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Cluster-Continuum Quasichemical Theory Calculation of the Lithium Ion Solvation in Water, Acetonitrile and Dimethyl Sulfoxide: Absolute Single Ion Solvation Free Energy Scales

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Abstract

Absolute single-ion solvation free energy is a very useful property for understanding solution phase chemistry. The real solvation free energy of an ion depends on its interaction with the solvent molecules and on the net potential inside the solute cavity. The tetraphenyl arsonium–tetraphenyl borate (TATB) assumption as well as the Cluster–Continuum Quasichemical Theory (CC–QCT) approach for Li^+ solvation allows access to a solvation scale excluding the net potential. We have determined this free energy scale investigating the solvation of the lithium ion in water (H_2O), acetonitrile (CH_3CN) and dimethyl sulfoxide (DMSO) solvents via the CC–QCT approach. Our calculations at the MP2 and MP4 levels with basis sets up to QZVPP+diff quality, and including solvation of the clusters and of the solvent molecules by the dielectric continuum SMD method, predict the solvation free energy of the Li^+ as –116.1, –120.6 and –123.6 kcal mol^{-1} in H_2O, CH_3CN and DMSO solvents, respectively (1 mol L^{-1} standard state). These values are compatible with the solvation free energy of the proton of –253.4, –253.2 and –261.1 kcal mol^{-1} in H_2O, CH_3CN and DMSO solvents, respectively. Deviations from the experimental TATB scale are only 1.3 kcal mol^{-1} in H_2O and 1.8 kcal mol^{-1} in DMSO solvents. However, in the case of CH_3CN, the deviation reaches a value of 9.2 kcal mol^{-1}. The present study suggests the experimental TATB scale is inconsistent for CH_3CN. A total of 125 values of the solvation free energy of ions in these three solvents was obtained. These new data should be useful for the development of theoretical solvation models.

Introduction

The interaction of ions with solvent molecules and their thermodynamic stability in the solution phase are fundamental problems in physical chemistry. Single-ion solvation free energy is critical for pK_a of acids,[1–15] redox potentials,[16–19] solubility products,[20] chemical equilibria,[21,22] kinetics,[21,23–29] spectroscopy[21,30] and many other properties. Thus, the availability of an accurate solvation free energy scale for single ions in different solvents is very important for the development of solvation models.[31–56] However, it has become evident that explicit and implicit solvation models should be calibrated against different free energy scales.[31,34] This is because a molecular cavity immersed in a solvent has two interfaces. The first interface is the gas–solvent surface. A point test charge going from the gas phase (zero potential) to inside the solvent region feels the variation of the electrostatic potential when crossing the interface, named the surface potential ($\Delta\phi_{sp}$), and the resulting electrostatic potential inside the liquid phase is named the Galvani potential (ϕ_G, see Figure 1). This gas–solvent interface is real. However, there is another, imaginary, interface built around the solvated ion, which the solvent molecules do not cross. Inside this region, the electrostatic potential created by the solvent molecules is different from the bulk solvent and corresponds to ϕ_R, the real potential felt by the ion (also named the net potential, ϕ_{np}).[36] The variation of the electrostatic potential on going from bulk solvent to inside the solute cavity is the local potential ($\Delta\phi_{lp}$). The relations between these quantities are:

$$\phi_{\mathrm{G}} = \Delta\phi_{\mathrm{sp}}, \quad (1)$$

$$\phi_{\mathrm{R}} = \phi_{\mathrm{G}} + \Delta\phi_{\mathrm{lp}} = \Delta\phi_{\mathrm{sp}} + \Delta\phi_{\mathrm{lp}}. \quad (2)$$

Any calculation of the solvation free energy of an ion inside a very large cluster with explicit solvent molecules leads to the real solvation free energy ($\Delta G^{*\mathrm{real}}_{\mathrm{solv}}$). On the other hand, when explicit solvent molecules are used with periodic boundary conditions, only the local potential is included, and the resulting solvation free energy is named the intrinsic solvation free energy ($\Delta G^{*\mathrm{int}}_{\mathrm{solv}}$). Thus, the Galvani (or surface) potential needs be added to $\Delta G^{*\mathrm{int}}_{\mathrm{solv}}$ to obtain the real solvation free energy.

$$\Delta G^{*\mathrm{real}}_{\mathrm{solv}} = \Delta G^{*\mathrm{int}}_{\mathrm{solv}} + q\phi_{\mathrm{G}}. \quad (3)$$

Another solvation thermodynamic quantity is the bulk solvation free energy ($\Delta G^{*\mathrm{bulk}}_{\mathrm{solv}}$). In this case, both the surface and local potential contributions are excluded from the real solvation free energy and the relation between these two quantities is:

$$\Delta G^{*\mathrm{real}}_{\mathrm{solv}} = \Delta G^{*\mathrm{bulk}}_{\mathrm{solv}} + q\phi_{\mathrm{R}}. \quad (4)$$

When we consider a dielectric continuum solvation model,[43,57–60] these surface potentials do not exist. As a consequence, the solvation free energy of any ion computed using a continuum model, or even a hybrid cluster–continuum approach with a few solvent molecules, corresponds to $\Delta G^{*\mathrm{bulk}}_{\mathrm{solv}}$. These quantities need be related to experimental values.

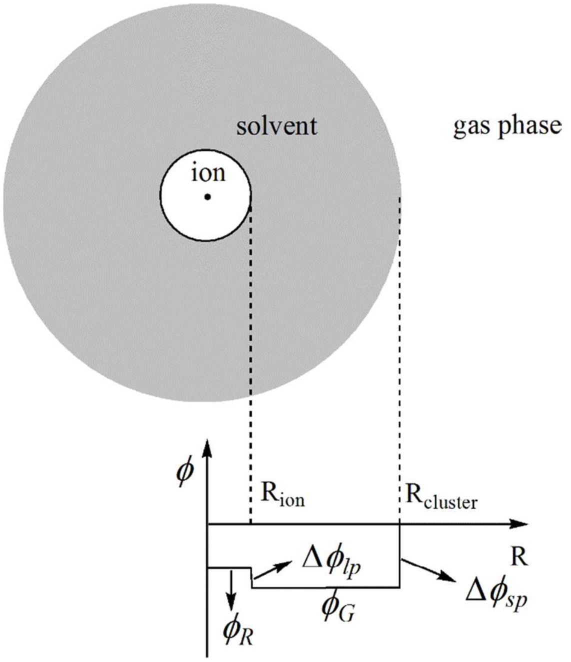

Figure 1: Electrostatic potential felt by a test charge crossing the real gas–solvent interface and the imaginary ion–solvent interface.

Experimental approaches aimed at determining the solvation free energies are usually based on extrathermodynamic assumptions. The most used include the TATB (tetraphenyl arsonium tetraphenyl borate)[53,61,62] and the CPA (Cluster Pair Approximation).[49,50] The TATB considers two ions of opposite charges, the tetraphenyl arsonium (TA^+) cation and the tetraphenyl borate (TB^-) anion, as references for determining the solvation free energy scale.[62] It is assumed that large and spherical ions like TA^+ and TB^- have the same solvation free energy. Thus, the approach corresponds to assigning half of $\Delta G^*_{\mathrm{solv}}$ of the TA^+ plus TB^- pair of ions to each one. As a consequence, it does not include the net potential and provides the bulk solvation free energy scale.

The other widely used method is the CPA and related approaches, which are based on the thermodynamic properties of small ion–solvent clusters in the gas phase.[33,38,47,49,50] Usually, clusters with up to 10 water molecules are studied and extrapolations are made to the bulk. The main assumptions of this approach are that the difference in the solvation free energy between the $M^+(H_2O)_n$ and $X^-(H_2O)_n$ clusters is small even for small n and becomes zero in the limit of $n \to \infty$. Nevertheless, this idea has been challenged. Asthagiri *et al.* have argued that the CPA approach includes the solvent surface potential[63] and Vlcek and co-workers have shown that the convergence requires more than a few solvent molecules.[33] In fact, the CPA method leads to the real solvation free energy and the corresponding solvation free energy scale does not match the TATB approach.

