

# An Atomic Insight into the Chemical Origin and Variation of the Dielectric Constant in Liquid Electrolytes

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**Abstract:** The dielectric constant is a crucial physicochemical property of liquids in tuning solute–solvent interactions and solvation microstructures. Herein the dielectric constant variation of liquid electrolytes regarding to temperatures and electrolyte compositions is probed by molecular dynamics simulations. Dielectric constants of solvents reduce as temperatures increase due to accelerated mobility of molecules. For solvent mixtures with different mixing ratios, their dielectric constants either follow a linear superposition rule or satisfy a polynomial function, depending on weak or strong intermolecular interactions. Dielectric constants of electrolytes exhibit a volcano trend with increasing salt concentrations, which can be attributed to dielectric contributions from salts and formation of solvation structures. This work affords an atomic insight into the dielectric constant variation and its chemical origin, which can deepen the fundamental understanding of solution chemistry.

## Introduction

The dielectric constant, namely relative permittivity, reflects the response of a matter toward an external electric field and has become one of the most important topics in physical science. The contribution to dielectric constant of a material can be classified into the ionic conduction, the dipolar relaxation, the atomic polarization, and the electronic polarization, which dominate at different frequencies of the electric field.<sup>[1]</sup> The variation of dielectric constant in the high-frequency range is primarily contributed by the atomic polarization and electronic polarization while the ionic conduction and dipolar relaxation function at the low-frequency region. Conventional dielectric studies mainly focus on solid materials. Corresponding working mechanisms

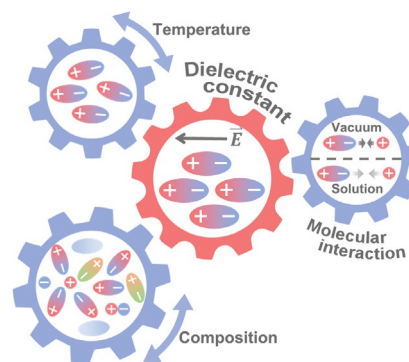
and applications are well probed while the vital role of dielectric constant in regulating solution structures and related physicochemical properties is recently highlighted.<sup>[2,3]</sup> Solutions are usually applied in a specific electric field in various electrochemical systems, such as batteries, fuel cells, and electrolytic cells. Therefore, the static dielectric constant (hereinafter referred to as “dielectric constant” ( $\epsilon$ )) at relatively low frequencies is mainly concerned for solutions.<sup>[4]</sup>

The dielectric constant affects both the solution structure and related physicochemical properties by regulating the interactions between solution components. Specifically, according to the classical physical laws, the electrostatic interactions between ions or molecules are significantly weakened by the solvation effect, in which the dielectric constant plays a major role (Figure 1).<sup>[5]</sup> Furthermore, many physicochemical properties of solutions are directly influenced by the ion–solvent, cation–anion, and solvent–solvent interactions in solution. For example, the dissolution of salts in solvents is determined by the competition between the cation–anion interaction in solid salts and the ion–solvent interaction in solutions. Consequently, the dielectric constant has become one of the most important parameters in synthesizing materials or designing reactions in solutions, especially achieving wide applications in energy storage fields based on liquid electrolytes such as lithium (Li) batteries (LBs).<sup>[3,6]</sup>

LBs are widely employed in our daily life, powering the electric vehicles and portable electronics.<sup>[7]</sup> Building safe, high-energy-density, high-rate, and long-cycling LBs is the ultimate goal in energy storage research and has attracted worldwide interests, which is strongly dependent on highly stable and high-performance electrolytes.<sup>[8]</sup> Tremendous

