Simulation of a Solvate Ionic Liquid at a Polarisable Electrode with a Constant Potential

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Abstract

Solvate ionic liquids have the potential for use in a wide range of electrochemical devices. The interfacial nanostructure of these liquids largely determines the performance of such applications. In this work we have focused on the nanostructure and calculated the capacitance of a solvate ionic liquid–electrode interface, where the electrode has a constant potential, and is thus inherently polarisable. The first time, to our knowledge, a solvate ionic liquid has been simulated at such an electrode. Lithium cations from the lithium–glyme solvate ionic liquid are found within 0.5 nm of the electrode at all voltages studied, however, their solvation environment varies with voltage, with both lithium cation–anion and lithium cation–glyme complexes being observed in the first interfacial layer. Our study provides molecular insight into the electrode interface of solvate ionic liquids, with many features similar to pure ionic liquids. The profound differences between the structure observed in these simulations and
our previous study performed with fixed charge electrode boundary conditions make clear the importance of accurate modelling interfaces when studying solvate ionic liquids. The differences shown here are qualitatively greater than observed for conventional ionic liquids.

**Introduction**

Solvate ionic liquids are a new class of ionic liquids formed of a salt, usually a lithium salt, and a chelating solvent molecule. If the chelation is of significant longevity and prevalence, then a liquid comprised solely of ions like a conventional ionic liquid is formed.\(^1\) Solvate ionic liquids are relevant to a range of applications, most prominent is their possible usage as electrolytes for lithium–sulphur batteries.\(^2\,^3\) One such ionic liquid is lithium bistriflimide tetraglyme – Li(G4)TFSI. Tetraglyme (G4) is a chelating solvent from the glyme homologous series, the general formula of which is sketched in Fig. 1A. Li(G4)TFSI is formed by dissolution of lithium bistriflimide in tetraglyme (Fig. 1B), which is the specific liquid studied in this paper. In these liquids, such a large proportion of lithium cations are chelated to glyme molecules that the solution exists as liquid comprised almost solely of ions like a conventional ionic liquid.\(^1\)

Substances which behave as solvate ionic liquids exist on a continuum which runs from good solvate ionic liquids in which nearly all ions are coordinated to solvent molecules, through to concentrated solutions where a large number of solvent molecules in the liquid are free.\(^1\) Where a liquid sits on this continuum is the result of an interplay of the solvent identity,\(^1\,^4\) the specific metal cation\(^4\,^5\) and the anion within the ionic liquid.\(^6\) Solvents which coordinate more readily to the metal cation, will be less likely to be free and thus are more likely to form solvate ionic liquids. Therefore chelating and macrocyclic solvents are preferred to monodentate ones\(^1\,^4\) (though similar liquids based on amphoteric water have recently been described\(^7\)). To form a good solvent ionic the cation and the solvent molecule comprising the liquid must be matched in size, which will make coordination as favourable as possible.
In the case of chelating solvents this means matching coordination numbers,\(^5\) and in the case of macrocycle it is necessary to match ionic diameter and cavity size.\(^4\)

The most commonly used good solvate ionic liquids contain salts where the anion is related to the bistriflimide anion because these ions will less readily out-compete the solvent molecules in the liquids in coordinating to the lithium cations.\(^6\) There are two prominent methods which can be used to classify solvate ionic liquids. Firstly extraction of diffusion coefficients; which can be done by both classical molecular dynamics\(^8\) and NMR measurements.\(^6,9\) Diffusion coefficients for lithium cations and solvent molecules are more similar for good solvate ionic liquids than for poor solvate ionic liquids or concentrated electrolytes. Further to this thermal methods (such as thermogravimetric analysis) provide an easy method of classification for good solvate ionic liquids, which exhibit mass loss (due to the liberation of solvent molecules) at much higher temperature\(^4,10\) than for poor solvate ionic liquids and concentrated solutions. This is due to the higher proportion of solvent molecules which