While the absolute solvation free energy of single ions in aqueous solvent has received much attention,[53,54,61,62,64–66] organic solvents have been less studied.[45,52] The available experimental data are usually the free energy of transfer between different solvents, based on the TATB assumption.[67,68] Pliego and Riveros have reported absolute solvation free energies of single ions in water and DMSO[52] using the proton solvation in water determined by the CPA method[50] and the free energy of transfer of the proton from water to DMSO.[68] Some years later, Kelly *et al.* combined theoretical and experimental data and applied the CPA method for CH_3OH, CH_3CN and DMSO solvents to obtain single-ion solvation free energy scales in these solvents.[45] Thus, the real (or net) potential was included in those studies. Westphal and Pliego applied the cluster–continuum approach to calculate the solvation free energy of the Li^+ ion in DMSO.[69] Although this approach does not include the real potential, the value of lithium solvation was comparable to the Kelly *et al.* scale.[45] More recently, the solvation free energy of the Li^+ ion in methanol has also been investigated by the cluster–continuum approach.[70] The results have indicated that a high level of theory is needed to converge to the interaction energy between the methanol solvent molecules and the small Li^+ ion. In addition, the obtained solvation free energy scale was close to the TATB-based scale and different from the Kelly *et al.* scale. Other theoretical studies of single-ion solvation have also been recently reported for methanol[56] and acetonitrile solvents.[71]

Considering that the bulk solvation free energy scale is more adequate than the real solvation free energy scale for continuum or hybrid cluster–continuum solvation models, it is worthwhile to have a bulk scale for important organic solvents and water. In addition, if the $\Delta\phi_{\mathrm{lp}}$ term is approximately constant for molecular size cavities, then the ϕ_{R} potential will be a constant for each solvent and independent of the solute. We are using this assumption in this study. Thus, the aim of this paper is to apply accurate electronic structure methods in conjunction with the Cluster-continuum Quasichemical Theory (CC–QCT) approach[63,69,72–74] to calculate the solvation free energy of the Li^+ ion in water, acetonitrile and dimethyl sulfoxide. In the following step, the solvation free energy values of some single ions were determined in these solvents.

Theoretical Methods

Cluster-continuum Quasichemical Theory of Solvation

The Cluster–Continuum model proposed by Pliego and Riveros[72] is similar to the quasichemical theory of Pratt and co-workers[63,73] and it is referred to as the Cluster–Continuum Quasichemical Theory (CC–QCT) of Solvation. This approach has been discussed in detail elsewhere[69,70,72] and we are just going to present the main results. The idea behind the approach is to consider the central ion plus some strongly bound solvent molecules as a chemical species. The formation of this cluster is represented as a chemical reaction between the $A^{\pm}$ ion and n solvent molecules S according to equation 5:

$$\mathrm{A}^{\pm}{}_{(\mathrm{g})} + n\mathrm{S}_{(\mathrm{sol})} \rightarrow (\mathrm{A}^{\pm}(\mathrm{S})_{n})_{(\mathrm{sol})} \qquad (5)$$

Thus, the solvation free energy is given by the following equation:

$$\Delta G^{*}_{\mathrm{solv,n}}(\mathrm{A}^{\pm}) = \Delta G^{*}_{\mathrm{clust}}(\mathrm{A}^{\pm}(\mathrm{S})_{n}) + \Delta \mathrm{G}^{*}_{\mathrm{solv}}(\mathrm{A}^{\pm}(\mathrm{S})_{n}) - n\Delta G^{*}_{\mathrm{solv}}(S) - nRT\ln[\mathrm{S}]. \quad (6)$$

The first term on the right-hand side is the Gibbs free energy for the formation of the cluster in the gas phase (1 mol L^{-1} standard state). The second term is the solvation energy of the cluster, the third term corresponds to the solvation free energy of n solvent molecules and the last term is related to the density number of the solvent, which is equal to 55.34, 19.12 and 14.08 mol L^{-1} for water, acetonitrile and dimethyl sulfoxide, respectively. The CC–QCT approach was tested by Roux and Yu for solvation of Li^+, Na^+ and K^+ ions in aqueous solution against free energy perturbation calculations.[75] Those authors have found that the method is accurate for the case of Li^+ ion, which has the highest binding energy to the water solvent molecules.

An important issue is the standard state used in the solvation free energy definition. Throughout this work, we have used the standard state of 1 mol L^{-1} for both gas phase and solution phase, which is indicated by the symbol *. The relation between this solvation free energy scale with a definition that uses 1 atm standard state in the gas phase, represented by the symbol ^{o}, corresponds to:

$$\Delta G^{*}_{\mathrm{solv}}(\mathrm{X}) = \Delta G^{\circ}_{\mathrm{sol}}(\mathrm{X}) - 1.89\ \mathrm{kcal/mol} \qquad (7)$$

This relation (valid at 25 °C) was used to convert some solvation data taken from the literature.

Ab initio calculations

Previous studies on Li^+ interaction with CH_3OH and DMSO solvent molecules have indicated that these systems are very sensitive to the level of theory and require an extended basis set. Thus, we have used the most reliable approach for each cluster that was possible with our present computational resources. For $Li^+(H_2O)_4$ and $Li^+(CH_3CN)_4$ clusters, geometry and frequency calculations were performed at the MP2 level with the def2-TZVPP basis set[76] augmented by diffuse sp functions on oxygen and nitrogen atoms (named TZVPP+diff). For the larger $Li^+(DMSO)_4$ cluster, we have used MP2 optimization and frequency with the smaller def2-SVP[76] function augmented by diffuse sp functions on sulfur and oxygen atoms.

To obtain more reliable geometries in the liquid phase, we have performed optimizations using the continuum model CPCM (Conductor-like Polarizable Continuum Model)[77] in conjunction with the MP2 method with the same basis sets used in the gas-phase calculations. These CPCM optimizations make use of the FIXPVA method,[78] and we have performed the calculations with 240 tesserae to generate a smooth potential of mean force surface. The atomic radii used in optimizations were the default values in the GAMESS program (using 1.40 Å for Li) and the scale factor was chosen as 1.20 for water, 1.35 for DMSO[51] and 1.40 for acetonitrile.[79]

Accurate electronic energies were obtained through single-point calculations at the MP2 and MP4 levels (full, all electrons included in the correlation) on the liquid-phase optimized structures. For the smallest $Li^+(H_2O)_4$ cluster, the calculations were performed at the MP2 and MP4 level with up to def2-QZVPP basis set[76] augmented with sp diffuse functions on oxygen (named QZVPP+diff). Additional CCSD(T) (full electrons correlated) calculations with the TZVPP+diff basis set were performed to confirm the convergence of the MP4 method. For the $Li^+(CH_3CN)_4$ and $Li^+(DMSO)_4$ clusters, single-point energy calculations were performed at the MP2 level with TZVPP+diff and QZVPP+diff basis sets. We should comment that these basis sets are similar to the minimally augmented Karlsruhe basis sets of Truhlar and co-workers.[80]

The final part of the calculations is the single-point solvation free energy for each species. We have used the SMD model[40] with the accurate MP2/TZVPP+diff method to obtain reliable solvation free energy values. The SMD method includes electrostatic and nonelectrostatic solvation free energy contributions and it has a good performance for solvation of neutral species.[40,81–83] Thus, we believe that large $M^+(S)_4$ clusters with internal charge should be well described by this method. All of the gas-phase calculations were performed with the Firefly program,[84] and the solution-phase calculations were performed with a recent version of the GAMESS program.[85]

Anharmonicity in the Li–acetonitrile clusters

Acetonitrile can bind to the central Li^+ ion through the nitrogen atom, and the four acetonitrile molecules point out to the corners of a tetrahedral. The methyl groups on these extremes can undergo almost free rotations, leading to very small real or imaginary frequencies. Therefore, this is a case where correction for these very low harmonic vibrational modes is critical. For example, we have found an imaginary frequency as low as 5i cm^{-1} for the acetonitrile rotation motion around the N–C–C axis. In the present study, we have considered these four rotational modes of the four acetonitriles in the $Li^+(CH_3CN)_4$ cluster as free rotations. Thus, considering that I_r is the moment of inertia, the partition function for this two-dimensional rotation is:[86–88]

$$q_{\mathrm{rot}} = \frac{(2\,\pi\,k_{\mathrm{B}} T I_{\mathrm{r}})^{1/2}}{\hbar\sigma}, \tag{8}$$

and the contribution of these rotations to the Gibbs free energy is given by:

$$G_{\mathrm{rot}} = -4RT\ln q_{\mathrm{rot}}, \tag{9}$$

where R is the ideal gas constant. In the case of real frequencies related to rotation of one acetonitrile molecule, the corresponding harmonic frequency contributions to the Gibbs free energy were excluded. In summary, the four vibrational modes of the $Li^+(CH_3CN)_4$ cluster that are related to the acetonitrile rotation around the N–C–C axis have been treated as two-dimensional free rotations for computation of the Gibbs free energy. We have calculated that q_{rot} = 3.678 and the total contribution of these four acetonitrile molecules to the free energy is –3.09 kcal mol^{-1}.

