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Ion Association Constants for Lithium Ion Battery Electrolytes from First-Principles Quantum Chemistry

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We provide a quantum chemical computational framework to calculate ion association constants relevant to lithium ion battery electrolytes. We compare our method to reported experimental values as the solvent, cation, and anion are varied. For solvent, anion, and cation variations, the standard errors are respectively 0.2 eV, 0.12 eV, and 0.11 eV for the chosen data set, where Pearson correlation values are all above 0.92.
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The degree to which a salt is associated directly affects the solvation structure, the electrochemical stability and the transport properties of electrolytes. In this article we present a simple methodology to estimate the ion association constants K_A of 1-1 non-aqueous electrolytes using ab initio computational methods, which we then compare against experimentally reported values relevant to lithium ion battery (LIB) systems.

Conventional wisdom holds that ion association is deleterious as it reduces the conductivity of LIB electrolytes.[1,2] However, newly emerging LIB electrolyte formulations, such as those described as low permittivity[3–6] or superconcentrated,[7,8] are promising alternative candidates. In these active research areas, associated salt plays unconventional roles. For example, neutral associated salt complexes may aid in surface passivation[7] or help dissociate salt via their contributions to the overall electrolyte permittivity.[9] A concise and validated methodology to calculate the K_As of a salt is therefore of practical and renewed interest.

Previous computational work has focused on determining pK_A values of aqueous solutes including understanding the effects of computational method, solvation model, and choice of thermodynamic cycle on the accuracy of these calculations.[10–12] Work toward performing analogous computations for nonaqueous electrolytes with cations other than H^+,[13] however, are far less established. While binding energies have been computed for a variety of battery-relevant electrolytes,[2,14,15] the methods used typically focus on trends in the electronic energy of the gas-phase species often omitting the entropic contributions or solvation effects necessary for comparison to experimental K_A values.[14] To the best of the authors' knowledge, no previous work reports computed ionic K_A values comparable to available experimental values and relevant to LIB systems. Herein, we provide a computational methodology for directly calculating such K_As.

We provide a straightforward method that is inexpensive and can be used for predictive screening for electrolyte selection. We simplify the possible equilbria via the assumption of contact-ion pairs as the relevant ion associated species. We evaluate this approximation by comparing the results to experimental K_As. Although simplistic, we find that this assumption provides reliable trends in the prediction of association behavior.

First, we introduce the relevant equilibria relations for ion-association. We then discuss the computational methods used. The choice of experimental data set is motivated, to which we compare computed K_As. Finally, we discuss limitations of the model, possible improvements, and example LIB electrolyte systems where knowledge of the extent of ion association may be particularly relevant.

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Theory

For a cation M^+ and anion N^- in solution, an equilibrium may be established with the neutral contact-ion pair MN:

$$M^+ + N^- \rightleftharpoons MN \qquad [1]$$

The change in Gibbs free energy of the above reaction can be denoted as ΔG_A, and for infinite dilution as ΔG_A^0. ΔG_A^0 can be related to the association constant at infinite dilution K_A^0 via the following relationship:[16]

$$K_A^0 = exp\left[\frac{-\Delta G_A^0}{RT}\right]/(1mol/L) \qquad [2]$$

If ideality is assumed, then $K_A^0 = K_A$, and K_A^0 can be directly related to the fraction of free ions α at a given concentration c via the mass action law:[16]

$$K_A^0 = \frac{1-\alpha}{c\alpha^2} \qquad [3]$$

We note that that for appreciable concentrations, e.g. up to 1 M, there exist semi-empirical expressions for the activity coefficients of the various salt species, which would allow construction of speciation diagrams,[17] the details of which are outside the scope of this paper.

