

Electrolytes for Aluminum Ion Batteries: A Molecular Dynamics Study

Maryam Kosar^{1*}, S. Maryamdokht Taimoory¹, Owen Diesenhaus¹, John F. Trant^{1*}

¹ Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario N9B 3P4 Canada.

² Current Address: Department of Mechanical Engineering, University of Wisconsin-Madison, Madison, WI, 53706 USA

* Corresponding Authors' emails: jtrant@uwindsor.ca, maryam.kosar@uwindsor.ca

Abstract

A vital component in the fight against climate change is the development of highly efficient energy storage for renewable resources. The aluminum ion battery (AIB) is a promising technology, but there is a lack of understanding of the desired nature of the batteries' electrolytes. These properties cannot simply be extrapolated from other metal ion batteries, as the ionic charge carriers in these batteries are not simply Al^{3+} ions but the anionic AlCl_4^- and Al_2Cl_7^- , which form in the electrolyte. This study aims to illustrate the effect of mole ratios and organic solvents to improve the AIB electrolytes with the aid of computational techniques. To this end, molecular dynamics simulations were carried out on varying ratios forming acidic, neutral and basic mixtures of the AlCl_3 salt with 1-ethyl-3-methylimidazolium chloride (EMImCl) ionic liquid (IL) and an organic solvent electrolyte (dichloromethane (DCM) or toluene). The data obtained from both viscosity and diffusion calculations indicate that the solvents could improve the transport properties. Both DCM and toluene lead to lower viscosities, higher diffusion coefficients, and higher conductivity. Detailed calculations demonstrated solvents can effectively improve the formation of $\text{AlCl}_3 \cdots \text{Cl}$ (AlCl_4^-) and $\text{AlCl}_4^- \cdots \text{AlCl}_4^-$ (Al_2Cl_7^-) especially in acidic mixtures. Densities which were averaged around 1.25 g/cm^3 for pure electrolyte mixture of AlCl_3 -EMImCl were of comparable values to the experimental reports. These results are all in agreement with experimental findings, and strongly suggest that DCM in acidic media with AlCl_3 and EMImCl might provide a promising basis for battery development.

Keywords:

Aluminum battery, Electrolytes, Ionic liquids, Organic solvents, Molecular dynamics simulation.

Introduction

Battery technology is constantly improving and increasingly looking towards the post-lithium world by employing more readily accessible metals such as Na, Ca, Mg, K, and especially Al. Al is an inexpensive, earth-abundant element. It is chemically very stable and has a higher redox potential, -1.76 V vs standard hydrogen electrode (SHE), than other metals. Al also has a high gravimetric capacity (2,980 mAh/g) and volumetric capacity (8,046 mAh/cm³), four times that of Li⁺. Additionally, it is nontoxic and stable in the air, major benefits compared with the unfortunate “frequent fires and explosions” that can occur with lithium batteries.¹⁻² Theoretically, Al batteries with the same capacity as extant Li batteries would be far lighter and far smaller. However, challenges remain with Al batteries that prevent their wide scale deployment. Aluminum ion batteries (AIBs) suffer from poor diffusivity due to the difficult intercalation/de-intercalation of Al³⁺ cations. Multivalent cations’ diffusion suffers from poorer kinetics due to the higher electrostatic interactions when compared to monovalent Li ions.³ Species involved in the (de)intercalation process in IL Al batteries are mainly AlCl₄⁻ and Al₂Cl₇⁻; compared to Li⁺ in Li batteries, they are rather slow moving due to their larger radii.⁴⁻⁵ The trivalent nature of the ion also complicates matters as an electrode needs to accept three electrons in order to bind a single cation, and it needs to reversibly bind multiple cations. Furthermore, formation of an oxide layer on the anode must also be prevented as it hinders the electrochemical reaction; however, pretreatment with a coating, or the addition of electrolyte additives can suppress the emergence of this passivation layer.^{1-2, 6-15} Another restriction is that ions in higher oxidation states, such as M²⁺ or M³⁺, demonstrate low plating efficiency and formation of an insulating solid electrolyte interface layer, *i.e.*, dendrites, is inevitable. In this case, electrolyte/electrode interface design is very important.⁶

