprotic solvents with functional groups, including ether, ketone, nitrile, and ester, are HBA only, while fluoroprotic solvents are HBD only. They terminate the HB network due to outbalanced HBD and HBA characteristics. The former are usually low in A_N but high in D_N, so they solvate Zn^{2+} as well as terminate the HB network; the latter are often high in A_N but with minimal D_N, so they solvate the anions as well as terminate the HB network. Gao *et al.* recently used HFIP's sole-solvating power to the anion ($\alpha = 1.96$, $\beta = 0$), and this mixed solvent of LS:H (9:1 by volume) increases Zn(TFSI)'s dissolution in H_2O from 5.4 to 20.6 M, forming nanometric AGG colloid.[27] In fact, fluorination, along with aromatization, is a common approach to reducing the electron density of "O" by delocalizing its lone electron pairs to nearby fluorine through induction force, whilst the adjacent "H" in fluoroalcohols starts exhibiting increased HB donating effect. This explains the high-α and low-β characteristics of fluoroalcohols.

In contrast, solvents like AN with small α and β, which interact with H_2O only *via* van der Waals forces, are ideal HB

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Figure 2. Metrics of hydrogen bonding in selecting a modulating solvent, with data provided in Table S2.

breakers demonstrating "chaotropic" characteristics. Some ionic liquids and surfactants with relatively large alkyl components also fall into this category.[67,68] These solvents demonstrate overlaps with WIS, thereby leading to anion-reinforced,[69] HB-weakened electrolyte structure. Ultimately, this enhances Zn^{2+} transport by increasing the number of mobile ions and optimizing desolvation kinetics.

Epic Understatement of the Selection of an Anione

A seldomly discussed aspect in aqueous WSEs is salt selection, particularly the anion. As Lewis's bases in hydrolysis, anions exhibit a tendency to donate electrons, thus entering the Zn^{2+} solvation sheath through ionic interactions. In Figure 3, we categorize these anions based on their electron-donating abilities into low-D_N anions, high-D_N anions, and those within the solvation-adjustable region specific to aqueous electrolytes.

To make an aqueous WSE, we recommend using anions with low lattice energy (U_L) and D_N values lower than, but close to, that of H_2O, i.e., OTf^- ($D_N = 16.9 \, kcal\,mol^{-1}$). Low U_L ensures a decent Zn^{2+} concentration, while a high D_N allows the anion to

enter the solvation sheath more easily. Adding a WIS, such as nitriles, esters, and ethers, reduces the solvation power of the electrolyte system and introduces more anions into Zn^{2+}'s primary solvation sheath, facilitating the desolvation process and minimizing H_2 production. Otherwise, with inherently low-D_N anions,[70] achieving the same high-CIP sheath at the same salt concentration necessitates a WIS with even lower D_N values. For instance, $TFSI^-$ ($D_N = 5.4 \, kcal\,mol^{-1}$) would require solvents with D_N values smaller than itself, such as alkanes (insoluble in aqueous electrolyte) or highly fluorinated ones (cost and toxicity concerns). Practically, water-soluble WIS with $D_N < 5 \, kcal\,mol^{-1}$ is limited to fluoroalcohols. Their high A_N indicates their anion-solvating power, which in return hinders anion incorporation into Zn^{2+}'s solvation sheath. Alternatively, using high-D_N anions, e.g., SO_4^{2-},[71] H_2O already acts as a WIS that does not dominate in entering the solvation sheath and promotes CIP formation, which, in reality, is contrary because the high U_L of these high-D_N salts raises the dissociation barrier, limiting the formation of mobile Zn^{2+} solvates, thus reducing overall ion mobility in the electrolyte. Therefore, developing an WSE for AZMBs should focus on using OTf^-. For non-aqueous WSEs, redefining the solvation-adjustable region is necessary.

Figure 3. Gutmann's donor number (D_N) and the radii of the anions and the lattice energy of the corresponding zinc salts (data provided in Table S3). The color scale indicates the empirical solubility limit of each salt. Aqueous-instable salt, *i.e.*, $Zn(PF_6)_2$ lacks solubility data and is dyed grey. D_N of F^-, SO_4^{2-}, $H_2PO_4^-$, ClO_3^-, and $HCOO^-$ are estimated (details provided in Table S3 and S4).

Overall, the goal is to ensure sufficient salt dissociation as well as facilitate the predominance of CIPs in Zn^{2+}'s solvation sheath.

In addition to the D_N-indicated anion-cation interaction and A_N-indicated solvent-anion interaction, Hofmeister *et al.* discussed the anion-H_2O interaction:[72] anionic kosmotropes enhance the orderliness of tetrahedral HB network of H_2O, while chaotropes enhance its chaoticity in the order of $PO_4^{3-} <$ $SO_4^{2-} < HPO_4^{2-} < H_2PO_4^- < HCOO^- < OTf^- < Cl^- < NO_3^- < OAc^- <$ $BF_4^- < ClO_4^- < PF_6^-$ (inorganic) and $OTf^- < FSI^-$, $< FTFSI^- <$ $TFSI^- < PTFSI^-$ (organic)[73] quite agreeable with their decreasing D_N values. For example, SO_4^{2-}, with its high net negative charge and small size, is classified as an anionic kosmotrope that results in fewer available H_2O molecules for Zn^{2+} solvation, while also exhibiting strong ionic interactions, resulting in increased CIP formation and reduced salt dissociation, *i.e.*, a "salt out" phenomenon. The low-net-charge and large-size ClO_4^-, BF_4^-, or $TFSI^-$, with their electronegativity dispersed by a large number of F or O atoms, however, lie at the opposite extreme and are considered chaotropes, interacting very weakly with H_2O, which allows Zn^{2+} to be fully hydrated and thoroughly H_2O-separated