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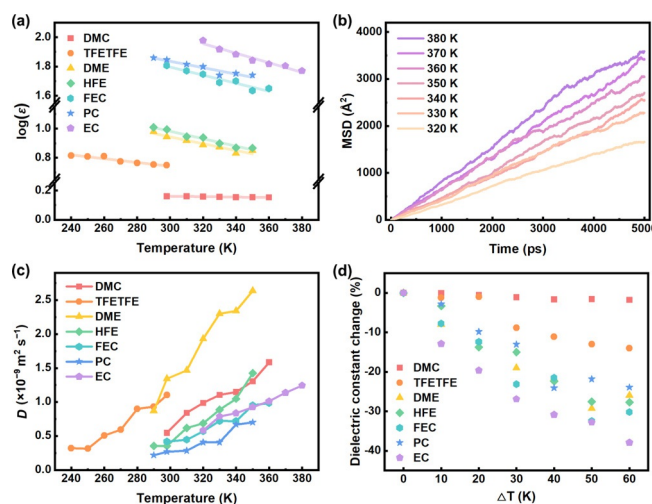
**Figure 1.** Relations between the temperature, electrolyte composition, dielectric constant, and interaction at the molecular level.

studies have demonstrated that the electrolyte performance is directly determined by its solvation structure, where the dielectric constant plays an important role.<sup>[9]</sup> The dielectric constant of routine pure solvents or aqueous solutions is well established. However, electrolytes used in LBs generally consist of many components, including organic solvents, lithium salts, and various additives. It is difficult and expensive to construct a high-quality and large-quantity database of dielectric constant for all electrolytes through experiments, which seriously blocks the rational design and high-throughput screening of high-performance electrolytes.

In this contribution, the dielectric constant of liquid electrolytes is comprehensively investigated by molecular dynamics (MD) simulations to acquire a deep insight into the dielectric constant of solutions, including its atomic origin and variation. The temperature and electrolyte compositions are two key factors to determine the dielectric constant of solutions (Figure 1). The dielectric constant reduces with increasing temperature due to the intense motion of molecules and their enhanced ability to overcome the intermolecular dipole–dipole interactions at high temperatures. A linear and a polynomial variation of dielectric constant are observed for solvent mixtures with a weak and a strong molecule interaction, respectively. Besides, high-concentration and localized high-concentration electrolytes, in which the ions not only contribute to the dielectric constant but also alter the arrangement of solvent molecules owing to formation of solvation shells, are probed in detail for their important applications in high-energy-density LBs. A volcano plot is therefore obtained between the dielectric constant and lithium salt concentration. Moreover, the dielectric constant increases at the presence of diluents. This work not only affords an atomic insight into the dielectric constant variation with change of temperature and electrolyte composition but also establishes a high-throughput method for investigating the dielectric constant and further constructing a corresponding database for electrolytes.

## Results and Discussion

Typical carbonates, ethers, fluorinated solvents, and additives used in LBs are first considered for the calculation of dielectric constant, including diethyl carbonate (DEC), ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (HFE), 1,1,2,2-tetrafluoroethyl-2,2,2-trifluoroethyl ether (TFETFE), 1,3-dioxolane (DOL), 1,2-dimethoxyethane (DME), pentylene carbonate (PIC), butylene carbonate (BC), 2,3-butylene carbonate (BC23), propylene carbonate (PC), ethylene carbonate (EC), fluoroethylene carbonate (FEC), and vinylene carbonate (VC) (Figure S1a–n). Their experimental dielectric constant values range from 2 to 126, covering the  $\epsilon$  of most solvents.<sup>[10]</sup> Three different charges, Charge Model 1–Austin Model 1 (CM1A), Charge Model 5 (CM5), and Advanced restrained electrostatic potential charge (RESP2), were accordingly compared to ensure the reliability of the theoretical method.<sup>[11]</sup> The dielectric constant of the above solvents at 298 K (except for EC at 315 K) is



**Figure 2.** Effects of temperature on the dielectric constant of solvents. a) Dielectric constant dependence on temperatures. b) The mean square displacement (MSD) of EC at different temperatures. c) Variation of diffusion coefficients as temperature increases. d) Dielectric constant change percentage in the range of 60 K temperature increment.

summarized in Figure S2. Three charge models deliver a very similar dielectric constant for most solvents, such as DEC, EMC, DMC, DOL, PIC, BC, and FEC, while the 1.14\*CM1A charge outperforms a lot in some other solvents, especially for EC and VC. Therefore, the 1.14\*CM1A charge is chosen for the following calculations. Details of the calculation method are provided in Materials and Methods.