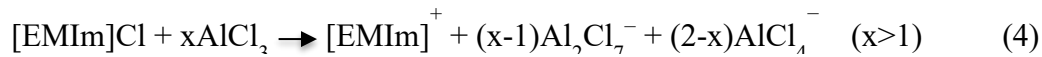
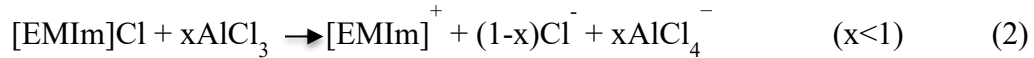
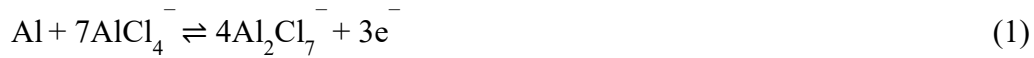
The choice of electrolyte is critical for determining battery efficiency. It needs to facilitate ion mobility, restrain the electrochemical window to prevent undesirable “side” redox reactions, exhibit low viscosity, have a large thermal operation window, be non-flammable, and remain chemically inert to avoid corrosion and battery degradation.¹⁶ Aqueous electrolytes were used in early Al batteries, but after 2010 their application was limited due to anode corrosion, hydrogen evolution side reactions, and passive oxide film formation.¹⁴ In order to overcome these issues, nonaqueous electrolyte systems were explored and see increasing investigation, and progress has been rapid.^{5, 13, 17-20} In 2011, Jayaprakesh designed an Al-ion battery using V₂O₅ nano-wires as the

cathode, Al metal as the anode, and 1-Ethyl-3-methylimidazolium chloride (EMImCl) as the electrolyte. The battery had promising electrochemical stable cycling over 20 charge–discharge cycles.¹⁸ In 2013 Rani reported high reversibility and capacity retention in an Al-ion battery containing AlCl₃– 1-Butyl-3-methylimidazolium bromide (BMImBr). The charge capacity of the fluorinated graphite electrode was 300 mAh g⁻¹ and the columbic competency of the cell was 75 %.²¹ In 2015, Wang improved the electrochemical performance of the Al battery with AlCl₃-BMImCl electrolyte by using a V₂O₅ on Ni foam as the cathode. He could achieve a discharge capacity of 239 mAh/g and a relatively high voltage plateau at 0.6 V.⁹ In 2015, Sun reported a very high voltage plateau at ca. 1.8 V vs. Al³⁺/Al in an AlCl₃-EMImCl Al battery.²² Lin disclosed an even stronger Al-ion battery using AlCl₃-EMImCl electrolyte and a graphitic cathode with a stable cycling life up to 7,500 charge/discharge cycles exhibiting a discharge voltage of ~2.0 V at 70 mAh/g specific capacity with an ultrafast charge/discharge rate.²³ In 2017, Ferrara *et. al.* studied the effect on the physicochemical properties of differing the molar ratios of AlCl₃/[EMIm]Cl in the range of 1.1–1.7. The electrolytes were tested in a standard Al-ion cell and at relatively high current densities ($i > 200 \text{ mA g}^{-1}$) and confirmed that a 1.2 Al₂Cl₇⁻/AlCl₄⁻ molar ratio was the most effective ratio.²⁴ In 2019, Yang and co-workers looked into the effect of the substituents of imidazolium IL on the performance of electrolyte and proposed a way to design ILs to optimize the performance of Al battery through electrolytes.¹⁴ They concluded that the reduction of Al₂Cl₇⁻, the intercalation/deintercalation of AlCl₄⁻ and the electrodeposition/electrostripping of Al can be improved by designing the substituents like [MPIM] which weaken the intramolecular forces between the IL cation and chloroaluminate anions.