Figure 1: Panel A: a diagram showing the general formula of a glyme polymer or oligomer. Panel B: a scheme showing the mixing of lithium bistriflimide LiTFSI with tetraglyme G4 to form the solvate ionic liquid Li(G4)TFSI. Coloured atoms indicate the colour code used in Fig. 2.
are “trapped” by direct coordination to the ions. Further to these primary methods of classification solvate ionic liquids have also been studied by use of AFM\cite{11,12} and neutron scattering experiments.\cite{3} One result of particular interest to the authors of this paper is that Li(G4)TFSI based solvate ionic liquids intercalate into graphite without exfoliation, while a concentrated solution of the same salt (with roughly a 2:1 molar ratio of salt to solvent) exfoliates graphite during the intercalation process.\cite{13}

In our previous work, we simulated the nanostructure of Li(G4)TFSI at electrodes using the constant surface charge method.\cite{14} The observed nanostructure was unusual, with little direct coordination of lithium cations to the electrode. However, it did not fully match the interfacial structure observed in atomic force microscopy experiments\cite{11,12} and molecular dynamics simulations of a different solvate ionic liquid.\cite{15} This work aims to unify the results of experiments and simulations, by performing molecular dynamics simulations using a constant potential electrode method. We aim to achieve this by answering the following questions:

- Do solvate ionic liquids adopt the experimentally observed multilayer\cite{11} structure in fixed potential molecular dynamics simulations?

- To what extent does lithium cations dechelate to coordinate directly to the electrode surface?

- What is the coordination environment observed for interfacial lithium cation?

**Methods**

The simulations were performed using the constant potential method implemented by Wang et al.,\cite{16} which was previously used in a study of the highly related water in salt electrolytes by Li.\cite{17} et al.. This method is based on previous work by Reed et al.,\cite{18} and Siepmann et
with the three-dimensional version of Ewald summation as defined by Wilson and Gingrich\textsuperscript{20} in the slab geometry defined by Yeh and Berkowitz.\textsuperscript{21} This methodology contrasts with a number of other methodologies for simulating constant potential electrodes.\textsuperscript{22} Most notably the two dimensional Ewald summation used in the metalwalls code developed by Salanne,\textsuperscript{23,24} or the Smooth PME based method used in the collaborative work of Bedrov and Borodin.\textsuperscript{25,25–27} Wang et al.’s implementation operates through the use of the LAMMPS molecular dynamics software.\textsuperscript{28} In addition to the aforementioned study by Li et al. the constant potential method was previously used in simulations of ionic liquids\textsuperscript{29,30} as well as of lithium-based electrolytes.\textsuperscript{26}

The constant potential method works by fixing the electric potential (\(\Psi_i\)) on each electrode atom so that it is equal to the external potential (\(V\)). This equation can be solved for each atom by 3D Ewald summation incorporating the Yeh–Berkowitz slab correction.\textsuperscript{21} To render the Ewald sum non-conditionally convergent the electrode atoms are modelled as Gaussian distributions of charge with a characteristic width \(\eta\). This work uses the same characteristic width, where \(\eta^{-1} = 19.79\text{nm}^{-1}\), as in previous studies.\textsuperscript{16,18}

Force fields used for the ionic liquid were developed by Shimizu et al.,\textsuperscript{8} and are the same as used in our previous study.\textsuperscript{14} These force fields are based on the OPLS-AA force field\textsuperscript{31} with the CL&P parameters used for bistriflimide,\textsuperscript{32} and the Åqvist force field used for lithium cations,\textsuperscript{33} all these force fields are all atom force fields and thus every component in the system is modelled explicitly. As in the previous studies, ion charges are scaled to obtain accurate transport properties. For unlike pairs the standard OPLS-AA combination rules are used.\textsuperscript{31}

The simulation box has a length of 10 nm in the \(z\)-direction. It consists of two electrodes – three-layered graphene sheets with an inter-layer separation of 0.335 nm. Which are separated by 8.000 nm from one another. The lateral dimensions of each sheet are set as 4.673 nm by 4.331 nm, the same as the box dimensions in \(x\)- and \(y\)-directions. An implicit vacuum slab of 20 nm is placed between the two ends of the box. It is worth noting that the electrodes
simulated in this system are modeled atomistically, as previous studies have suggested that there are large differences between atomistic and smooth electrode models for fixed potential simulations.\textsuperscript{34} Electrostatic forces acting on the particles within the system are calculated by means of the particle–particle particle–mesh solver of Ewald summation.\textsuperscript{35–37} For the force calculation step, the Coulomb and van der Waals cutoffs are set to 1.4 nm, and the particle–particle particle-mesh accuracy set so that forces are calculated with a maximum relative error of $1 \times 10^{-6}$.