The electrolyte performance in wide-temperature range is of great interest recently.<sup>[12]</sup> Hence the influence of temperature on dielectric constant is considered in the following (Figure 2). In general, the dielectric constant of all solvents decreases as temperature rises within the range of their respective melting and boiling points, which can be explained by the molecular thermal motions (Figure 2a). Specifically, solvent molecules are more directionally aligned due to the dipole–dipole interactions between solvents at low temperatures than high temperatures. A high temperature enables molecules to overcome the dipole–dipole force and delivers a quick molecular thermal motion in solutions, which can be inferred from the continuous increase of mean square displacement and diffusion coefficient with increasing temperature (Figure 2b, c and Figure S3). Since the dependence of diffusion coefficients on temperatures conforms with an Arrhenius equation, the increment of diffusion coefficients varies with the same temperature increase interval of 10 K.<sup>[13]</sup> The total dipole moment of simulated systems becomes smaller due to accelerated molecular motions, further leading to a reduced dielectric constant.

The relationship between dielectric constant and temperature can be well described by an exponential function (formula 1), which is similar to the Arrhenius equation (Values of parameters  $A$  and  $E^*$  are listed in Table S1).

$$\epsilon(T) = A e^{\frac{E^*}{k_B T}} \quad (1)$$

The parameter  $E^*$  is defined as the energy barrier of overcoming dipole–dipole interactions between molecules herein, which can indicate the sensitivity of the  $\epsilon$  of a solvent to change with temperature. A solvent with a larger  $\epsilon$  and stronger intermolecular interactions possesses a higher energy barrier and its dielectric constant is more sensitive to temperature change (Figure 2d and Figure S4). For example, the binding energy between EC molecules is  $-0.16$  eV, corresponding to an energy barrier over  $1.3 \times 10^{-25}$  eV. The dielectric constant of EC ( $\epsilon = 86.94$  at 315 K) is reduced by approximately 40 % when temperature increases from 320 to 380 K. On the contrary, DMC ( $\epsilon = 1.44$  at 298 K, binding energy equals to  $-0.10$  eV) almost keeps the same dielectric constant at high temperatures as at 298 K due to that binding strength between DMC is much weaker than that between EC and energy barrier for DMC is also about two orders of magnitude lower than that for EC.

Besides temperature, dielectric constant variation with change of solution compositions is another important topic for battery studies as regulating electrolyte components is one of the most efficient and convenient methods to improve battery performances.<sup>[10,14]</sup> Mono-solvent can hardly meet all requirements for practical LBs and mixed solvents are often adopted. Therefore, dielectric constant variation of binary solvents is considered first in the following. After that, the influence of lithium salts on electrolyte dielectric constant is further studied. Especially, high-concentration and localized high-concentration electrolytes are focused on due to their superior performance with lithium metal anodes.<sup>[15]</sup>

The mixed carbonate solvents are widely used in commercialized LBs and their dielectric constants vary a lot for linear and cyclic molecules. Therefore, the EC/DMC and PC/EMC mixtures with various ratios are taken as examples to probe the dielectric constant of binary solvents (Figure 3a). Neither of these two systems follows a linear superposition rule. For example, when EC accounts for 50 % of the total mixture, the dielectric constant of EC/DMC should be about 54.02 according to linear addition rule but it is, in truth, only 22.94. In pure EC solvents, EC molecules prefer a directional alignment due to its large dipole moment, polarity, and strong intermolecular interactions (Figure S1 and Figure S4). Once EC is mixed with DMC, DMC molecules break the ordered arrangement of EC molecules due to the entropy of mixing, which explains the solid state of EC but liquid state of EC/DMC mixtures at room temperature and also agrees with the larger diffusion coefficients of EC and DMC at low EC