A suitable electrolyte should be electrochemically stable and electronically insulating but not ionically conducting. Several non-aqueous systems have been studied in the AIBs so far, including inorganic molten salts, eutectic liquids, organic solvents and room temperature ionic liquids (**RTILs**).²⁵ Inorganic molten salts, eutectic liquids, and organic solvents require elevated temperatures for operation, making them unfeasible for widespread use. Eutectic liquids and organic solvents containing aluminum salts have low conductivity. Aluminum salts have shown poor solubility in organic solvents. Flammability of organic solvents (not eutectic liquids) is a limiting factor but addition of the ionic liquid in aluminum salt organic solvent mixture have rectified these shortcomings.^{6, 20}

RTILs, displaying high ionic conductivity, low vapor pressure, non-flammability, a relatively wide electrochemical window and reversible stripping/plating of the aluminum electrode at low temperatures are the most promising electrolytes in AIBs as they are with most other metals.^{8, 13} The most commonly employed RTIL is EMImCl. RTIL electrolytes are composed of a solid or liquid RTIL compound and the solid AlCl₃ salt, which together form a liquid binary mixture. In addition, the composition and pH of the RTIL electrolyte is an important parameter for cell engineering because it affects the electrochemical performance of the cathode and the whole design of the cell.

Unlike other metal-ion batteries, in the AIBs, the Al³⁺ cation is transformed into the anionic mobile charge carriers AlCl₄⁻ and Al₂Cl₇⁻.⁶



The electro stripping and electro plating ability of the RTIL electrolytes is dependent on the charge carrier species, which is affected by their Lewis acidity, or the molar ratio of AlCl₃ to the RTIL.¹⁵ The Al₂Cl₇⁻ and Cl⁻ are strong Lewis acids and bases respectively. Excess Al₂Cl₇⁻ leads to an acidic mixture; excess Cl⁻ lead to a basic mixture. At a neutral pH, the AlCl₄⁻ predominates. Table 1 and Figure 2 give a good insight into the species and constitution of the mixture.²⁶ The electro deposition and stripping are feasible in the acidic mixture in which there is an excess of AlCl₃ and Al₂Cl₇⁻ species. However, should the mixture become too acidic, the melting point rises rapidly as a function of increasing X_{AlCl₃}(mol%), meaning the electrolyte is no longer liquid at operational temperatures above 66% AlCl₃ content. This would be the limiting condition.

Table 1. Molar ratios of EMImCl and AlCl₃ in a mixture of EMImCl-AlCl₃ with different Lewis acidity and dominant species.

χ_{EMImCl} (mol %)	χ_{AlCl_3} (mol %)	Lewis acidity	Predominant anions
33.3	66.7	Acidic	Al ₂ Cl ₇ ⁻ , AlCl ₄ ⁻
50	50	Neutral	AlCl ₄ ⁻
66.7	33.3	Basic	AlCl ₄ ⁻ , Cl ⁻

The properties of electrolytes are strongly affected by the addition of additional solvents. A suitable solvent is the one in which both ionic liquids and the salts are soluble, but which doesn't react with any other component.²⁴ In lithium-ion batteries, dimethyl carbonate (DMC) and diethyl carbonate (DEC) have usually been used as solvents. However, DMC and DEC suppress the electrochemical reaction of AlCl_4^- and they have been less promising in Al batteries; consequently, toluene, methylene chloride (DCM) and benzene have instead been used as electrolyte additives in aluminum batteries.²⁷ Experiments have demonstrated that organic solvents can increase the performance of the AIBs, but solvent choice is important as acetone, acetonitrile or THF lead to unpleasant highly exothermic reactions as the electron-deficient AlCl_3 or Al_2Cl_7^- interact with the solvent.²⁸⁻²⁹ Recently, Park *et al* reported the enhancement in conductivity, ionic mobility and diffusion coefficients of the ions by the addition of benzene to an EMImCl- AlCl_3 electrolyte solution.²⁷ Similarly, Sun *et al* reported a 13 (toluene) or 10 (methylene chloride) percent enhancement in the current density upon the addition of solvent to the EMImCl- AlCl_3 electrolyte.²⁸ Interaction of the lone pair electrons in DCM with AlCl_3 decreases current density although DCM has lower viscosity compared to that of toluene which compensates. Xia *et al* looked at the influence of the addition of 1,2-dichloroethane, dichloromethane, benzene, and toluene individually to an $\text{AlCl}_3/\text{Et}_3\text{NHCl}$ electrolyte solution at different volumetric ratios.³⁰⁻³¹ The organic solvents, *i. e.*, DCM and toluene, enhance the electrochemical properties of the system by interacting with both cations and anions, increasing the distance between them, leading to an increase in the diffusivity which not only improves the physicochemical properties, but also stabilizes Al_2Cl_7^- . These solvents also help to decrease the viscosity of the system, increasing conductivity.^{30, 32-33}