from the anions by forming solvent-separated ion pairs (SSIPs) and solvent-shared ion pairs, known as "salt in." Increasing the salt concentration can forcibly incorporate these anions into the Zn^{2+} solvation sheath to form water-in-salt electrolytes with an increased number of CIPs. In particular, OTf^-, with a D_N comparable to H_2O, allows for similar chances of being retained in Zn^{2+} solvation sheath as CIPs than incentivizing H_2O to solvate Zn^{2+}, in which case introducing low-cost, lower ε_r AN becomes an economical approach to modulate CIP and SSIP ratio. Till now, OTf^-,[74] BF_4^-,[75] and ClO_4^-[76] have been identified to exhibit a salt-in effect on PC in water, where H_2O-insoluble PC becomes soluble after the salt is added, forming a chaotropic salt electrolyte, with enhanced low-temperature performance in a battery. Large cations, *i.e.*, 1-ethyl-3-methyl-imidazolium ($Emim^+$) in ionic liquids,[77] also exert a strong chaotropic effect, expanding the choice of secondary solvents in aqueous electrolytes, thereby advancing the development of organic based electrolytes.

We consider that the essence of weak solvation lies in the regulated electrolyte structure, particularly the transport scheme of Zn^{2+} and the size of ion-solvent nanoclusters.[78] For

example, when SSIP is oversaturated, sub-nanometric CIP-connected ion-molecule clusters form and evolve into larger nanometric ion-ion clusters.[79] By introducing AN to shield ionic interactions, a balance of ionic interactions and solvation is built, so that the ions are distantly but tightly solvated in these AGG clusters. Otherwise, without the weak-solvation condition, these clusters can grow and eventually precipitate.

Summary and Outlook

Electrolyte is a sub-nanometric dispersion of ions and solvent molecules. More specifically, the philosophy of formulating an aqueous WSE can be interpreted from three angles: H_2O-to-Zn^{2+} hydration, anion-to-Zn^{2+} interaction, and anion/WSE-to-H_2O chaotropism, as summarized in Figure 4. Using this framework and aforementioned solvent descriptors, the WIS for aqueous electrolytes is guided to be aprotic with small A_N and D_N, small α and β, as well as decent ε and E^N_T, such as EC, PC, AN, and SL[53] These WIS molecules de-strengthen ion-solvent clusters, dilute the AGGs in salt-in-water electrolytes,[80] and increase the entropy of solvated structures. Anions with decent D_N are suggested, such as OTf⁻, NO_3^-, OAc⁻,[81] Cl⁻,[82,83] $H_2PO_4^-$, SO_4^{2-}, opposing to low-D_N anions, such as TFSI⁻, BF_4^-, ClO_4^-.[50] It might be worth noting that the high D_N of an anion is a compromise of solubility, and it is important to balance the number of conducting ion units and the portion of CIP in each vehicle of solvated Zn^{2+}.

Future studies around WSE should fine-tune the weak solvation at a molecular level, which includes the selection of functional groups and introduction of steric hindrance of alkyl chains, *i.e.*, cyclization, halogenation, aromatization, or alkylation. For example, a strong solvent of dimethyl sulfoxide after alkylation and cyclization becomes SL, exhibiting weak solvat-

ing characteristics;[53] zinc dodecylbenzenesulfonate (*i.e.*, Zn-(DBS)₂),[84] akin to Zn(OTf)₂, is an aromatization and alkylation result of OTf⁻, demonstrating high-D_N characteristics but steric-induced sluggish ion mobility.[85] This framework is also applicable to advanced electrolyte systems including high entropy electrolytes,[86–88] which use multiple components synergistically to enhance performance,[89] and non-aqueous electrolytes, where organic solvents replace H_2O as the primary solvent, expanding the electrochemical stability window of aqueous electrolyte chemistries.
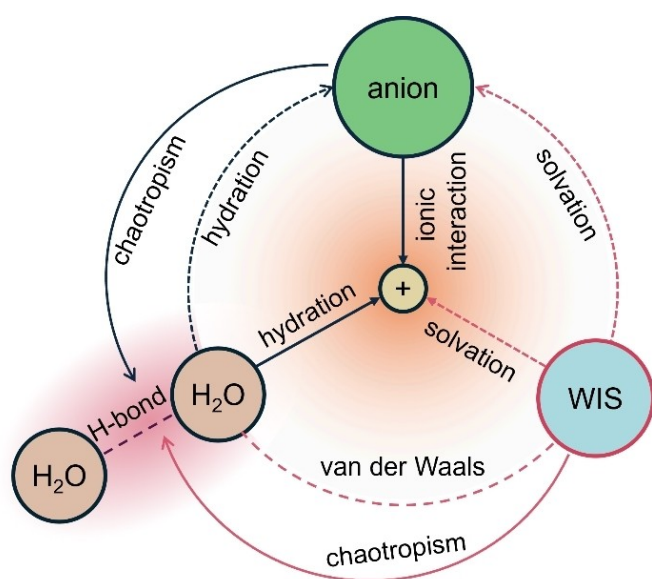
Conflict of Interests

The authors declare no conflict of interest.

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Figure 4. A framework concluding important interactions between each two components in a weakly solvating aqueous electrolyte. The two stems of cation solvation and hydrogen bonding of H_2O are highlighted.

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