Results and discussion

Solvation of Li$^+$ ion in water

Theoretical and experimental studies of Li$^+$ in aqueous solution converge to the view that there are four coordinating water molecules in its first solvation shell.[63,74,89] Thus, in the study of Li$^+$ solvated by water, we have used the Li$^+$(H$_2$O)$_4$ cluster, and the obtained structure is presented in Figure 2. For the Li–O distance, we have found a value of 1.95 Å at the CPCM/MP2/TZVPP+diff level. This value is in excellent agreement with a recent experimentally derived value of 1.942 Å reported by Mähler and Persson.[90]

The calculation of the solvation free energy value of Li$^+$ in aqueous solution ($\Delta G^{*\text{bulk}}_{\text{solv}}$) is presented in Table 1. The interaction energies of Li$^+$ with four water molecules calculated at the MP2(full) and MP4(full) levels with TZVPP+diff and QZVPP+diff basis sets are close, suggesting that these calculations have converged. Test with the CCSD(T)/TZVPP+diff method shows it is 0.35 kcal mol^{-1} from MP4/TZVPP+diff value. Thus, our best level of theory, MP4(full)/QZVPP+diff method, predicts a value of –104.7 kcal mol^{-1}. For comparison, a value reported by Asthagiri *et al.*[63] calculated at the B3LYP/6-311+G(2d,p) level is –106.8 kcal mol^{-1}. Inclusion of thermal corrections leads to a $\Delta G^{*}_{\text{clust}}(\text{Li}^+(\text{H}_2\text{O})_4)$ value of –75.8 kcal mol^{-1}, while Asthagiri *et al.* have reported a value of –77.7 kcal mol^{-1} for this property after correcting for the standard state used in this report. Including solvation of the cluster, solvation of the water molecules, and the water density term, leads to a $\Delta G^{*\text{bulk}}_{\text{solv}}(\text{Li}^+)$ value of –116.1 kcal mol^{-1}. For comparison, the value of Asthagiri *et al.* using the dielectric continuum model for solvation of the cluster is –120.5 kcal mol^{-1}. Asthagiri *et al.* have also calculated the solvation of the Li$^+$(H$_2$O)$_4$ cluster using thermodynamic integration with the TIP3P and SPC/E water models. In these calculations, they have reported values of –115.1 and –112.7 kcal mol^{-1} for Li$^+$ solvation, respectively. However, as we have discussed in the introduction, these values are $\Delta G^{*\text{int}}_{\text{solv}}$.

A comparison with experimental data is worthwhile. Taking the experimental value[53] from Marcus, –117.3 kcal mol^{-1}, which is compatible with the TATB assumption, indicates a deviation of only 1.2 kcal mol^{-1} from our theoretical value! On the other hand, Tissandier *et al.*[50] have found a value of –128.4 kcal mol^{-1} using the CPA method. Although the solvation values derived from the CPA method have been widely accepted, Vlcek *et al.*[33] have recently used simulation methods to shown that the CPA approach does not converge for the small clusters used in the Tissandier *et al.* studies. In addition, they have confirmed that the CPA approach includes the surface potential contribution, a fact first pointed out by Asthagiri *et al.* more than 10 years ago.[63] Based on these considerations, we believe that our value of –116.1 kcal mol^{-1} obtained in this work is the most reliable theoretical value for the bulk solvation free energy of the Li$^+$ ion in aqueous solution to date.

Table 1. Calculation of the solvation free energy of the Li$^+$ in water, acetonitrile and dimethyl sulfoxide by the CC-QCT method.[a]

	$Li^+(H_2O)_4$	$Li^+(ACN)_4$	$Li^+(DMSO)_4$
MP2/SVP +diff	-	-	-168.47
MP4/SVP + diff	-	-	-169.15
MP2/TZVPP + diff	-102.99	-121.69	-148.04
MP4/TZVPP + diff	-103.20	-	-
CCSD(T)/TZVPP + diff	-103.55	-	-
MP2/QZVPP + diff	-104.27	-123.66	-148.45
MP4/QZVPP + diff	-104.66	-	-
ΔG_{clust}^*	-75.82	-95.16	-108.89
$\Delta G_{solv}^*(Li^+(S)_4)$ [b]	-58.49	-41.09	-39.42
$n\Delta G_{solv}^*(S)$ [b]	-27.76	-22.60	-31.00
nRT ln [S]	9.51	6.99	6.27
$\Delta G_{solv}^{*bulk}(Li^+)$[c]	-116.06	-120.64	-123.58

a - Units of kcal/mol. b - Solvation free energies obtained at SMD/MP2/def2-TZVPP level.
c - Bulk single ion solvation free energy obtained with the Cluster-Continuum approach. Standard state of 1 mol L^{-1} for both gas phase and solution.

Solvation of Li$^+$ ion in acetonitrile

The next solvent is acetonitrile. Eldik and co-worker[91] have studied $LiClO_4$ in mixtures of nitromethane and acetonitrile by ^{7}Li-NMR spectroscopy. They have concluded that the Li$^+$ ion is coordinated by four acetonitrile molecules. In addition, those authors have investigated the stability of tetra- and pentacoordinated ions by theoretical calculations at the PCM/B3LYP/6-311+G** level of theory. Their calculations have indicated that the pentacoordinated Li^+ is 3.7 kcal mol^{-1} less stable than the tetracoordinated form.

In the present study, we have considered the lithium ion solvated by acetonitrile as represented by the $Li^+(CH_3CN)_4$ cluster and the corresponding structure is shown in Figure 2. The Li–N distance is calculated to be 2.02 Å. The interaction energy of the Li^+ with four acetonitrile molecules was calculated at the MP2(full) level with up to QZVPP+diff basis set. This level of theory predicts a value of –123.7 kcal mol^{-1}, almost 20 kcal mol^{-1} more negative than the interaction of the Li^+ with four water molecules and 10 kcal mol^{-1} more negative than the interaction with four methanol molecules.[70] Including thermal corrections changes the $\Delta G^{*}_{\text{clust}}(\text{Li}^{+}(\text{CH}_{3}\text{CN})_{4})$ to a value of –95.2 kcal mol^{-1}. When the solvation of the $Li^+(CH_3CN)_4$ cluster and the solvation of the CH_3CN are included, as well as the density number contribution, the final solvation free energy of the Li^+ ion in acetonitrile becomes –120.6 kcal mol^{-1}, which is 4.5 kcal mol^{-1} more negative than Li^+ solvation in aqueous solution. Thus, although the lithium ion remains more solvated in acetonitrile solution than in aqueous solution, in line with the free energy for cluster formation in the gas phase, the difference decreases substantially. This behavior can be rationalized considering that the $Li^+(CH_3CN)_4$ cluster is larger than the $Li^+(H_2O)_4$ cluster. As a consequence, the former is less solvated by the bulk solvent.