This current study aims to find an improved electrolyte for the Al batteries by incorporating solvent. We apply computational methods to examine the RTIL electrolytes for the AIBs. The experimental research to determine promising materials as AIB electrolytes requires trial and error, which is a tedious and expensive process. Computational models and simulations can be used to explain the effects observed for current electrolytes and can predict the function of future materials. With the aid of molecular dynamics (MD) simulations we study the electrolytes in acidic, basic, and neutral concentrations. We also look at the effect of different ratios of organic solvents on the performance of the Al battery. The analysis of the solvation of AlCl_3 and the suitability of the

different electrolyte mixtures will help build a greater understanding of the electrolytic structure, which will inform the further search for enhanced electrolyte materials.

Methods

Molecular dynamics simulations were carried out using the Materials Science (MS) suite in the 2020.3 version of the Schrodinger package. Three kinds of boxes eg., AlCl₃:EMImCl, AlCl₃:EMImCl:toluene, and AlCl₃:EMImCl:DCM with different mole ratios of AlCl₃ and EMImCl (2:1, 1:1 and 1:2) representing the acidic, neutral and basic systems were built. Solvent ratios were 3, 2, 1.5 for toluene and 5, 3.2 and 2.5 for DCM for the aforementioned systems respectively. All the ratios were selected based on the calculations on the previously reported experimental results where Fannin *et. al.* considered the molecular weight of a mixture of AlCl₃-IL was given by

$$M = M_{\text{Im}} + 133.34N/(1-N)$$

where M_{Im} is the molecular weight of IL and N is the mole fraction of AlCl₃.³⁴ Volumes of the IL can be derived from this equation and based on the results of Xia *et. al.* a volume ratio of IL: solvent (DCM/toluene) was chosen 1:1 to give us the highest conductivity.³⁰ Having the volume and density, one can calculate the mass and molar ratios of the solvents. Molar ratios of AlCl₃: IL were also chosen based on the acidity of the mixtures.^{30, 34} Initial configurations for each system were generated with the 2D-Sketcher plugin in the MS suite (Figure 1). All ~1000 molecules of interest i.e., AlCl₃, EMImCl and solvents (DCM or toluene) were placed randomly in the simulation boxes with dimensions of $\sim 55 \times 55 \times 55 \text{ \AA}^3$ using the disordered system builder plugin. The OPLSe non-polarizable force field was used for modelling the species in this study, although we were aware of the probable non-realistic effects of the non-polarizable force field in the reproduction of the transport properties. The reason behind selecting this non polarizable force field was that the computer times related to the minimization procedure of the polarization term of polarizable species when using polarizable force fields increases tremendously, and exponentially with the number of polarizable species. A similar simplification was used by Salanne and coworkers who treated the EMI⁺ cation as a non-polarizable species, justifying this decision by considering that polarization effects are dominated by the chloride anions. They concluded the dynamical properties calculated with non-polarizable models are slower than is observed in experiments though they can reproduce the structure very well.³⁵ Kubisiak *et. al.* compared a

polarizable and non-polarizable force field for the study of a sodium ion battery and the agreement between the computational and the experimental results was satisfactory.³⁶ Based on these precedents, we likewise treated the EMIm⁺ cation as a non-polarizable species since the polarization effects are dominated by the chloride anions. Initial relaxation and energy minimization were performed on all 9 systems for 1000 steps. The systems were then equilibrated for 5.0 ns in an NVT ensemble following by a 100 ns NPT production run (at 1.0 atm and 300 K). Analyses contained but not limited to the calculation of the radial distribution function (RDF), interaction energies, densities, and transport properties such as viscosity, diffusion coefficients and molar conductivities.