In the simulations presented here, the 8 nm by 4.673 nm by 4.331 nm gap between the electrodes is packed to bulk density with 346 ion pairs and tetraglyme molecules. The initial configurations are generated with the packmol algorithm\textsuperscript{38} followed by steepest descent energy minimisation. The temperature of the system is set to 300 K with atom velocities set to replicate the Boltzmann distribution; the temperature is raised from 300 K to 500 K over the course of 1 ns. At this point, the constant potential boundary condition is applied to the electrodes. Equal and opposite external potentials are applied to the two electrodes allowing us to simulate boxes with potential differences between electrodes ($\Delta \Psi$) of 0 V to 4 V. The system is then cooled from 500 K to 300 K over the course of 1 ns. A run is then performed at 300 K for 7 ns with the first 3 ns treated as an equilibration run and the subsequent 4 ns treated as the production run. This process is repeated for four replicas at each voltage to confirm the system is in thermodynamic equilibrium. The Nosé–Hoover thermostat is used throughout the simulations.\textsuperscript{39,40} A timestep of 1 fs is used for all simulations. Fixed charge simulations were run for $\Delta \Psi$ values of 1 V and 2 V. The average charges from the fixed potentials were smoothly spread across all atoms. Simulations were run for 1 replica using the same methodologies as for the fixed potential simulations.
Results and Discussion

Fig. 2 shows the normalised interfacial density ($\rho_N/\rho_{bulk}$) of the three components for $\Delta \Psi = 0, 1, 2, 3$ and $4$ V (with the data reproduced in Fig 3 for each specific component to allow for easier comparison of specific trends between potentials). To get a better idea of the form of the coordination shells, the following guide atoms, which are indicated in Fig.1, are used for each molecule: the 5 tetraglyme oxygen atoms shown in red, bistriflimide nitrogen atoms shown in blue, and lithium cations shown in purple. As is observed for all liquids at a solid interface the presence of the surface leads to the formation of an ordered structure. The specific features of which will be explored over the coming paragraphs.

Firstly, for every potential difference lithium cations are present in the first layer of the structure. This stands in contrast to fixed charge simulations. In Fig 3 we present data for each species at electrodes of positive negative and neutral potentials. Further to this however we include a plot for a fixed charge electrode with the same net surface charge as observed for a potential of $-2$ V (full plots of the liquid at fixed charge electrode in the style of Fig 2 can be found in the supplementary information). On examination of these plots we see that unlike for lithium cations at fixed potential electrode these lithium cations at the fixed charge electrode do not come in contact with the electrode. This is because the unpolarisable electrode present in the fixed charge simulations cannot exert an attractive force great enough on the lithium cation to cause dechelation from the tetraglyme molecule, as we see for the fixed potential electrode.

Secondly, a multilayer structure is observed at both electrodes for all non-zero $\Delta \Psi$. At the negative electrodes in Figs. 2 and 3, an area of cationic excess can be observed at a distance of $1.1$ nm, and an area of net anionic density at a distance of $1.4$ nm. These features are symptomatic of the overscreening multilayer structure observed for conventional ionic liquids. The same features are seen at positive electrodes where the anionic excess can be observed at a distance of $0.8$ nm and the cationic excess at distances of roughly $1.2$ nm. Which, is again symptomatic of an overscreening multilayer structure. These areas of net excess take place
Figure 2: Plots showing the normalised interfacial number density ($\rho_N/\rho_{bulk}$) of the components of solvate ionic liquids. These plots show densities through the whole simulation cell for simulations run with potential differences of $\Delta \Psi = 0$, 1, 2, 3 and 4 V between electrodes. The negative electrode sits on the left of the graph, while the positive electrode sits on the right of the plot. The line colours correspond as follows: pink for $\text{Li}^+$, blue for the Nitrogen atom in TFSI$^-$, and red for the Oxygen atoms in G4. These colours as indicated explicitly in Fig. 1.
Figure 3: Plots showing the normalised interfacial number density ($\rho_N/\rho_{bulk}$) of the components of solvate ionic liquids. Plots are shown for $\Delta \Psi = 2$ V (in cyan for the negative electrode and dotted magenta for the positive one) and 0 V (dashed green). Arrows are drawn to highlight the tendency of changing of the peaks up on potential variation. The filled curves represent the data obtained in fixed charge simulations corresponding to $\Delta \Psi \approx -2$ V.