Recently, Bryantsev[71] has reported a mixed cluster–continuum calculation of Li^+ ion solvation in acetonitrile using DFT calculations. He has found a value of –125.8 kcal mol^{-1}. This difference of 5.2 kcal mol^{-1} in relation to our value has three sources: first, the level of electronic structure theory. Second, the treatment of internal motion of acetonitrile molecules and third, the hybrid approach that he has used. The mixed cluster–continuum approach used by Bryantsev does not converge to the solvation free energy value that would be obtained using free energy perturbation, while the CC–QCT used in this work does, as shown by Roux and Yu for lithium ion in aqueous solution.[75]

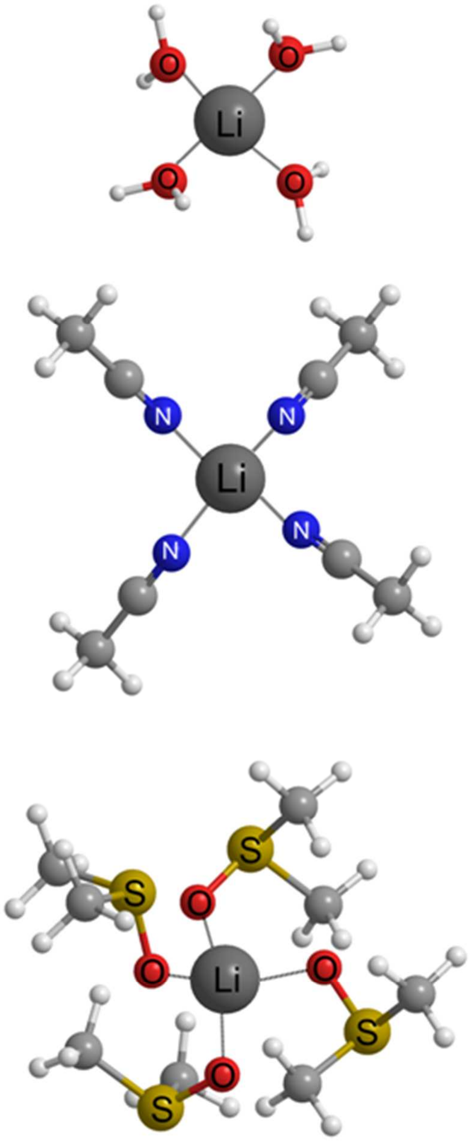

Figure 2. Structure of the $Li^+(H_2O)_4$, $Li^+(ACN)_4$ clusters obtained at CPCM/MP2/TZVPP+diff level and of the $Li^+(DMSO)_4$ cluster obtained at CPCM/MP2/SVP+diff level.

The experimental value can be obtained using the solvation free energy of the lithium ion in aqueous solution (–117.3 kcal mol^{-1}) plus the free energy of transfer between water and acetonitrile (6.8 kcal mol^{-1}) reported by Marcus,[53,68] leading to a value of –110.5 kcal mol^{-1}. This value, consistent with the TATB method, is 10 kcal mol^{-1} more positive than our value. Although equations 8 and 9 introduce some uncertainty in the final clustering free energy, this contribution is only 3 kcal mol^{-1} and the error in the used method should be smaller than this value. Thus, the experimental data indicate less solvation of lithium ion in acetonitrile in relation to aqueous solution. Based on our calculations on gas-phase clusters, which indicate stronger interaction of Li^+ with acetonitrile than with water, these experimental data seem unsound. To include more comparisons, our value is compatible with the following solvation free energy of the proton in acetonitrile: –253.8 kcal mol^{-1}, to be discussed later in this report, while Kelly *et al.* have obtained an even more negative value of –260.2 kcal mol^{-1} (in this case, corresponding to $\Delta G^{*\mathrm{real}}_{\mathrm{solv}}$). Thus, the difference between our value and the TATB method for this system is interesting, considering the good agreement obtained for water and methanol[70] solutions.

Solvation of Li^+ ion in DMSO

Our group studied lithium ion solvation in DMSO 10 years ago.[69] In that study, we found that the Li^+ is coordinated by four DMSO molecules. It was observed that the calculated interaction energy of Li^+ with DMSO is very sensitive to the level of theory, requiring an extended basis set and full inclusion of the core electrons in the correlated calculation. A similar conclusion on the coordination number of four was reached by Onthong *et al.* using molecular dynamics calculations.[92] Experimental studies also support the view that Li^+ is coordinated by four DMSO molecules.[93]

The structure of the $Li^+(DMSO)_4$ clusters obtained in this study is presented in Figure 2. We have obtained a value of 1.93 Å for the O–Li length at the CPCM/MP2/SVP+diff level, which can be compared with the previous value of 1.96 Å obtained at the B3LYP/6-31G(d) level. The calculation of the interaction energy between the Li^+ and the four DMSO molecules goes from –168.5 kcal mol^{-1} at the MP2(full)/SVP+diff level to –148.5 kcal mol^{-1} at the MP2(full)/QZVPP+diff level. We should observe that the calculation with the TZVPP+diff basis set is close to that of the QZVPP+diff basis set, and the MP4 calculation has a small effect in relation to MP2. Therefore, we are confident that the interaction energy is converged. For comparison, our best calculation in the previous study, MP2(full)/6-311+G(2df,2p), predicts a value of –157.0 kcal mol^{-1}, in considerable error by 8.5 kcal mol^{-1} from our best calculation in this work.

Including the thermal corrections, the free energy for the cluster formation ($\Delta G^{*}_{\mathrm{clust}}(\mathrm{Li^+(DMSO)_4})$) is calculated to be –108.9 kcal mol^{-1}. This value is much more negative than that observed for H_2O and CH_3CN complexation with the lithium ion, suggesting DMSO is more coordinating than those other solvents.

The effect of cluster solvation, DMSO solvation and density number leads to the final $\Delta G^{*\mathrm{bulk}}_{\mathrm{solv}}(\mathrm{Li}^+)$ value of –123.6 kcal mol^{-1}, 11.9 kcal mol^{-1} more positive than our previous calculation of –135.5 kcal mol^{-1}. This is a substantial difference and it can be attributed to the high sensitivity of the interaction energy in relation to the level of theory.

A comparison with experimental data is encouraging. Thus, using the Marcus value for Li^+ solvation in aqueous solution (–117.3 kcal mol^{-1}) and its free energy of transfer from H_2O to DMSO (–4.1 kcal mol^{-1}), the experimental $\Delta G^{*\mathrm{bulk}}_{\mathrm{solv}}(\mathrm{Li}^+)$ becomes –121.4 kcal mol^{-1}, a deviation of only 2.2 kcal mol^{-1} from our new theoretical value. The excellent agreement between the theoretical and experimental data observed for this system is outstanding.

Looking at Table 1, we can observe good consistency between the solvation free energy of the Li^+ ion in the three solvents and the free energy for formation of the $Li^+(S)_4$ cluster in the gas phase. If we include the solvation in methanol from our previous work, the consistency remains, using the gas-phase free energy for $Li^+(CH_3OH)_4$ formation of –82.3 kcal mol^{-1} and the solvation free energy of Li^+ of –118.1 kcal mol^{-1}. Furthermore, our values for lithium solvation in H_2O, CH_3OH and DMSO are very close to the experimental values of Marcus. Hence, we are inclined to think that the experimental value for the lithium ion solvation in acetonitrile is not reliable.

Solvation free energy from the salt solvation data

The solvation free energy of the Li^+ in the three solvents, determined in this work, are the anchor values used to determine the single-ion free energy scale. For an MX salt, the solvation free energy in a solvent S can be experimentally determined and the following relation is valid:

$$\Delta G^{*}_{\mathrm{solv}}(\mathrm{M}^+\mathrm{X}^-,\mathrm{S}) = \Delta G^{*}_{\mathrm{solv}}(\mathrm{M}^+,\mathrm{S}) + \Delta G^{*}_{\mathrm{solv}}(\mathrm{X}^-,\mathrm{S}). \qquad (10)$$

Taking the data of Tissandier *et al.*[50] in aqueous solution for solvation of the MX salts, the $\Delta G^{*}_{\mathrm{solv}}$ of ions Na^+, K^+, Rb^+, Cs^+, F^- and Cl^- were obtained. In the case of acetonitrile and DMSO solvents, we have used the free energy of transfer of a pair of ions from water to organic solvent and the relation:

$$\Delta G^{*}_{\text{solv}}(\mathrm{M^{+}X^{-}, S}) = \Delta G^{*}_{\text{solv}}(\mathrm{M^{+}X^{-}, H_2O}) + \Delta G_{\text{transf}}(\mathrm{M^{+}X^{-}, H_2O \rightarrow M^{+}X^{-}, S}). \quad (11)$$

In the following step, equation (10) was also applied. The collected data are presented in Table 2.