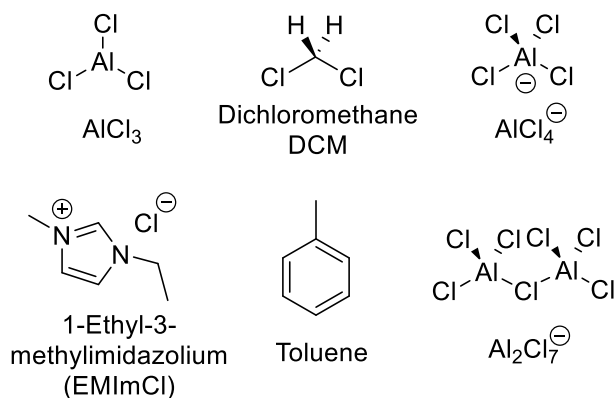


Figure 1. The chemical components present in the MD Simulation Boxes discussed.

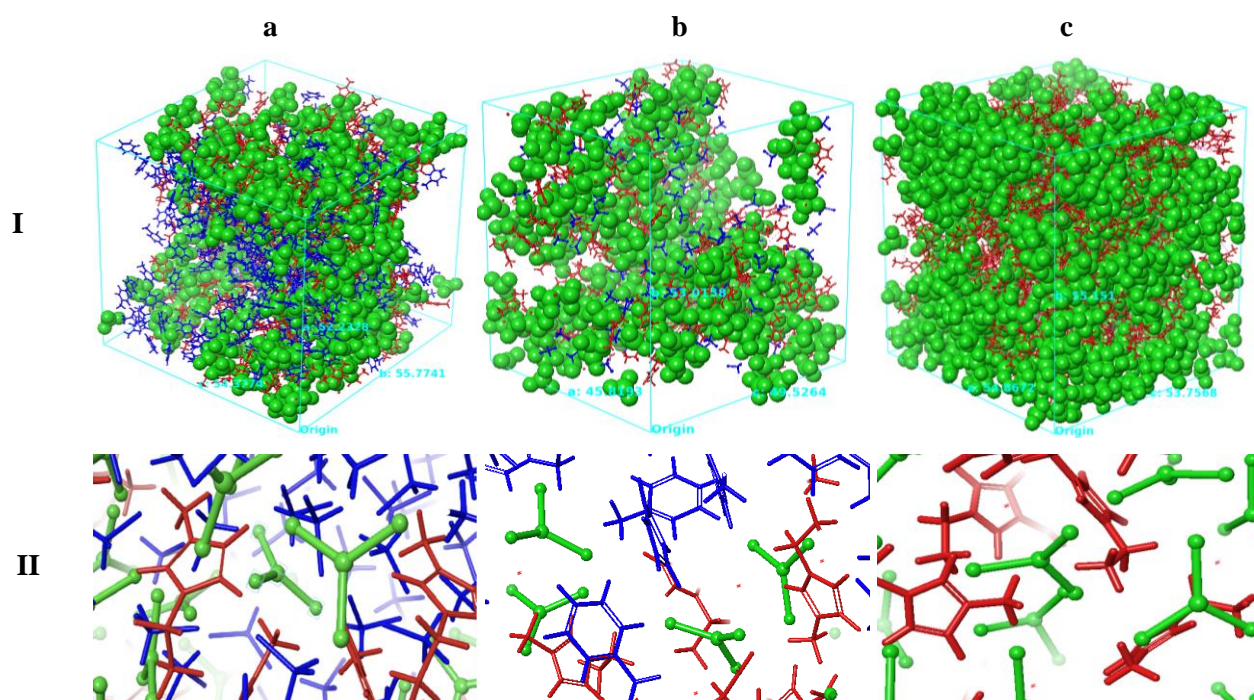


Figure 2. I) Complete views and II) expansions of the three sample boxes of simulations. a) AlCl_3 , EMImCl and toluene, b) AlCl_3 , EMImCl and DCM, and c) AlCl_3 and EMImCl. AlCl_3 , EMImCl and solvents are depicted in green, blue and red respectively.