Methods

Partial explicit solvation shell.—In order to calculate the free energy upon association $\Delta G_A^0 = G_{MN}^0 - (G_{M^+}^0 + G_{N^-}^0)$, we account for the various terms for a given species. We can relate the total Gibbs free energy $G_{species}^0$ to the electronic energy $E_{electronic}$, the solvation free energy δG_{solv}, the thermal energy $\Delta E_{thermal}$, and the entropy of the species S via the following expression:

$$G_{species}^0 = E_{electronic} + \delta G_{solv} + \Delta E_{thermal} - TS \qquad [4]$$

The terms in Equation 4 are here calculated using quantum chemistry. $E_{electronic}$ includes the electronic energy for the species with the geometry optimized in the liquid phase using the implicit solvent model PCM (polarizable continuum model).[18] The PCM models the liquid phase via a structureless dielectric medium surrounding a solute species, and also allows for the approximative calculation of δG_{solv}. The values for the static solvent permittivities used here were taken from the literature.[19,20] Figure 1a) shows the scheme used for the calculation of $E_{electronic} + \delta G_{solv}$, where an explicit solvent molecule is added for the electronic structure calculations of MN and M^+ to more accurately reflect the solvation environment.[12] For N^- simply the implicit solvent model is used, with no explicit solvent molecule (Figure 1b). Here we assume that explicit solvent molecules are not necessary to adequately represent the solvation environment of the anion, an assumption which we discuss in the Results section.

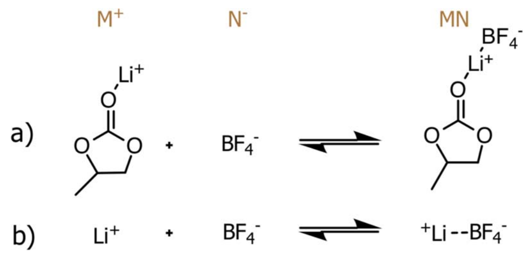

Figure 1. Scheme to calculate each of the components of the free energy of association (ΔG_A^0), exemplified using the salt $LiBF_4$ and solvent PC. a) Electronic energy ($E_{electronic}$) and solvation free energy (δG_{solv}) are calculated using one explicit solvent molecule. b) Thermal energy ($\Delta E_{thermal}$) and entropy (S) are calculated in implicit solvent.

In order to obtain S and $\Delta E_{thermal}$ for each respective solvated species, implicit solvent calculations were undertaken for each salt species (M^+, N^-, and NM) with no explicit solvent molecule (Figure 1b). The explicit solvent molecule is avoided in the calculation of S since entropic contributions related to solute-solvent interactions (such as librational modes) are, in principle, already accounted for by δG_{solv}. S includes a translational contribution for the free monoatomic cations M^+, and for N^- and NM, a translational, vibrational, and rotational contribution as well.[21,22] We note that the translational contribution calculated from the Sackur-Tetrode equation[23] is here evaluated for the appropriate standard concentration (1 mol/L), and that vibrational frequencies below 100 cm^{-1} are adjusted to 100 cm^{-1} to avoid spurious entropy contributions.[13,24,25] Furthermore, all calculations to obtain S and $\Delta E_{thermal}$ were undertaken using the PCM with a single dielectric constant, that of 2-methoxyethanol ($\epsilon = 16.96$), as variations calculated for S and $\Delta E_{thermal}$ across various ϵ are negligible. A detailed example for the application of equation 4 is provided in the supplementary information (SI).

All quantum chemistry calculations were undertaken with Gaussian16 software.[22] The wb97xd hybrid functional with Grimme's empirical 2D dispersion[26] was employed. It has been shown to provide adequate geometries and electronic energies at a reasonable cost.[26] The def2tzvp basis set was employed,[27] and it was preferred to Pople-type basis sets since def2 basis sets by default include effective core potentials, which are necessary for heavy alkali atoms (Rb and Cs). For solvation effects, IEFPCM[18,28] was used with the default cavity construction,[28] which utilizes the UFF force field. Corrections to the thermodynamic data were undertaken with the GoodVibes analysis code.[25] Initial configurations were found via conformational analysis[29–32] and energy minimization using the MacroModel package[33] with the semi-empirical OPLS forcefield.[34]

Full explicit solvation shell.—Electrostatic energies calculated with the above presented model are only accounted for by a single explicit solvent molecule and a structureless dielectric medium. Increasing the number of explicit solvent molecules in the electronic structure calculations may be helpful,[35–38] although significantly more expensive computationally. The treatment of explicit solvent molecules $\mathcal{S}$ may lead to release or capture upon association of x solvent molecules upon association. Consequently, the following equilibria relation can be established for K_A:

$$M^+\mathcal{S}_n + N^- \rightleftharpoons MN\mathcal{S}_{n-x} + x\mathcal{S} \quad [5]$$

The number of primary solvation shell solvent molecules n for $M^+\mathcal{S}_n$ and $n-x$ for $MN\mathcal{S}_{n-x}$ can be found variationally. Here, since the primary solvation shell is treated explicitly, S and $\Delta E_{thermal}$ for each species can be found simply via the Sackur-Tetrode equation (e.g. with translational, vibrational and rotational terms), with similar vibrational frequency corrections as those mentioned in the previous subsection. Here, S for the solvent $\mathcal{S}$ is calculated with the standard concentration of the neat solvent.