Table 2. Solvation data of inorganic salts in water and free energy of transfer to acetonitrile and DMSO.[a]

Salt	$\Delta G^{*}_{\text{solv}}$ (H_2O)[b]	ΔG^{*}_{t} ($H_2O \rightarrow$ ACN)[c]	$\Delta G^{*}_{\text{solv}}$ (ACN)	ΔG^{*}_{t} ($H_2O \rightarrow$ DMSO)[c]	$\Delta G^{*}_{\text{solv}}$ (DMSO)
LiF	-232.8	23.8[d]	-209.0	13.1	-219.7
LiCl	-203.1	16.9	-186.2	5.2	-197.9
NaCl	-177.8	12.9	-164.9	6.3	-171.5
KCl	-160.6	11.6	-149.0	6.4	-154.2
RbCl	-155.2	11.4	-143.8	6.9	-148.3
CsCl	-148.4	11.1	-137.3	6.2	-142.2

a - Units of kcal mol^{-1} and standard state of 1 mol L^{-1} in both gas and solution phases. b – Data taken from reference 50 . c - Data from references 67 and 68. d - For fluoride, free energy of transfer taken from ref. 94.

Solvation free energy from electrode potentials

For the ions H^+, Br^- and I^-, the solvation free energy data were obtained from the electrode potentials in H_2O, CH_3CN and DMSO, using an approach similar to our previous report in methanol. The reactions are:

$$\mathrm{Cl_2(g) + H_2(g) \rightarrow 2Cl^{-}\,(sol) + 2H^{+}\,(sol)} \qquad \text{(R1)}$$

$$\mathrm{Cl_2(g) + 2Br^{-}\,(sol) \rightarrow 2Cl^{-}\,(sol) + Br_2(g)} \qquad \text{(R2)}$$

$$\mathrm{Cl_2(g) + 2I^{-}\,(g) \rightarrow 2Cl^{-}\,(sol) + I_2(g)} \qquad \text{(R3)}$$

Taking the electrode potentials reported by Persson[20] (Table 3), we can calculate the reaction free energy for these processes through:

$$\Delta G^{\circ}_{\mathrm{sol}} = -nF\varepsilon^{\circ} \tag{12}$$

Table 3. Electrode potentials and reaction Gibbs free energy contributions for reactions R1, R2 and R3.

Reaction	ΔG°_{g} ^{a}	ε°/V^{b}			$\Delta\Delta G^{\circ}_{solv}$ ^{a}		
		Water	ACN	DMSO	Water	ACN	DMSO
R1	610.49	1.3585	0.424	1.145	-673.1	-630.0	-663.3
R2	-0.56	0.2935	0.181	0.145	-12.98	-7.79	-6.127
R3	-8.78	0.8235	0.540	0.509	-29.20	-16.13	-14.70

a - Units of kcal mol^{-1}. b – Data taken from reference 20.

These free energies can be decomposed into gas phase (also including the pure solid and pure liquid contributions) and the solvation free energy contribution:

$$\Delta G^{\circ}_{\mathrm{sol}} = \Delta G^{\circ}_{\mathrm{g}} + \Delta\Delta G^{\circ}_{\mathrm{solv}}. \tag{13}$$

The $\Delta G^{\circ}_{\mathrm{g}}$ term was obtained in the previous work,[70] and using equation (13) we can obtain the $\Delta\Delta G^{\circ}_{\mathrm{solv}}$ term, which leads to the solvation free energy of H^{+}, Br^{-} and I^{-} ions using equations (14) to (16):

$$\Delta G^{*}_{\mathrm{solv}}(\mathrm{H}^{+},\mathrm{S}) = \frac{1}{2}\Delta\Delta G^{\mathrm{o}}_{\mathrm{solv}}(\mathrm{R1}) - \Delta G^{*}_{\mathrm{solv}}(\mathrm{Cl}^{-},\mathrm{S}) - 2 \times 1.89\ \mathrm{kcal\ mol}^{-1}, \tag{14}$$

$$\Delta G^{*}_{\mathrm{solv}}(\mathrm{Br}^{-},\mathrm{S}) = \Delta G^{*}_{\mathrm{solv}}(\mathrm{Cl}^{-},\mathrm{S}) - \frac{1}{2}\Delta\Delta G^{\mathrm{o}}_{\mathrm{solv}}(\mathrm{R2}), \tag{15}$$

$$\Delta G^{*}_{\mathrm{solv}}(\mathrm{I}^{-},\mathrm{S}) = \Delta G^{*}_{\mathrm{solv}}(\mathrm{Cl}^{-},\mathrm{S}) - \frac{1}{2}\Delta\Delta G^{\mathrm{o}}_{\mathrm{solv}}(\mathrm{R3}). \tag{16}$$

All of the solvation data for these simple ions obtained in this work are presented in Table 4 for these three solvents.

Comparison with solvation data from the literature

The single-ion solvation free energy values obtained in this work correspond to bulk solvation ($\Delta G^{*\text{bulk}}_{\text{solv}}$). A comparison with experimental data must be done with a similar quantity, such as the free energy scale based on the TATB method.[61,62] Thus, we have chosen to do a direct comparison with the Marcus data[53] in aqueous solution, instead of the values derived from the CPA method,[50] because this approach corresponds to $\Delta G^{*\text{real}}_{\text{solv}}$. For the experimental data in acetonitrile and dimethyl sulfoxide,[67,68] we have added the experimental free energy of transfer of the single ions to their solvation values in aqueous solution. All of the experimental solvation data are presented in Table 4.

In aqueous solution, the theoretical $\Delta G^{*\text{bulk}}_{\text{solv}}$ values are more positive for cations and more negative for anions than the experimental values of Marcus. The resulting root mean squared (RMS) deviation is 1.6 kcal mol^{-1}, an excellent agreement considering the independent approaches used to determine these values. We should also observe that the TATB assumption may have some uncertainties. For example, Schurhammer *et al.*[95–97] have investigated the solvation of TA^{+} and TB^{-} ions in water solution using different water models. They have consistently found that the TB^{-} ion is better solvated than the TA^{+} ion, although the values have presented a wide range. Because those authors have calculated $\Delta G^{*\text{int}}_{\text{solv}}$, some contribution to this difference is due to the $\Delta\phi_{\text{lp}}$ term, as pointed out by Shi and Beck.[34]

In the case of acetonitrile, the deviations are high, reaching an RMS value of 9.9 kcal mol^{-1}. Our theoretical results are more negative for cations and more positive for anions than the Marcus values. These high deviations in acetonitrile solution are intriguing when we consider that for water (this work) and methanol[70] solutions, the agreement is very good. Thus, the data of Marcus have indicated that the proton is 10.7 kcal mol^{-1} less solvated in acetonitrile than in aqueous solution. Our data have indicated a very different value: the proton is only 0.2 kcal mol^{-1} less solvated in acetonitrile than in aqueous solution. For comparison, a CPA study by Kelly *et al.* in acetonitrile has indicated a solvation free energy value of –260.2 kcal mol^{-1} for the proton. Although this is a $\Delta G^{*\text{real}}_{\text{solv}}$ quantity, when compared with the Marcus value, the difference is 16.2 kcal mol^{-1}, indicating a very negative ϕ_{R} value of –0.70 V in acetonitrile. However, an experimental study by Case *et al.*[98] has found a surface potential (in fact, ϕ_{R}) of –0.10 V. This potential corresponds to a free energy of just 2.3 kcal mol^{-1}. Thus, using equation (4) and the $\Delta G^{*\mathrm{real}}_{\mathrm{solv}}(\mathrm{H}^+)$ value of Kelly *et al.* leads to an estimated $\Delta G^{*\mathrm{bulk}}_{\mathrm{solv}}(\mathrm{H}^+)$ value of –257.9 kcal mol^{-1}, differing by 4.7 kcal mol^{-1} from our value! Fawcett[18] has also suggested a value of –256.2 kcal mol^{-1} for the proton solvation in acetonitrile, whereas Pomogaeva and Chipman[99] have found that a solvation scale based on the Fawcett value of the proton leads to better performance of their new solvation method when compared with the Kelly *et al.* scale.[45] These observations are remarkable and provide more support for the value found in this work. On the other hand, our result suggests a problem with the experimental scale of Marcus.