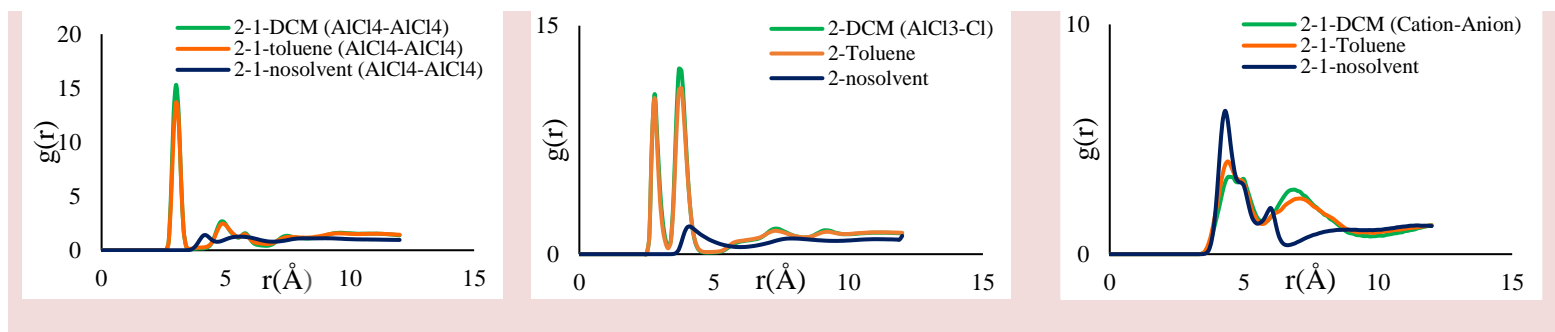
Results

As a preliminary step, we wanted to generate the smallest possible model that could provide useful data. We examined a series of models with the same ratio of components. We found that smaller models did not perform well as there were insufficient collisions to simulate the environment. We propose that this is a useful minimum box.

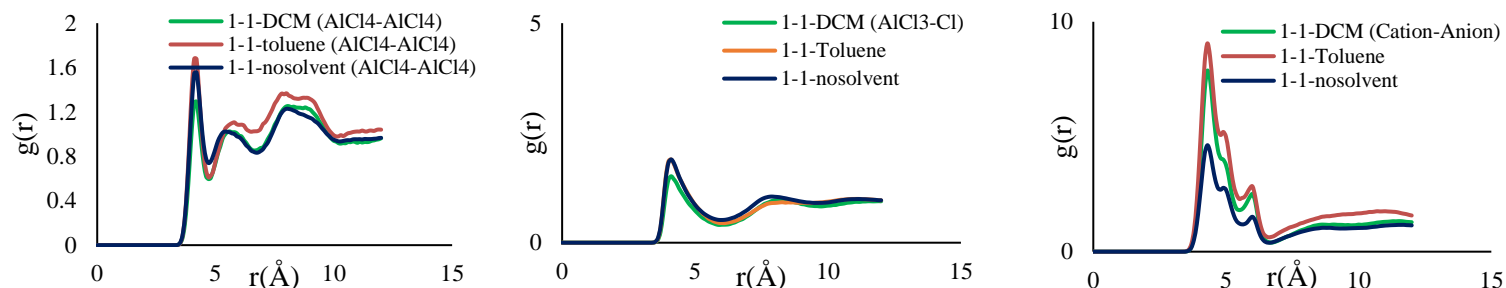
I. Radial Distribution Function

The radial distribution function (**RDF**) represents the average distribution of atoms around any given atom within the system. It is a classical tool to analyze the structure of the liquids and their mixtures, through the effective pairwise interaction between two species, A and B. RDF has been extensively used to understand intermolecular arrangements of different species in solution and their interactions in a mixture.

The RDFs between $\text{AlCl}_4^- \cdots \text{AlCl}_4^-$, $\text{AlCl}_3 \cdots \text{Cl}^-$ and $\text{EMIm}^+ \cdots \text{Cl}^-$ have been measured for the acidic, neutral and basic systems (**Figure 3**).