Table I. ΔG_A as a function of salt and solvent, both computed here (ΔG_A Comp) and reported experimentally (ΔG_A Exp).

Solvent	Salt	ΔG_A Comp (eV)	ΔG_A Exp (eV)	Exp ref
DMC	$LiClO_4$	−1.405	−0.765	9,19
methyl acetate	$LiClO_4$	−0.558	−0.467	19,39
Me-THF	$LiClO_4$	−0.562	−0.489	19,40
glyme	$LiClO_4$	−0.542	−0.363	41
glyme	$LiBF_4$	−0.614	−0.414	41
THF	$LiClO_4$	−0.572	−0.403	42
THF	$LiBF_4$	−0.643	−0.417	42
THF	$LiAsF_6$	−0.505	−0.290	16,43
methyl formate	$LiClO_4$	−0.244	−0.344	19,44
2-methoxyethanol	$LiClO_4$	−0.159	−0.138	16,45
2-methoxyethanol	$NaClO_4$	−0.282	−0.147	16,45
2-methoxyethanol	$KClO_4$	−0.305	−0.150	16,45
2-methoxyethanol	$RbClO_4$	−0.307	−0.153	16,45
2-methoxyethanol	$CsClO_4$	−0.397	−0.156	16,45
AN	$LiClO_4$	0.026	−0.079	19,46
AN	$NaClO_4$	0.003	−0.071	47
AN	$KClO_4$	−0.059	−0.086	47
AN	$RbClO_4$	−0.017	−0.088	47
AN	$CsClO_4$	−0.162	−0.091	47
DMA	$LiClO_4$	0.018	−0.033	20
PC	$LiClO_4$	0.002	−0.026	48
PC	$LiBF_4$	−0.041	−0.055	48
PC	$LiPF_6$	0.122	−0.019	48
PC	LiTriflate	−0.074	−0.071	48
PC	LiTFSI	0.019	−0.010	48
PC	$LiAsF_6$	0.032	−0.002	49

Validation.—In order to evaluate the accuracy and validity of the method presented in the Partial explicit solvent shell section, we compared our calculated K_As to reported K_As, which have been measured via conductometric or dielectric techniques[16] at room temperature. Such techniques allow estimation of the concentration of salt species and relevant equilibrium constants. Conductivity measurements allow inference of thermodynamic data such as the ion-pairing association constant due to the measurable decrease in conductivity arising from the presence of neutral ion-pairs.[16] Dielectric spectroscopy measurements also allow the inference of association constants since the frequency dependant dielectric response is a function of the 'cooperative motions of all dipolar species',[16] e.g. solvent and associated salt complexes.[64] The chosen K_As are all representative of systems at infinite dilution, and as such our computational model does not add corrections for non-idealities: henceforth $K_A^0 = K_A$ and $\Delta G_A^0 = \Delta G_A$. $LiClO_4$ was chosen as the salt for the data set with varying solvent due to the numerous available measured K_As.[19] Since variations in cation or anion can result in K_A differences sometimes smaller than the systematic error of the experimental method, our choices favor studies where the relevant K_As were found in the same study. All references and experimental values are listed in Table I. We note that there exists a large body of experimental work studying ion-pairing in battery relevant electrolytes at concentrations ∼1 M[50–54] but that these do not report infinite dilution equilibrium constants: in fact the activity coefficients of the salt species at the concentrations studied in those studies are significant, can vary widely from system to system[16,17] and would not be comparable to results from quantum chemistry alone. Development of a methodology to account for the effects of finite concentration on our computed equilibrium constants, for example using activity coefficients from Debye-Huckel theory,[16,17] is the subject of further work.