For the other dipolar aprotic solvent investigated, dimethyl sulfoxide, the agreement between our free energy scale and that of Marcus is very good. The calculated RMS deviation is 2.1 kcal mol^{-1}. Considering that the $\Delta G^{*\mathrm{real}}_{\mathrm{solv}}(\mathrm{H}^+)$ obtained by Kelly *et al*. by the CPA method is –273.3 kcal mol^{-1}, we can use our $\Delta G^{*\mathrm{bulk}}_{\mathrm{solv}}(\mathrm{H}^+)$ to estimate that ϕ_{R} = –0.52 V for DMSO. It is also interesting to note that our results point out that small anions are more solvated in DMSO than in acetonitrile by ~10 kcal mol^{-1}.

Table 4. Absolute bulk solvation free energies of some inorganic ions in water, acetonitrile and DMSO.[a]

	Water		Acetonitrile		DMSO	
Ions	This work	Marcus[b]	This work	Marcus[c]	This work	Marcus[c]
H^+	-253.4	-254.7	-253.2	-244.0	-261.1	-259.3
Li^+	-116.1	-117.3	-120.6	-110.5	-123.6	-121.4
Na^+	-90.8	-91.0	-99.3	-88.2	-97.2	-94.0
K^+	-73.6	-74.3	-83.5	-72.7	-80.0	-77.2
Rb^+	-68.2	-69.5	-78.3	-68.2	-74.1	-71.9
Cs^+	-61.4	-63.5	-71.7	-62.4	-67.9	-66.6
F^-	-116.7	-114.9	-88.4	-97.9	-96.1	-97.7
Cl^-	-87.0	-85.0	-65.6	-74.9	-74.3	-75.7
Br^-	-80.5	-79.1	-61.7	-73.2	-71.2	-73.3
I^-	-72.4	-69.5	-57.5	-65.0	-67.0	-66.1

a – Units of kcal mol^{-1}. b - Data taken from ref. 53. c - Data taken from refs.53, 67, 68.

Solvation free energy of single organic ions from pK_{a} data

A database of the solvation free energy of organic ions in the three solvents, including different functional groups, is very useful for calibration of the solvation models. In this work, we are focusing on a solvation scale for continuum and hybrid cluster–continuum solvation models. The equations used to calculate the solvation free energy of A^- anions and BH^+ cations were discussed in previous publications and are given by:[52,66,70]

$$\Delta G^{*}_{\text{solv}}(\text{A}^-) = (1.364)\text{p}K_\text{a}(\text{HA}) - \Delta G^{\text{o}}_{\text{bas}}(\text{A}^-) + \Delta G^{*}_{\text{solv}}(\text{HA}) - \Delta G^{*}_{\text{solv}}(\text{H}^+) - 1.89\ \text{kcal mol}^{-1}, \tag{17}$$

and

$$\Delta G^{*}_{\text{solv}}(\text{BH}^+) = (-1.364)\text{p}K_\text{a}(\text{BH}^+) + \Delta G^{\text{o}}_{\text{bas}}(\text{B}) + \Delta G^{*}_{\text{solv}}(\text{B}) + \Delta G^{*}_{\text{solv}}(\text{H}^+) + 1.89\ \text{kcal mol}^{-1}. \tag{18}$$

We have used extensive pK_a data in these three solvents, gas-phase basicity, solvation free energy of the neutral molecule and the solvation free energy of the proton determined in this work to obtain the solvation free energy of the corresponding ion. These data were taken from the literature and previous compilations.[45,47,52,70,100–101] The obtained solvation free energy values are presented in Tables 5 and 6.

It is interesting to analyze the solvation data in these different solvents. In aqueous solution, the much higher solvation free energy of the anions than the cations is evident. For example, for the OH^- and H_3O^+ hard ions, the former is 20 kcal mol^{-1} more solvated. Even for larger ions like PhO^- and $PhNH_3^+$, the difference is 22 kcal mol^{-1}. The natural interpretation of this observation is that the small hydrogen atom bound to oxygen in water is able to stay closer to the anion than the larger oxygen atom of water is close to the cation, leading to better solvation of anions. In methanol,[70] this higher solvation of anions in relation to cations remains, although the difference in solvation between anions and cations decreases. In addition, anions are better solvated in water than in methanol, while cations are better solvated in methanol than in water.

In the case of CH_3CN and DMSO, we can observe an unexpected behavior: organic anions are more solvated than cations. For example, the PhO^- ion is 6.3 kcal mol^{-1} more solvated than $PhNH_3^+$ in DMSO. For smaller organic ions, the difference increases. Thus, the CH_3O^- ion is 23 kcal mol^{-1} more solvated than the $CH_3NH_3^+$ ion in DMSO. The usual thinking about dipolar aprotic solvents is that the anion solvation is less important and the cation solvation is more important. In other words, the positive part of the solvent molecules (O and N atoms of DMSO and CH_3CN, respectively) should have stronger interaction with the cations than the $–CH_3$ moiety interacts with the anions. Our results suggest that this is not the case.

Table 5. Absolute bulk solvation free energies of anions in water, acetonitrile and DMSO based on pK_a data.[a]

Anions	Water	Acetonitrile	DMSO
F^-	-117.5		-99.6
Cl^-	-87.1		
Br^-	-81.1		
I^-	-72.4		
OCl^-	-93.1		
OBr^-	-88.4		
OI^-	-84.0		
CN^-	-82.8		-75.9
N_3^-	-83.2		-80.4
NO_2^-	-		-72.7
NO_3^-	-	-65.4	
HO^-	-117.4		-102.1
HO_2^-	-109.8		
MeO^-	-107.6		-93.9
EtO^-	-103.6		-89.8
$i\text{-}PrO^-$	-98.5		-86.0
$t\text{-}BuO^-$	-94.5		-82.1
PhO^-	-82.3	-72.5	-73.9
$p\text{-}NO_2\text{-}C_6H_4O^-$	-70.3	-64.7	-64.3
$HCOO^-$	-88.7		
CH_3COO^-	-89.8	-75.2	-79.1
$PhCOO^-$	-83.7	-73.1	-76.9
$CH_3SO_3^-$	-84.2		-70.2
$CH_2NO_2^-$	-88.4		-79.1
CH_2CHO^-	-88.2		
$CH_3C(=O)CH_2^-$	-88.1		-81.3
$PhCOCH_2^-$	-82.7		
CH_2COOEt^-	-78.9		
HS^-	-84.1		
CH_3S^-	-86.2		
PhS^-	-75.8		-69.4
$CH_3SOCH_2^-$	-79.7		-82.6
PH_2^-	-71.9		
NH_2^-	-104.7		-99.4
$PhNH^-$	-76.3		-78.2

$HCONH^{-}$	-		-79.3
CH3CONH^{-}	-92.6		-80.7
CH_2CN^{-}	-78.2		-79.2
CH_3CHCN^{-}	-78.1		
HCC^{-}	-88.6		
$PhCH_2^{-}$	-		-77.5

a – Units of kcal mol^{-1}. The utilized properties are presented in the supporting information.

When we compare the solvation of organic anions between CH_3CN and DMSO, the values are close. In the case of cations with large exposure of the center of charge, like NH_4^+ and $PhNH_3^+$, the solvation free energy values are also close. This similar solvation in both solvents has an important practical consequence: a unique set of atomic cavities in the continuum solvation model could be useful for both dipolar aprotic solvents, and this behavior may be true for other similar aprotic solvents. However, in the case of cations with less exposition of the center of charge, such as pyridineH$^+$, acetonitrile is able to solvate more efficiently. A possible explanation is that the almost linear structure of CH_3CN allows more molecules to stay close to the center of charge of the ion, while the S=O group of DMSO has voluminous $-CH_3$ groups attached, not allowing more solvent molecules to stay close to the center of charge of the ion.