at different relative locations due to the different thickness of the first interfacial layer, with the first interfacial layer of negative external potentials being considerably thicker. Looking again at the plots of the fixed charge electrode in Fig. 3 it can be observed that there is no multilayer structure with the second peak in the lithium cation density occurring 0.5 nm behind the first at 1 nm, which is symptomatic of solvation layering and not the multilayer structure, which has greater periodicity.

Thirdly, within the first interfacial layer there appear to be two Li$^+$ peaks – the first at 0.3 nm and a second at 0.4 nm. An additional peak follows these peaks at about 0.55 nm,
which sees its density rise with an increasingly negative surface charge. The size of peaks at 0.3 nm and 0.4 nm has a more complicated dependence on the external potential. The peak at 0.3 nm is representative of lithium cations in closest possible contact with the electrode, and the peak at 0.4 nm is due to ions which have some coordinating ligands on the electrode side of their coordination shell. At the negative electrode the peak at 0.3 nm increases in size relative to the peak at 0.4 nm with increasingly negative potential difference, indicating that with increasingly negative electrode potential the lithium cations move closer to the surface to screen the surface charge.

![Figure 4](image_url)

Figure 4: Coordination number with distance for interfacial lithium cations, within 0.6 nm of the negative electrode. For potential differences of $\Delta \Psi = 0$ V (green), 2 V (cyan), and 4 V (blue). The dotted black line is for lithium cations in the middle of the simulation box at $\Delta \Psi = 2$ V. Panel A shows the average lithium cation–tetraglyme oxygen ($\langle$Li$^+$–G4$\rangle$) coordination number. Panel B shows the average lithium cation–anion nitrogen ($\langle$Li$^+$–TFSI$^-$\rangle) coordination number. Panel C shows the coordination number among those lithium cations which are coordinated to a tetraglyme molecule. Panel D shows lithium cation–anion nitrogen coordination numbers for Li$^+$ which are coordinated to tetraglyme oxygens (solid lines) and Li$^+$ that are not coordinated to tetraglyme oxygens (dashed lines).

We move now to consider the coordination environments of the lithium cations in the first interfacial layer. Before doing this however we must discuss the coordination environments previously described for the bulk system by Shimizu et al. $^8$ and at fixed charge interfaces by ourselves in our previous study. $^{14}$ In the bulk the chelation of tetraglyme to lithium cations was found to be near total, with a coordination number of 3.86 observed, there is
some coordination of Li⁺ to anions also with an average coordination number of 1.90. In the bulk phase there was no coordination complexes consisting of lithium cations and multiple tetracylgyme molecules. In contrast to this in our previous study at fixed charge electrodes (and in the data presented for fixed charge electrodes in this paper) we found that surplus glyme concentration in the near interfacial layer leads to the formation of coordination complexes consisting of two glyme molecules to one lithium cation. The number of such complexes was seen to increase with increasing surface charge. Due to the stronger interaction with the lithium cation than with the surface these complexes were seen instead of Li⁺ dechelation.