Results

Partial explicit solvation shell.—Figure 2 shows the computed K_A as a function of experimentally reported K_A for the $LiClO_4$ salt dis-

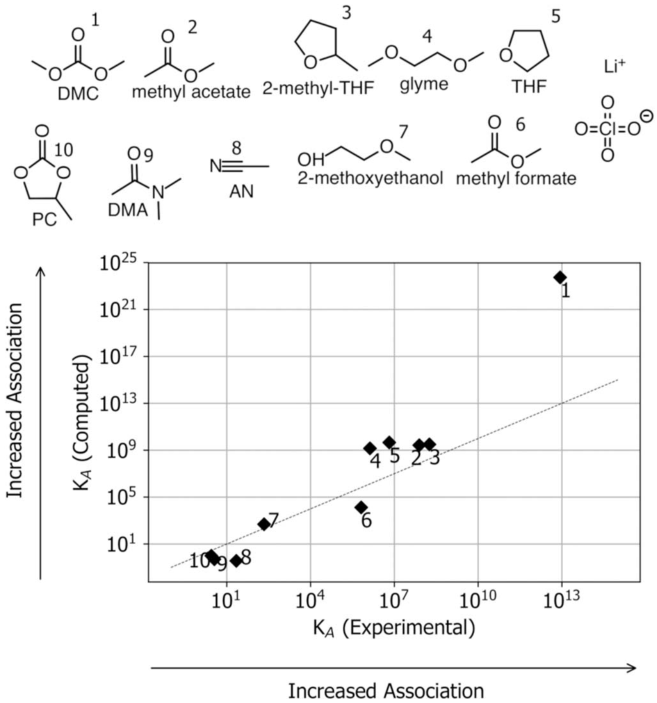

Figure 2. Computed K_A as a function of experimental K_A for $LiClO_4$ based electrolytes. The different solvents studied are shown above.

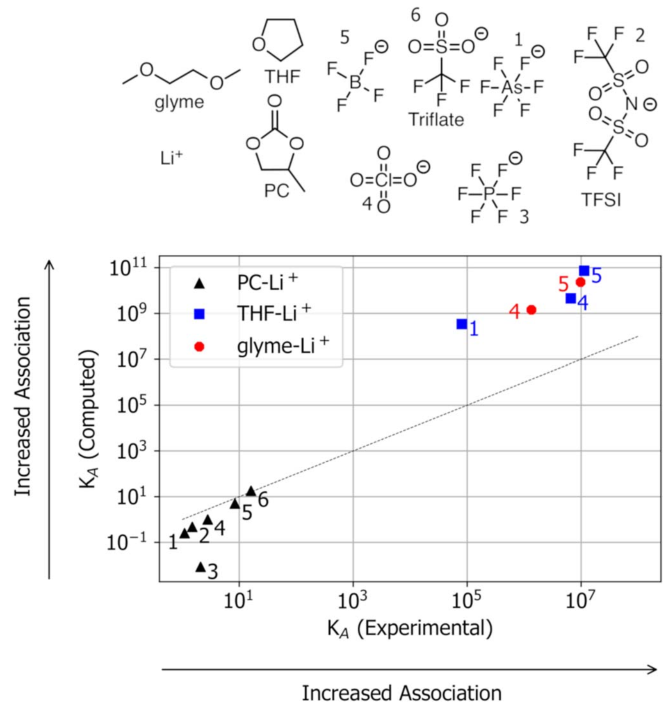

Figure 3. Computed K_A as a function of experimental K_A for Li^+ based electrolytes with various anions in PC, glyme and THF. The different anions and solvents studied are shown above.

solved in various solvents, using the methods described in the Partial explicit solvent shell methods section. The experimental and computed trends agree, with a Pearson correlation value of 0.96, while the standard error of ΔG_A is 0.21 eV. The dielectric constant is generally a reliable descriptor for relative trends in association between solvents which are of considerably different polarity,[16,19] and its effect is directly encompassed by the PCM used in our model. However, the permittivity as a descriptor may fail between solvents of similar permittivity. A notable example is glyme ($\epsilon = 7.0$) and tetrahydrofuran ($\epsilon = 7.4$), where glyme, despite its lower permittivity, exhibits a lower K_A for $LiClO_4$. This is commonly attributed to the chelating ability of the glymes which allows more oxygens to coordinate with the solute.[41,55–57] Consistent with this rationale, the inclusion of an explicit solvent molecule in the calculation allows for the relative K_A ordering between both solvents to be predicted. In Figure 2, we note one striking outlier, dimethyl carbonate (DMC), which, although accurately reported to exhibit the highest K_A among the studied solvents, presents an overestimated calculated ΔG_A by 0.6 eV. This may be due to an imprecise calculation of δG_{solv} for the species, which we discuss in the following section.