Table 6. Absolute bulk solvation free energies of cations in water, acetonitrile and DMSO based on pK_a data.[a]

Cations	Water	Acetonitrile	DMSO
H_3O^+	-97.8		
$CH_3OH_2^+$	-80.6		
$CH_3CH_2OH_2^+$	-75.9		
$(CH_3)_2OH^+$	-67.3		
$(CH_3CH_2)_2OH^+$	-59.0		
$(CH_3)_2C{=}OH^+$	-64.3		
$(PhCOCH_3)H^+$	-52.6		
$(CH_3COOEt)H^+$	-56.0		
$(CH_3)_2SH^+$	-52.0		
$(CH_3SOCH_3)H^+$	-55.7		
NH_4^+	-72.7	-82.6	-82.1
$CH_3NH_3^+$	-64.0	-73.2	-71.2
$(CH_3)_2NH_2^+$	-56.1		
$(CH_3)_3NH^+$	-48.7		
$EtNH_3^+$	-60.5		

$(Et)_2NH_2^+$	-50.7		
$(Et)_3NH^+$	-42.2	-53.1	-46.6
$PrNH_3^+$	-59.0		
$nBuNH_3^+$	-58.5		-65.8
$PhNH_3^+$	-60.3	-69.8	-67.6
pyridineH$^+$	-48.6	-59.5	-53.5
$(HCONH_2)H^+$	-70.0		
$(CH_3CONH_2)H^+$	-61.3		

a – Units of kcal mol^{-1}. The utilized properties are presented in the supporting information.

A comparison between water and the dipolar aprotic solvents suggests that anions are more solvated in water than in DMSO or CH_3CN. The smaller the ion, the higher the difference of the solvation free energy. For cations, we observe the reverse, and the solvation free energy is more negative by ~10 kcal mol^{-1} in dipolar aprotic solvents. Therefore, the classical view that going from protic solvent to dipolar aprotic solvent leads to higher reactivity of anions because dipolar aprotic solvents decrease their solvation remains true.[102] However, this fact is not uniquely responsible for the enhancement of the reactivity. The higher solvation of cations is critical to solubilize the salt and to form free ions in solution. Otherwise, ion pairs would be formed, leading to reduced reactivity.[103,104]

Our results in acetonitrile raise doubts about the Marcus solvation free energy scale. To provide more support for our scale, let us pay attention to the solvation free energy of the *p*-nitrophenoxide anion in CH_3CN and DMSO. The values presented in Table 5 are –64.7 and –64.3 kcal mol^{-1}, respectively. These values are close and expected for solvation of charge-dispersed anions like *p*-nitrophenoxide. On the other hand, if the Marcus scale was correct, the solvation free energy of this anion would become 10 kcal mol^{-1} more negative in acetonitrile. This fact would have two implications: first, the solvation of this anion would be much higher in CH_3CN than DMSO. Second, the solvation free energy value of the *p*-nitrophenoxide anion would be as negative as that in water solution. These consequences seem unphysical and in our opinion it is a strong indication that our scale is correct and physically sound.

Conclusions

A solvation free energy scale, excluding the net electrostatic potential inside the solute cavity, has been obtained for water, acetonitrile and dimethyl sulfoxide solvents from the solvation free energy of the Li^+ ion. The solvation of this ion was determined by the cluster–continuum quasichemical theory of solvation. Our values for the solvation free energy of the proton are close to the Marcus values in the case of H_2O and DMSO, studied in this work, as well as for the CH_3OH solvent, investigated in a previous report. For acetonitrile, the discrepancy reaches 9 kcal mol^{-1}. The Marcus scale is compatible with the TATB assumption and an analysis of the coherence of our scale suggests the experimental TATB scale in acetonitrile is not reliable. We have obtained 73 solvation free energy values for anions and 52 values for cations in these three solvents. Our scale provides a realistic description of solute–solvent interactions without the net potential and it could be valuable for the development of solvation models.

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References

1 A. K. Tummanapelli and S. Vasudevan, *Phys. Chem. Chem. Phys.*, 2015, **17**, 6383.
2 J. Ho, *Phys. Chem. Chem. Phys.*, 2015, **17**, 2859.
3 V. Radtke, D. Himmel, K. Pütz, S. K. Goll and I. Krossing, *Chem. Eur. J.*, 2014, **20**, 4194.
4 J. Ho, *Aust. J. Chem.*, 2014, **67**, 1441.
5 S. Sastre, R. Casasnovas, F. Muñoz and J. Frau, *Theor. Chem. Acc.*, 2012, **132**, 1.
6 J. Ho and M. L. Coote, *Theor. Chem. Acc.*, 2010, **125**, 3.
7 K. S. Alongi and G. C. Shields, in *Annual Reports in Computational Chemistry*, ed. A. W. Ralph, Elsevier2010, vol. Volume 6, pp. 113.
8 F. Eckert, I. Leito, I. Kaljurand, A. Kütt, A. Klamt and M. Diedenhofen, *J. Comp. Chem.*, 2009, **30**, 799.
9 F. Eckert, M. Diedenhofen and A. Klamt, *Mol. Phys.*, 2009, **108**, 229.
10 E. L. M. Miguel, P. L. Silva and J. R. Pliego, *J. Phys. Chem. B*, 2014, **118**, 5730.
11 G. I. Almerindo, D. W. Tondo and J. R. Pliego Jr, *J. Phys. Chem. A*, 2004, **108** 166.

12 J. R. Pliego Jr and J. M. Riveros, *J. Phys. Chem. A*, 2002, **106**, 7434.
13 Y. Fu, L. Liu, R. Li, R. Liu and Q. Guo, *J. Am. Chem. Soc.*, 2004, **126**, 814.
14 D. M. Chipman, *J. Phys. Chem. A*, 2002, **106**, 7413.
15 A. M. Toth, M. D. Liptak, D. L. Phillips and G. C. Shields, *J. Chem. Phys.*, 2001, **114**, 4595.
16 J. Cheng, X. Liu, J. VandeVondele, M. Sulpizi and M. Sprik, *Acc. Chem. Res.*, 2014, **47**, 3522.
17 A. V. Marenich, J. Ho, M. L. Coote, C. J. Cramer and D. G. Truhlar, *Phys. Chem. Chem. Phys.*, 2014.
18 W. R. Fawcett, *Langmuir*, 2008, **24**, 9868.
19 W. A. Donald, R. D. Leib, J. T. O'Brien, M. F. Bush and E. R. Williams, *J. Am. Chem. Soc.*, 2008, **130**, 3371.
20 H. D. Inerowicz, W. Li and I. Persson, *J. Chem. Soc. Faraday Trans.*, 1994, **90**, 2223.
21 C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VHC, Weinheim, Germany, 2011.
22 I. Soteras, D. Blanco, O. Huertas, A. Bidon-Chanal and F. J. Luque, in *Continuum Solvation Models in Chemical Physics: From Theory to Applications*, eds. B. Mennucci and R. Cammi, John Wiley & Sons, Chippenham, Wiltshire, Great Britain2007, pp. 323.
23 D. G. Truhlar and J. R. Pliego, Jr., in *Continuum Solvation Models in Chemical Physics: From Theory to Applications*, eds. B. Mennucci and R. Cammi, John Wiley & Sons, Chippenham, Wiltshire, Great Britain2007, pp. 338.
24 J. R. Pliego Jr, *J. Phys. Chem. B*, 2009, **113**, 505.
25 D. W. Tondo and J. R. Pliego Jr, *J. Phys. Chem. A*, 2005, **109**, 507.
26 S. J. Klippenstein, V. S. Pande and D. G. Truhlar, *J. Am. Chem. Soc.*, 2014, **136**, 528.
27 A. Fernandez_Ramos, J. A. Miller, S. J. Klippenstein and D. G. Truhlar, *Chem. Rev.*, 2006, **106**, 4518.
28 B. Ensing, M. De Vivo, Z. W. Liu, P. Moore and M. L. Klein, *Acc. Chem. Res.*, 2006, **39**, 73.
29 R. F. Ribeiro, A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2011, **115**, 14556.
30 B. J. C. Cabral, K. Coutinho and S. Canuto, *J. Chem. Phys.*, 2013, **138**, 225102.
31 Y.-L. Lin, A. Aleksandrov, T. Simonson and B. Roux, *J. Chem. Theory Comput.*, 2014, **10**, 2690.
32 C. Houriez, M. Meot-Ner and M. Masella, *J. Phys. Chem. B*, 2014, **118**, 6222.
33 L. Vlcek, A. A. Chialvo and J. M. Simonson, *J. Phys. Chem. A*, 2013, **117**, 11328.
34 Y. Shi and T. L. Beck, *J. Chem. Phys.*, 2013, **139**, 044504.
35 M. W. Lee and M. Meuwly, *Phys. Chem. Chem. Phys.*, 2013, **15**, 20303.
36 T. L. Beck, *Chem. Phys. Lett.*, 2013, **561–562**, 1.
37 P. H. Hunenberger and M. M. Reif, *J. Chem. Phys.*, 2011, **134**, 144103.
38 W. A. Donald and E. R. Williams, *J. Phys. Chem. B*, 2010, **114**, 13189.
39 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Chem. Theory Comput.*, 2009, **5**, 2447.
40 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378.
41 K. Leung, S. B. Rempe and O. A. von Lilienfeld, *J. Chem. Phys.*, 2009, **130**, 204507.
42 E. Harder and B. Roux, *J. Chem. Phys.*, 2008, **129**.