Moving now to the coordination environments of the systems explored in the current paper Fig. 4 shows plots of coordination number against the separation distance between the lithium cation and the oxygen atoms which are considered to be coordinating (r) for interfacial lithium cations at negative electrodes in systems with ΔΨ = 0 V, 2 V, and 4 V. Further to this we show the same plot for lithium cations in the the middle 4 nm of the simulation box, the pseudo bulk region, for the case where ΔΨ = 2 V,. We find that the coordination numbers in the pseudo-bulk region, seen in dotted black in Panels A and B, are largely the same as seen in the bulk, with a slight increase in the lithium cation–tetraglyme oxygen (Li⁺–G4) coordination number and a slight decrease in the lithium cation–anion nitrogen (Li⁺–TFSI⁻) coordination number. However looking at the interfacial ion coordination numbers in panels A and B we see a very different result. In all cases the the Li⁺–G4 coordination number has fallen to around 2.2, while the Li⁺–TFSI⁻ coordination numbers have been seen to increase markedly. This is at first highly perplexing, as the process of chelation is normally considered an “all or nothing” effect due to the massive entropic favourability of polydentate coordination, and thus we do not expect to frequently see intermediate coordination numbers in complexes with chelating ligands. This data can be shown to be compliant with this general thermodynamic principle by splitting the lithium cations at the interface into two sub categories: those which are coordinated to a tetracylgyme molecule and those that are not coordinated to tetracylgyme at all. Panel C shows the coordination number among those
lithium cations which are coordinated to a tetraglyme molecule, these lithium cations exhibit a very high coordination number, in excess of 4.8, as we would expect. Panel D shows the lithium cation–anion nitrogen coordination numbers for both lithium cations additionally coordinated to tetraglyme oxygens (solid lines) and lithium cations that are not coordinated to tetraglyme oxygens (dashed lines). The coordination numbers plotted in Panel D for these two types of lithium cation are very different. There is limited lithium cation–anion nitrogen coordination for the tetraglyme complexed lithium cations, with coordination numbers in all cases being far below 1, but in the case of those uncoordinated to tetraglyme we see coordination numbers between 3 and 4, around the number seen in molten lithium bistriflimide (3.72). This suggests the presence of two distinct types of Li\(^+\) coordination complexes at the interface, lithium cation–tetraglyme chelate complexes, which will carry a net positive charge, and lithium cation–anion complexes, which will carry a net negative charge. Finally we note here that there are negligible complexes containing two tetraglyme molecules at fixed potential electrodes, in stark contrast to our previous result for fixed charge electrodes. The question now arises: why do we observe these two different, and distinct types of lithium complex at the electrodes? We can postulate that the polarisable electrode induces the presence of these two different types of coordination complexes. However, to make certain it is necessary to look at the local structure against the surface charge distribution on the electrode surface.

A closer look can be taken at these two types of coordination complexes by looking closer at the interfacial layer in the simulation trajectories. The coordination environments of the lithium cations in the first interfacial layer, within 0.5 nm of the electrode, are captured by the simulation snapshots in Fig. 5. The two main types of Li\(^+\) coordination environment are apparent in the snapshots. Both the type where interfacial Li\(^+\) are coordinated to the oxygen atoms in a single tetraglyme molecule as in the bulk, and the second where lithium cations are coordinated to the oxygen atoms in multiple bistriflimide anions. The presence of these two types of cluster is observed irrespective of surface charge. Generally, the
bistriflimide anions form chain-like structures owing to the bistriflimide anions coordinating to two different lithium cations at the same time. This bridging coordination leads to the formation of extended chains of bistriflimide lithium cation coordination. The simulation box, however, appears to be far too small to get a full idea of how these chains would terminate and whether some sort of longer range structure may be observed. As previously suggested this structure appears stabilised by the inherent charge polarisability of electrodes modelled with the constant potential method.\textsuperscript{16,41,42} It can be seen in the colourmap in Fig 5 that the electrode can be polarised depending on its local environment. The area nearest to the extend strings of lithium cation–bistriflimide complexes, which will have a net negative charge, take on a more positive surface charge, and those areas of the electrode closest to the lithium cation–tetraglyme clusters will take on a more negative surface charge.
The plots in panel B of Fig 5 show the statistical distribution of charges on the electrode atoms throughout the simulations. In a case with limited polarisation of the electrode we would expect to see distributions that were roughly Gaussian, yet we do not see this here. In fact the distribution is highly asymmetric with large tails being seen in the negative direction in all these cases. These tails are caused by the highly polarising effect of lithium cations in near contact with the electrode, stabilisation of these ions is performed by the pooling of large amounts of negative charge on the electrode atoms nearest to the cations. This leads to large negative charges being observed on certain individual electrode atoms. The number of lithium cations close to the electrode increases at the negative electrode with increasing potential difference and decreases at the positive electrode with increasing potential difference. The presence of these tails is most pronounced for high potential negative electrodes and least pronounced for high potential positive electrodes, with neutral electrodes showing tails of intermediate size. Such a result gives weight to the idea that the polarisability of the fixed potential electrode stabilises dechelated and partially dechelated lithium cations in comparison to the unpolariseable fixed charge electrode.