percentages than that at high EC percentages (Figure S5 and Figure S6). The square of the average total dipole moment ( $\langle M \rangle^2$  in formula S1) can be viewed as a measure of the order of a system. For a totally disordered system,  $\langle M \rangle^2$  is supposed to be zero because the dipole moments of molecules counterbalance each other. In the EC/DMC mixture, the smaller EC percentage, the smaller  $\langle M \rangle^2$ , which corresponds to a more disordered system (Figure S5c). As a result, the dielectric constant of EC/DMC mixtures is lower than the linear combination of  $\epsilon$  of pure EC and DMC. The FEC/DMC and BC/DEC mixtures exhibit a similar trend, indicating the wide applicability of the principle in mixtures of solvents with significantly different intermolecular interactions and dielectric constants (Figure S7). For solvents with similar polarities such as HFE/DMC and DME/DOL binary mixtures, mixing does not make a big difference to molecular orientations because the  $\langle M \rangle^2$  of mixtures remains at a low level (Figure S8). The diffusion coefficients of HFE and DMC at different HFE percentages resemble each other as well (Figure S9). The dielectric constants of such mixture systems follow the linear superposition rule at different ratios.

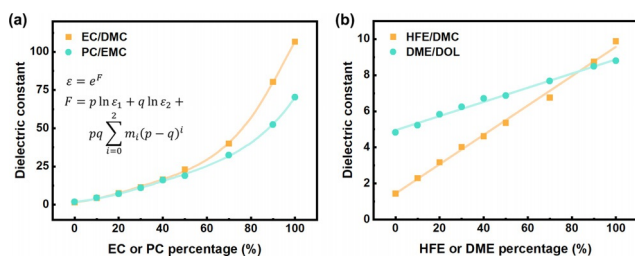
In order to quantitatively describe the nonlinear dielectric constant variation in a binary mixture, a polynomial model is constructed to describe dielectric constant of the mixture components (formula 2 and 3).<sup>[16]</sup>

$$\epsilon = e^F \quad (2)$$

$$F = p \ln \epsilon_1 + q \ln \epsilon_2 + pq \sum_{i=0}^2 m_i (p - q)^i \quad (3)$$

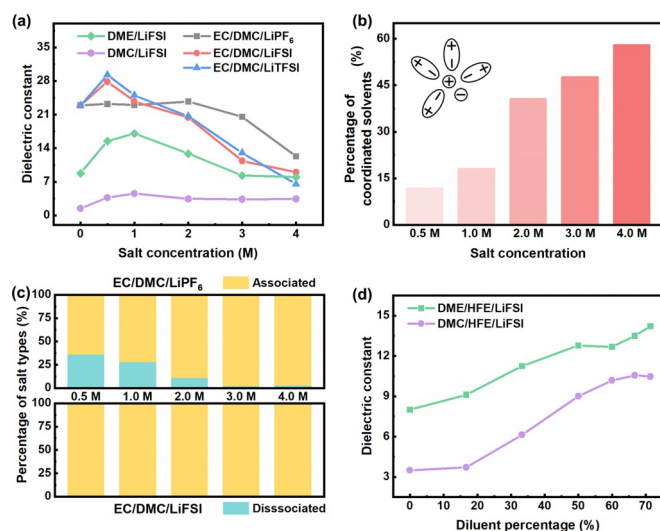
where  $\epsilon$  is the dielectric constant of mixtures,  $\epsilon_1$  and  $\epsilon_2$  dielectric constants of solvent 1 and 2 with a proportion of  $p$  and  $q$  ( $q = 1 - p$ ), respectively.  $m_i$  ( $i = 0, 1, 2$ ) are the model parameters. Accordingly, the model has an excellent prediction of dielectric constant of EC/DMC, PC/EMC, FEC/DMC, and BC/DEC mixtures with all coefficient of determination ( $R^2$ ) close to 1 (Table S2). In regard to mixed solvents lacking comprehensive dielectric constant data, the dielectric constant at any solvent ratio can be determined according to the polynomial model and only three data points are required to fit the model.