43 C. J. Cramer and D. G. Truhlar, *Acc. Chem. Res.*, 2008, **41**, 760.
44 H. S. Ashbaugh and D. Asthagiri, *J. Chem. Phys.*, 2008, **129**, 204501.
45 C. P. Kelly, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2007, **111**, 408.
46 G. Lamoureux and B. Roux, *J. Phys. Chem. B*, 2006, **110**, 3308.
47 C. P. Kelly, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2006, **110** 16066.
48 A. Grossfield, *J. Chem. Phys.*, 2005, **122**, 024506.
49 J. V. Coe, *Int. Rev. Phys. Chem.*, 2001, **20**, 33.
50 M. D. Tissandier, K. A. Cowen, W. Y. Feng, E. Gundlach, M. H. Cohen, A. D. Earhart, J. V. Coe and T. R. Tuttle, *J. Phys. Chem. A*, 1998, **102**, 7787.
51 J. R. Pliego Jr and J. M. Riveros, *Chem. Phys. Lett.*, 2002, **355**, 543.
52 J. R. Pliego Jr and J. M. Riveros, *Phys. Chem. Chem. Phys.*, 2002, **4**, 1622.
53 Y. Marcus, *J. Chem. Soc. Faraday Trans.*, 1991, **87**, 2995.
54 P. Hunenberger and M. Reif, *Single-Ion Solvation: Experimental and Theoretical Approaches to Elusive Thermodynamic Quantities* RSC Publishing, Cambridge, UK, 2011.
55 J. R. Pliego Jr and J. M. Riveros, *J. Phys. Chem. B*, 2000, **104**, 5155.
56 J. J. Fifen, M. Nsangou, Z. Dhaouadi, O. Motapon and N.-E. Jaidane, *J. Chem. Theory Comput.*, 2013, **9**, 1173.
57 J. Tomasi, in *Continuum Solvation Models in Chemical Physics: From Theory to Applications*, eds. B. Mennucci and R. Cammi, John Wiley & Sons, Chippenham, Wiltshire, Great Britain2007, pp. 1.
58 J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999.
59 J. R. Pliego Jr, *Quim. Nova*, 2006, **29**, 535.
60 F. J. Luque, C. Curutchet, J. Munoz-Muriedas, A. Bidon-Chanal, I. Soteras, A. Morreale, J. L. Gelpi and M. Orozco, *Phys. Chem. Chem. Phys.*, 2003, **5**, 3827.
61 Y. Marcus, *J. Chem. Soc. Faraday Trans. 1*, 1987, **83**, 339.
62 Y. Marcus, *J. Chem. Soc. Faraday Trans. I*, 1987, **83**, 2985.
63 D. Asthagiri, L. R. Pratt and H. S. Ashbaugh, *J. Chem. Phys.*, 2003, **119**, 2702.
64 R. G. Pearson, *J. Am. Chem. Soc.*, 1986, **108**, 6109.
65 Y. Marcus, *J. Chem. Soc. Faraday Trans. 1*, 1986, **82**, 233.
66 J. R. Pliego Jr and J. M. Riveros, *Chem. Phys. Lett.*, 2000, **332**, 597.
67 Y. Marcus, *Chem. Rev.*, 2007, **107**, 3880.
68 C. Kalidas, G. Hefter and Y. Marcus, *Chem. Rev.*, 2000, **100**, 819.
69 E. Westphal and J. R. Pliego Jr, *J. Chem. Phys.*, 2005, **123**, 074508.
70 J. R. Pliego and E. L. M. Miguel, *J. Phys. Chem. B*, 2013, **117**, 5129.
71 V. Bryantsev, *Theor. Chem. Acc.*, 2012, **131**, 1.
72 J. R. Pliego Jr and J. M. Riveros, *J. Phys. Chem. A*, 2001, **105**, 7241.
73 P. Grabowski, D. Riccardi, M. A. Gomez, D. Asthagiri and L. R. Pratt, *J. Phys. Chem. A*, 2002, **106**, 9145.
74 S. B. Rempe, L. R. Pratt, G. Hummer, J. D. Kress, R. L. Martin and A. Redondo, *J. Am. Chem. Soc.*, 2000, **122**, 966.
75 B. Roux and H. Yu, *J. Chem. Phys.*, 2010, **132**, 234101.
76 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.
77 V. Barone and M. Cossi, *J. Phys. Chem.*, 1998, **102**, 1195.
78 P. Su and H. Li, *J. Chem. Phys.*, 2009, **130**, 074109.
79 E. S. Boes, P. R. Livotto and H. Stassen, *Chem. Phys.*, 2006, **331** 142.
80 J. J. Zheng, X. F. Xu and D. G. Truhlar, *Theor. Chem. Acc.*, 2011, **128**, 295.
81 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 4538.

82 S. Genheden, A. Cabedo Martinez, M. Criddle and J. Essex, *J. Comput. Aided Mol. Des.*, 2014, **28**, 187.

83 C. C. Zanith and J. R. Pliego, Jr., *J. Comput. Aided Mol. Des.*, 2015, **29**, 217.

84 A. A. Granovsky, Firefly version 7.1.F, http://classic.chem.msu.su/gran/gamess/index.html.

85 M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis and J. A. Montgomery Jr, *J. Comp. Chem.*, 1993, **14**, 1347.

86 D. A. McQuarrie, *Statistical Mechanics*, University Science Books, Sausalito, CA, 2000.

87 K. Bhattacharyya, *Chem. Phys. Lett.*, 1989, **159**, 40.

88 H.-y. Pan, *Chem. Phys. Lett.*, 1988, **151**, 35.

89 S. Varma and S. B. Rempe, *Biophys. Chem.*, 2006, **124**, 192.

90 J. Mähler and I. Persson, *Inorg. Chem.*, 2012, **51**, 425.

91 E. Pasgreta, R. Puchta, A. Zahl and R. van Eldik, *Eur. J. Inorg. Chem.*, 2007, **2007**, 1815.

92 U. Onthong, T. Megyes, I. Bako, T. Radnai, K. Hermansson and M. Probst, *Chem. Phys. Lett.*, 2005, **401**, 217.

93 E. Pasgreta, R. Puchta, M. Galle, N. van Eikema Hommes, A. Zahl and R. van Eldik, *ChemPhysChem*, 2007, **8**, 1315.

94 K. Izutsu, *Electrochemistry in Nonaqueous Solutions*, Wiley-VCH2009.

95 R. Schurhammer, E. Engler and G. Wipff, *J. Phys. Chem. B*, 2001, **105**, 10700.

96 R. Schurhammer and G. Wipff, *J. Phys. Chem. A*, 2000, **104**, 11159.

97 R. Schurhammer and G. Wipff, *New J. Chem.*, 1999, **23**, 381.

98 B. Case, N. S. Hush, R. Parsons and M. E. Peover, *J. Electroanal. Chem.*, 1965, **10**, 360.

99 A. Pomogaeva and D. M. Chipman, *J. Phys. Chem. A*, 2015, **119**, 5173.

100 A. Kutt, I. Leito, I. Kaljurand, L. Soovali, V. M. Vlasov, L. M. Yagupolskii and I. A. Koppel, *J. Org. Chem.*, 2006, **71**, 2829.

101 J.-N. Li, Y. Fu, L. Liu and Q.-X. Guo, *Tetrahedron*, 2006, **62**, 11801.

102 A. J. Parker, *Chem. Rev.*, 1969, **69**, 1.

103 J. R. Pliego Jr and J. M. Riveros, *J. Mol. Catal. A - Chem.*, 2012, **363-364**, 489.

104 J. R. Pliego Jr and D. Pilo-Veloso, *Phys. Chem. Chem. Phys.*, 2008, **10**, 1118.