Figure 3 shows the computed K_A as a function of experimentally reported K_A for salts of varying anion dissolved in propylene carbonate (PC), glyme and tetrahydrofuran (THF) solvents. The relative K_A ordering is fairly reproduced — in this case between varying anions for a single solvent. However, $K_A(LiPF_6)$ is calculated to exhibit lower association as compared to K_A(LiTFSI) and $K_A(LiAsF_6)$ in PC as compared to experimental results, where $K_A(LiAsF_6) < K_A(\text{LiTFSI}) < K_A(LiPF_6) < K_A(LiClO_4) < K_A(LiBF_4) < K_A(\text{LiTriflate})$. For glyme and THF, the relative trend of $K_A(LiAsF_6) < K_A(LiClO_4) < K_A(LiBF_4)$ is accurately predicted. We note that binding energies calculated by previous computational studies also generally agree with this trend.[14] Although it is likely that explicit hydrogen bonding plays a role for ClO_4^- in the 2-methoxyethanol solvent, the computed K_A is comparable to the other cases in the studied data set. For the data in Figure 3, the standard error of ΔG_A is 0.12 eV and the Pearson correlation value is 0.96. We note that previous computational work, e.g. on pK_As, involves errors of similar magnitude.[10,12,13] PF_6^- exhibits a much larger volume than BF_4^-, resulting in a lower volumetric charge density, and both properties prompt a weakened electrostatic interaction between oppositely charged ions for $LiPF_6$ over $LiBF_4$. However, the argument invoking size fails to explain why triflate leads to a higher K_A than the smaller BF_4^-. In general, quantum chemistry accounts for charge density as well as specific interatomic interactions, the latter being evidently important for LiTriflate. Regarding solvent-anion interactions, we note the following: conventional organic solvents typically exhibit a well-defined negative end of the dipole, but a less well-defined positive end of the dipole, i.e. the charge is less localized.[58,59] This would entail that anions interact in a weaker fashion with solvents than cations do, and hence differences in K_A between various anions are unlikely to be dominated by solvent-anion interactions.

Figure 4 shows the computed K_A as a function of experimentally reported K_A for ClO_4^- salts of varying alkali metal cation dissolved in acetonitrile (AN) and 2-methoxyethanol solvents. Here the experimental trend is well reproduced by our computational model. As previously reported,[47] increasing alkali metal cation size results in decreasing solvent-cation electrostatic interactions, which in turn correlates with higher K_As. Two minor deviations from the relative experimental association strengths are noted. The experimental K_As indicate that Li^+-AN is more associated than Na^+-AN, in disagreement with the computed values. However, as shown in Table I, the experimental data point for Li^+-AN is taken from a different study than the other M^+-AN values: between different experimental reports there are often errors on the order of 0.02 eV,[19,48] which is comparable to the measured difference in the K_As of Li^+-AN and Na^+-AN. Previous computational work by Jonsson and Jonhannsen[14] found that Na salts typically bind more strongly than Li salts, in agreement with the present work. Secondly, the computed K_As for Rb^+-AN and K^+-AN suggest that the Rb^+ analog is less associated than the K^+ counterpart, in disagreement with experimental values. Overall, for the data shown in Figure 4, the standard error between experimental and computed K_As is 0.11 eV and the Pearson correlation value is 0.93. Here, the differences between varying cations, although correct in their relative ordering (besides the above mentioned cases), are exaggerated. This may be due to inaccurate solvation energies of the various cations, which we discuss in the