Different from the above binary solvents, the introduction of salts is much more complicated because of the association of salts and the formation of solvation structures. On one hand, the cations and anions from salts can be separated far apart by solvents and the electrolyte is infinitely polarizable under an external electric field, exactly corresponding to the situation of static dielectric constant measurement. In experiments, the dielectric constant at magnitude of million or billion Hz is used to represent the static dielectric constant of electrolytes and the dissociated ion pairs are no longer an unreasonable contribution to  $\epsilon$ .<sup>[17]</sup> Therefore, only contact ion pairs (CIPs) and solvents are considered when calculating the dielectric constant of electrolytes through formula S1.<sup>[18]</sup> On the other hand, cations will be solvated by solvents. Positive charges carried by spherical cations can induce the centripetal orientation of solvent dipoles, further influencing the dielectric constant.



**Figure 3.** Dielectric constant of binary solvent mixtures. a) Dielectric constant of EC/DMC and PC/EMC mixed solvents. b) Dielectric constant of HFE/DMC and DME/DOL mixed solvents (Solvent percentages are all in molar percentage).





**Figure 4.** Effects of salts and diluents on the dielectric constant of electrolytes. a) Dielectric constant of EC/DMC/LiPF<sub>6</sub>, EC/DMC/LiFSI, EC/DMC/LiTFSI, DME/LiFSI, and DMC/LiFSI at different salt concentrations (EC and DMC with a molar ratio of 1:1). b) Change of the percentage of coordinated solvents with increasing salt concentration in EC/DMC/LiFSI electrolyte. c) Statistics of the percentage of different salt types contained in EC/DMC/LiPF<sub>6</sub> and EC/DMC/LiFSI at different salt concentrations. d) Dielectric constant of electrolytes with diluents: 4.0 M DME/HFE/LiFSI and 4.0 M DMC/HFE/LiFSI ("4.0 M" means the electrolyte concentration is 4.0 M before the addition of diluents).

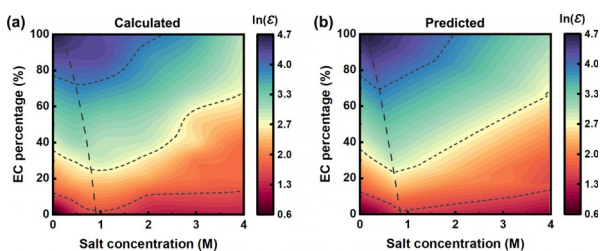
A volcano plot is obtained when correlating the dielectric constant of electrolytes with the salt concentration due to the compromise between the enlarged  $\epsilon$  from CIPs and decreased  $\epsilon$  from solvents in the solvation shell (Figure 4a). For instance, in the EC/DMC/LiFSI electrolyte, the dielectric constant increases from 22.94 to 27.83 when the salt concentration increases from 0.0 to 0.5 M because the Li<sup>+</sup>–FSI<sup>−</sup> CIPs possess a larger dipole moment than EC and DMC molecules (Figure S1). Subsequently, the dielectric constant decreases when the electrolyte become more concentrated. At the same time, dielectric constant of solvents in the electrolyte exhibits a gradual reduction throughout the process of salt concentration increasing (Figure S10), agreeing with the statistical analysis of the electrolyte structure and the change of diffusion coefficients of species in the electrolyte (Figure 4b and Figure S11). Li<sup>+</sup> coordinated solvents account for only 11.8% of total solvent molecules in 0.5 M EC/DMC/LiFSI electrolyte but approximately 60% in 4.0 M EC/DMC/LiFSI electrolyte and diffusion coefficients of EC and DMC decline to about one fiftieth of the values in the 0.5 M electrolyte. The reduced diffusion coefficients indicate that more solvents are frozen in the Li<sup>+</sup> solvation shell (inset in Figure 4b) and not able to move and orientate freely with increasing salt concentration. Therefore, the contribution of solvents to the electrolyte dielectric constant reduces, which is known as the dielectric saturation.<sup>[19]</sup>