Finally, we move to a discussion of the capacitance. As fluctuations in charge on the electrode are related to correlations with liquid species in the near vicinity. The differential capacitance can be extracted from the oscillations in electrode charge within time by using the relationship,

$$ C(\Delta \Psi) = \frac{\partial Q}{\partial \Delta \Psi} = \frac{\langle \delta Q^2 \rangle}{k_B T} $$

(1)

where $C(\Delta \Psi)$ is the potential dependent capacitance, $\Delta \Psi$ is the external potential difference, $k_B$ is the Boltzmann constant, $T$ is the temperature, and $\delta Q$ is defined as,

$$ \delta Q = Q - \langle Q \rangle, $$

(2)

where $Q$ is the charge of the whole electrode.

$C(\Delta \Psi)$ is the total capacitance of the simulated two-electrode system. Usually, in the-
ory and computations, a one-electrode capacitance is plotted against the potential drop from the electrode to the bulk-like region.\textsuperscript{44} On such a plot, the curve might have a single-hump or a double-hump shape. Herewith, both constant surface charge and constant potential methods provide the data for plotting such capacitance–potential drops,\textsuperscript{34} yet only the latter one allows for straightforward calculation of $C(\Delta \Psi)$. Fig. 6 shows the resulting total capacitance curve on the $\Delta \Psi$-scale. The curve has a maximum at roughly 2V, which is equivalent to the double-hump shape on the potential drop scale. A similar plot for a conventional ionic liquid was previously presented by Merlet \textit{et al.}\textsuperscript{42} Thus, the behaviour is symptomatic of an ionic liquid nanostructure, and together with the simulated nanostructure suggests that solvate ionic liquids behave in a manner similar to conventional ionic liquids\textsuperscript{45,46} and their solutions with lithium salts.\textsuperscript{47,48} However, this plot of capacitance against potential differs somewhat from that obtained for conventional ionic liquids using green functions to model a universally polarisable metal surface, while both results show a general decrease in capacitance with dilution, the prior prediction does not show the peak away from the zero potential we see here, but such was observed for dilute electrolytes.\textsuperscript{49,50} There are a couple of possible reasons for this difference, one is the presence of this peak may be due to the atomistic nature of the electrode, as in previous studies of the capacitance of water at platinum electrodes and ionic liquids at graphitic electrodes. Alternatively this may be due to a specific difficulty in modelling solvate ionic liquids using the methodology of Girotto \textit{et al.}\textsuperscript{49,50} In their 2017 paper the liquid is modeled using two parameters: one for ion size and the other the Bjerrum length.\textsuperscript{50} The problem is that the size of a solvate ionic liquid cation changes with chelation and dechelation, which has been shown in this paper to have some degree of surface dependence, this dynamic would also be expected to lead to broad changes in the translation component of the dielectric constant close to the interface and thus the Bjerrum length.

It should be noted that this capacitance curve does not reflect what would be seen for the diluted solution of lithium salt in an organic solvent. It will be interesting to see how
this curve and capacitance, in general, would evolve with time particularly when compared to conventional ionic liquid solutions.

In a somewhat related point due to the box size and simulations length, it has not been possible, as usual with simulations of this type to extract screening lengths. Recent work has however shown that concentrated electrolytes exhibit non negligible long range decay lengths, with theoretical and computational studies supporting these conclusions.

$$C(\Delta \Psi) / \mu F \, cm^{-2}$$

Figure 6: Calculated differential capacitance of the solvate ionic liquid at a graphitic electrode. The connecting lines are added to guide the eye.