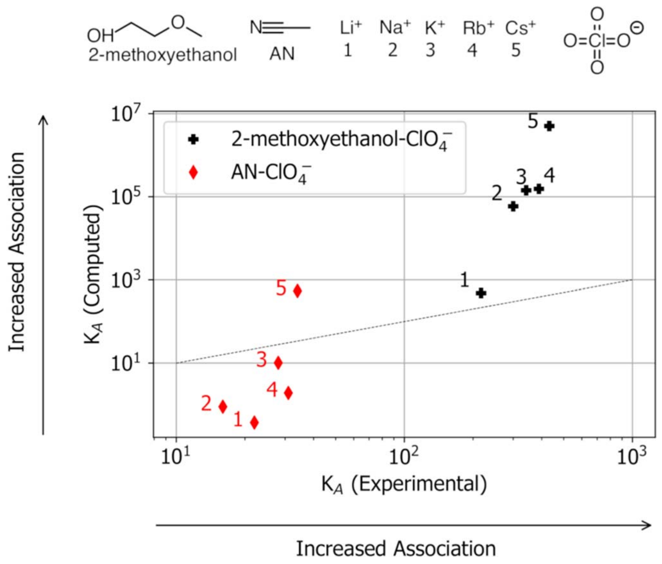

Figure 4. Computed K_A as a function of experimental K_A for various alkali metal cation based electrolytes. The different solvents and salts studied are shown above.

following section. We note that all ΔG_A values for the data shown in Figures 2, 3 and 4 are listed in Table I using Equation 2.

Full explicit solvation shell.—As noted in the previous section, the DMC-$LiClO_4$ K_A showed significant disagreement with experiment (e.g. 0.6 eV). To investigate the role of solvent number we employed a full explicit solvation shell of solvent molecules for the calculation of the DMC-$LiClO_4$ K_A, as detailed in the Methods section. By minimizing the $E_{electronic} + \delta G_{solv}$, solvent numbers of $n = 6$ and $n - x = 5$ were found for the free ion and the CIP, respectively. Using additional solvent molecules, the overestimation error in ΔG_A decreased from 0.6 eV to 0.2 eV. Previous work has shown that the PCM alone is not adequate for modeling DMC due to significant but unaccounted quadrupolar interactions.[60] To some extent, explicit solvents (sometimes referred to as cluster-continuum), can help correct the solvation energy errors.[37,53,61] We note that in the present work's methodology, the preparation of initial structures followed a conformational analysis with a semi-empirical force field (see Methods section), and that further corrections may be made via a conformational analysis with a more accurate method (e.g. first principles) and more advanced statistical sampling.[61]

Hence, we surmise that for very low permittivity media (e.g. $\epsilon < 5$), the PCM may require enhancement via explicit solvent shells, where otherwise solute-solvent interactions may not be well accounted for.[62]

Discussion and Conclusions

In the case of alkali cations, shown in Figure 4, although the relative trend in association strength is generally reproduced, the differences in K_A are exaggerated. We believe this is due to limitations of the PCM at accounting for differences in solvation energies between various alkali metal cations. We speculate that the Gaussian[22] default parameters employed here for the PCM cavity construction[28] may require additional tailoring.[63] Nonetheless, despite the apparent deviations, the standard error is modest (0.11 eV) with the largest error being 0.24 eV. Finally, we note that there may exist an equilibrium between various types of associated salt, e.g. solvent-separated ion pairs,[16] double solvent-separated ion pairs,[64] triple ions,[19] dimers,[9] etc., which could be included in a more elaborate model than the present one.

There exists a design space for electrolytes utilizing the properties of various salts, where knowledge of preferential association can be informative. Notably, LIB electrolytes comprised of binary mixtures of salt, unavoidably with varying K_A, are an active area of research. For example, a combination of $LiBF_4$ and $LiPF_6$ has shown promise in improving Coulombic efficiency of Li-ion cells.[65] Although nonidealities are left unaccounted for in the present model, preferential association will persist for a certain concentration range above the dilute limit.[66,67] Another example of binary salt systems for LIBs is Li^+ electrolytes with added $CsPF_6$ or CsTFSI, which have helped in passivation phenomena.[68–70] In low permittivity electrolytes, where polar associated salt species can help increase solution permittivity via polar contact-ion pairs,[3,5,9] the addition of a preferentially associated salt may be useful, as long as formation of larger but less polar aggregates (e.g. quadrupolar dimers) is minimized.

We presented and evaluated a methodology which was shown to be accurate in its predicted trends between various association constants K_A. Although limited in its ability to obtain accurate K_A differences across various cations, it was shown to be reliable for varying anions and solvents for a same cation. We hope that the current methodology can help guide future electrolyte salt selection for LIBs, as well as serve as a building block for more advanced computational models.

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