The volcano trend is similar in other electrolytes while the kind of salts and solvents can induce a slight difference (Figure 4a). Compared with electrolytes with LiFSI and LiTFSI, dielectric constant of EC/DMC/LiPF<sub>6</sub> does not exhibit obvious increment until 2.0 M, which is induced by

the large dissociation trend of LiPF<sub>6</sub> (Figure 4c). For example, the dissociated LiPF<sub>6</sub> occupies over one third of the total salt types in 0.5 M EC/DMC/LiPF<sub>6</sub> but the cations and anions become more associated with the increase of salt concentration. As a comparison, Li<sup>+</sup> and FSI<sup>−</sup> are nearly 100% associated at various concentrations due to the stronger Li<sup>+</sup>–FSI<sup>−</sup> interaction than Li<sup>+</sup>–PF<sub>6</sub><sup>−</sup> (Figure S12). As a result, the small amount of Li<sup>+</sup>–PF<sub>6</sub><sup>−</sup> CIPs in EC/DMC/LiPF<sub>6</sub> electrolytes explains why the increase of their dielectric constant lags behind electrolytes with other lithium salts. When substituting DME or DMC for EC/DMC in EC/DMC/LiFSI, the dielectric constant variation also shows a volcano trend. However, the dielectric constant of 4.0 M DME/LiFSI or DMC/LiFSI is very close to the value of pure DME or DMC. The dielectric constant variation of solvents in electrolytes indicates that addition of salts has negligible effects on solvents with small dielectric constant and polarity, especially for DMC (Figure S10), which is similar to the phenomenon in effects of temperature on the dielectric constant. As a result, the dielectric constant of DME/LiFSI and DMC/LiFSI at high concentrations resembles that of pure DME and DMC due to the balance between contributions from salts and slight reduction of dielectric constant caused by the formation of solvation sheaths.

The localized high-concentration electrolytes are also considered, including DME/HFE/LiFSI and DMC/HFE/LiFSI. The dielectric constant of these two electrolytes increases when diluents occupy a proportion from 0.0% to 71.4% (Figure 4d), since HFE possesses a larger dielectric constant than DME, DMC, and the corresponding electrolytes without HFE (Figure S2a and Figure 4a). According to the radial distribution function before and after introducing diluents, the coordination environment around Li<sup>+</sup> remains nearly unchanged because diluents have a very weak interaction with Li<sup>+</sup> (Figure S13). Hence, diluents are supposed to have a little influence on both the dielectric contributions of salts and the dielectric saturation of solvents, leading to the linear variation of dielectric constant. When taking the dielectric constant of solvents/diluents and solvents/salts into consideration separately, the former also changes linearly which is in consistence with the linear trend in binary mixtures (Figure S14a). However, the latter one shows a slight decrease trend especially when diluent percentage increases from 50% to 71.4% (Figure S14b). Although diluents do not change the local solvation structures around Li<sup>+</sup>, the three-dimensional network of salt clusters in high-concentration electrolytes can be broken into divided regions by diluents (Figure S15).<sup>[20]</sup> Because of the increasing diffusion coefficients of solvents, diluents, and ions in the DMC/HFE/LiFSI system (Figure S16), the dielectric constant of solvents/salts accordingly exhibits a slight decrease in localized high-concentration electrolytes.

Taking EC/DMC/LiFSI electrolytes as an example, both the influences of binary solvents ratios and salt concentrations on dielectric constant are further incorporated into one diagram (Figure 5a). The volcano trend with increasing salt concentration holds at different EC percentages. However, the peak position of dielectric constant gradually shifts from around 1.0 to 0.5 M when EC occupies a larger percentage.