2. Neutral



3. Basic

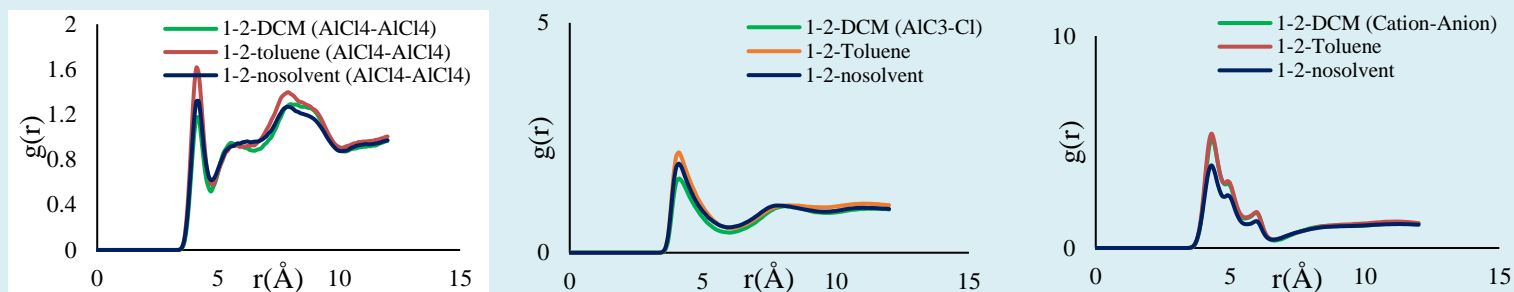


Figure 3. Radial distribution functions of a) AlCl_4^- - AlCl_4^- , b) AlCl_3 - Cl^- and c) EMIm^+ - Cl^- for the EMImCl - AlCl_3 mixtures in acidic, neutral and basic systems at 300 K.

The likelihood of *in situ* Al_2Cl_7^- formation from two AlCl_4^- ions is dependent on the acidity of the system.³⁷⁻³⁹ It requires the two negative ions to be able to come into close proximity.



In acidic mixtures when solvents are present, there are strong interactions of $\text{AlCl}_4^- \cdots \text{AlCl}_4^-$ at ~ 3 Å in their first solvation shell. The first peak is followed by a peak with lower intensity at ~ 5 Å which can be attributed to the formation of the $\text{Al}_3\text{Cl}_{10}^-$ in negligible amounts⁴⁰. When there is no solvent, there seems far fewer interactions of this type, implying that DCM and toluene are needed to facilitate the formation of Al_2Cl_7^- . In neutral and basic conditions, only some Al_2Cl_7^- is formed (note the small values on the y axis) and there seems to be no significant difference regardless of

whether solvents are involved; furthermore, the minimum occurring after the first maximum no longer corresponds to a value of zero. This suggests the possible formation of probable transient species like AlCl_5^{2-} or $\text{Al}_2\text{Cl}_8^{2-}$.

The two distinguishable peaks in acidic conditions of Figure 3.1.b can be attributed to the strong interactions between AlCl_3 and Cl^- . The two peaks show the Cl^- ions are gathered around AlCl_3 within 2.8 Å in the first shell, and 3.7 Å in the second shell, representing the two kinds of interactions between AlCl_3 and Cl^- . The $\text{AlCl}_3 \cdots \text{Cl}^-$ interaction at ~2.8 Å, and the peak at ~3.7 Å are due to the exchanged Cl^- ions which is a result of a jump from one Al coordination sphere to another. When there is no solvent, the interactions between AlCl_3 and Cl^- are weaker and thus there are no sharp peaks. The interesting point is that the solvents could ease this jump and result in two types of distinct interactions. However, the existence and occurrence of such jumps is more probable in the acidic mixture as the intensity of the second peak in neutral and basic is almost 10 times lower than that of the acidic mixture. The neutral and basic systems demonstrated similar patterns in terms of $\text{AlCl}_3 \cdots \text{Cl}^-$ interactions (Figures 3.2 & 3.b). The position of both peaks at the first solvation shell, ~3.7 Å, and the second one, ~8 Å, suggest weaker interactions between AlCl_3 and Cl^- but according to the data in the following table (Table 2), there are more Cl^- ions around the AlCl_3 in neutral and basic systems.