The results in this study differ significantly from the previous study with fixed charge electrodes. Primarily in the presence of a dechelation dynamic, which is induced by surface polarisability. Moreover, the nanostructure in this study does agree with previously obtained atomic force microscopy results, as a multilayer structure is observed. This study raises a question about the veracity of using simple constant charge simulations for systems featuring ions and coordinating solvents, to understand interfacial behaviour at electrodes. The heterogeneous surface charge distribution affects the solvation of lithium cations by the tetrtraglyme at the interface, a more profound effect than observed for the interfacial structure in conventional ionic liquids. However, constant charge simulations do still provide strong indications of how a liquid would behave at a charged dielectric surface, where the surface charge is equally distributed among the atoms of the same type. Moreover, these
simulations will be more illustrative of experiments performed on these types of surfaces, such as surface force or electrowetting experiments.\textsuperscript{55–58}

The coordination behaviour observed in this paper has wide-reaching implications for the implementation of solvate ionic liquids in technology. The presence of dechelation dynamics is likely to have a significant role in both charge transfer and wear of electrodes. The level to which this needs to be maximised and minimised is not apparent from this study. However, it is likely that it will be possible to control the level of dechelation of ions at the electrode while maintaining the bulk solvate ionic liquid type behaviour. This is because change to allow for easier dechelation at the electrode can be counteracted in the bulk by using an even less readily coordinating anion.\textsuperscript{1,5}

It is enticing to think that the behaviours observed here may be the reason for a previous result by Moon \textit{et al.}\textsuperscript{13} where concentrated solutions of lithium bistriflimide in tetraglyme exfoliate graphitic minerals, but solvate ionic liquids do not. The lithium cation–anion complexes observed at the graphitic interface for all studied surface potentials provide an alternative source for lithium cations which intercalate without a coordinating solvent. It is possible that such clusters would not exist in a diluted system as the greater amount of solvent molecules would lead to only lithium solvent complexes being observed, in line with a traditional Stern layer. This alongside an interest in seeing the effect of dilution on the capacitance curve, and the possibility of seeing the anomalous screening lengths observed experimentally for diluted lithium cation–glyme solutions,\textsuperscript{59} provides motivation for future simulations of diluted solvate ionic liquids at constant potential electrodes and in the bulk.

**Conclusions**

This study has shown that solvate ionic liquids adopt a multilayer type interfacial structure at constant electrode potential, a behaviour similar to that observed for conventional ionic liquids. The coordination environment of lithium cations in the first interfacial layer was
seen to be vastly different for the coordination environment in the bulk with a far larger number of lithium cations coordinated to bistriflimide anions.

The simulated structure is very different from the one obtained in past studies when a constant surface charge method was applied to the electrodes.\textsuperscript{14} Thus, accounting for the surface polarisability is crucial for simulations of the charge transfer at electrodes and the intercalation of lithium cations into graphitic electrodes.

**Supporting Information Description**

The SI includes the force field parameters for the studied systems, as well as fixed charge simulation results provided in full.

**Acknowledgements**

SWC thanks EPSRC and the Department of Physical and Theoretical Chemistry at the University of Oxford for his DTA studentship. High-performance computing was performed at the ARC supercomputing centre at the University of Oxford.\textsuperscript{60} This research was supported by the Estonian Research Council (grants IUT20-13 and PUT1107), by the EU through the European Regional Development Fund (TK141 “Advanced materials and high-technology devices for energy recuperation systems”), and by the Estonian–French cooperation program Parrot, funded by the Estonian Research Council and Campus France. This research was also supported by a short-term scientific mission funded by COST action MP1303. The authors thank Prof. Susan Perkin for all her help and support as well as Dr. Maksim Mishin and Prof. Maxim V Fedorov for useful discussions. The MDanalysis python library was used for simple parsing and data analysis operations for this paper\textsuperscript{61} and VMD was used for trajectory visualisation.\textsuperscript{62}
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