**Figure 5.** Dielectric constants of EC/DMC/LiFSI at different EC molar percentages and salt concentrations. a) Dielectric constants calculated by MD simulations and b) predicted by machine-learning model.

Contributions of solvent dipoles to the dielectric constant can be reduced due to the formation of solvation shells, especially for solvents with large dipole moments like EC. When EC accounts for a large percentage, the reduction of dielectric constant from solvents can prevail over the enlargement part due to CIPs even at a low salt concentration. The peak of dielectric constant hence shifts to low salt concentrations where there exist few solvation shells.

As a polynomial or exponential function is hard to describe the dielectric constant variation as electrolyte component changes, a machine-learning model based on artificial neural network (ANN) is further considered (Figure 5b and Figure S17). The EC and salt percentages were adopted as the inputs and the natural logarithm of dielectric constant was adopted as the output. After twenty thousand-step training, the ANN model delivers a good prediction of dielectric constant with a mean square error around 0.0088. Based on the ANN model, the two-dimensional diagram of dielectric constant variation with change of the EC percentage and salt concentration in EC/DMC/LiFSI electrolytes is obtained (Figure 5b), which is consistent with that from MD simulations. Therefore, the machine-learning model is very powerful to predict the dielectric constant of complicated electrolytes with multi solvents and salts.

As mentioned before, the dielectric constant can directly affect the interactions between ions or molecules, so as to modify solvation structures in solutions. Intermolecular interactions, in turn, are able to alter the dielectric constant according to our analyses of binary solvents, high-concentration electrolytes, and localized high-concentration electrolytes. The dielectric constant is thus a macroscopic description of the microstructures of solutions and in close relation to solution properties. Conventional experimental research is mainly carried out by trial and error to seek solution systems with suitable dielectric constant for specific purposes. For instance, a high dielectric constant is beneficial for the dissociation of cations and anions of salts and achieving high ionic conductivity. However, it will also impede reaction kinetics due to suppressed desolvation processes. Considering the abundant species that can be regulated, it is neither convenient nor economical to tailor solutions for different application scenarios through experiments. In this work, determination of dielectric constants of various solutions by MD simulations has advantages of high throughput and low cost. Other properties such as viscosity, diffusion coefficient, and so forth can also be calculated using MD simulations.

Combining theoretical calculations and existing experimental data, a database for solvents and electrolytes can be accordingly established. Further application of the machine-learning technique into data analysis and property prediction is capable of boosting rational design of solutions. The investigation of dielectric constants takes one step forward in such a statistically driven design approach, accelerating the design of new molecules and electrolyte recipes.<sup>[21]</sup>

## Conclusion

The dielectric constant variation of solutions with respect to temperatures and compositions is probed by MD simulations. The dielectric constants of solvents decrease with rise of temperature, which can be described by an Arrhenius-like function. The energy barrier is accordingly defined to reveal the intrinsic characteristics of solvents. The dielectric constants of binary solvents exhibit two distinct variation trends because of either strong or weak interactions between solvent molecules, which are well fitted by a polynomial and a linear model, respectively. A volcano plot is obtained for electrolytes with salts due to the compromise between the enlarged  $\epsilon$  from CIPs and decreased  $\epsilon$  from solvents in solvation shells. The addition of diluents to high-concentration electrolytes has a little influence on the above two effects as the solvation structures in concentrated electrolytes are preserved, thus delivering a linear correlation between the dielectric constant and the diluent percentage. Furthermore, a machine-learning model is developed to predict the dielectric constant of complicated electrolytes. This work unveils the chemical origin of dielectric constant variation of various electrolytes in lithium batteries at the molecular level and affords fruitful insight into the electrolyte solvation regulation, which helps to achieve the rational design and high-throughput screening of advanced electrolytes considering solvation effects. The general principle and method established in lithium battery electrolytes are supposed to be applicable to other chemical systems involving with solutions, such as fuel cells, sensors, and electrocatalysis.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** dielectric constant · liquid electrolytes · molecular dynamics simulations · solvent mixtures · temperature

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