As seen in Figure 3.1.c, the EMIm cation interacts strongly with the Cl anion at ~4.3 Å, which defines the width of the first solvation shell and a peak at ~7 Å due to the exchanged Cl^- ions as a result of a jump from one EMIm⁺ coordination sphere to another. This second peak is distinct especially in acidic conditions, although with lower intensity in the presence of DCM and toluene. This can be attributed to the Cl^- binding loosely to the cation due to the competitive interactions of the ring in toluene and chlorine atoms in DCM with the IL. For all other conditions the second shell emerges as a shoulder. This is due to the slight differences in bond length between the EMIm cation and the Cl anion. Note that for these calculations EMIm⁺ center of mass is considered for measuring the distance with Cl^- and the distances can roughly be assumed as collective average distances related to the six protons of the EMIm⁺ (located on the Imidazolium ring and chain) and Cl^- .

II. Interaction energies

Acidic

Neutral

Basic

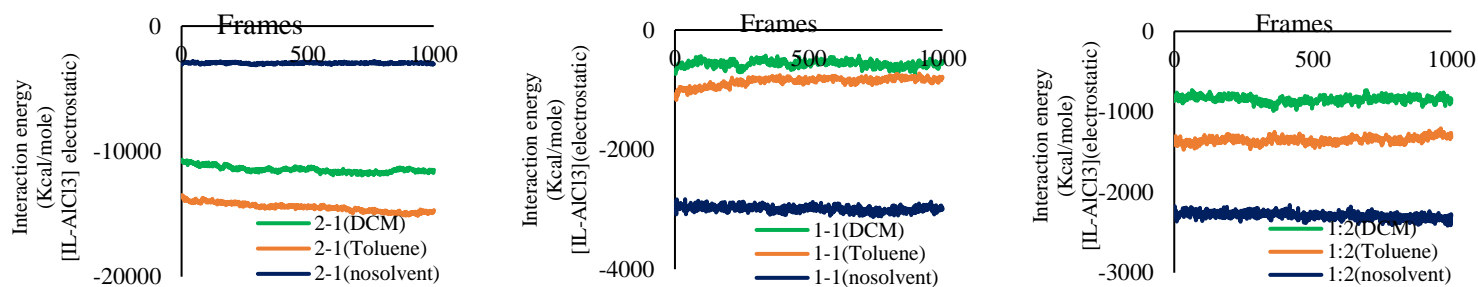


Figure 4. Interaction energies between AlCl₃ and EMImCl over the 100 ns simulation. For all acidic, neutral, and basic systems the interaction energies have been calculated in the absence and presence of solvents (DCM or toluene) for comparison.

In the acidic system (*i.e.*, when AlCl₃: IL: toluene/DCM is 2: 1: 3/5) electrostatic interaction energy between IL and AlCl₃ is stronger when DCM and toluene are present and this leads to an increase in solubility, diffusivity and a decrease in viscosities. This could be attributed to the competitive aromatic ring interaction of toluene and weak interaction of the lone pair electrons of the Cl atom in DCM with both AlCl₃ and IL. This interaction weakens the cationic-anionic interaction between N⁺ and Cl⁻ in the IL and therefore it can inject its Cl⁻ in the p-orbital of the Lewis acidic AlCl₃.

In basic and neutral conditions *i. e.*, AlCl₃: IL: toluene/DCM 1: 2: 1.5/2.5 and 1: 1: 2/3.2 respectively, the IL wins the competitive interaction with AlCl₃ and the strongest IL-AlCl₃ interaction energy is achieved when there is no DCM/toluene in systems. Since the chlorine atoms in DCM can partially interact with both IL and AlCl₃ the interaction energy between IL and AlCl₃ is always weaker in the presence of DCM compared to that of toluene.

III. Density

We measured the densities of our mixtures; those with DCM had the highest densities. The average densities for DCM mixtures were measured to be 1.35 g/cm³ (methylene chloride itself is 1.33 g/cm³) when toluene is the solvent the calculated densities were 1.10 g/cm³ (toluene itself is 0.867 g/cm³) while for the pure electrolytes the densities were 1.25 g/cm³ (EMIMCl is 1.43 g/cm³). Figure 5 shows the density of the 1: 1 pure mixture when no solvents were applied during the whole simulation time. The experimentally reported value of densities for the 1: 1 pure electrolyte was 1.18 g/cm³³² and 1.29 g/cm³⁴¹ which is comparable to our result. This suggests that the computational model is properly distributing the molecules.

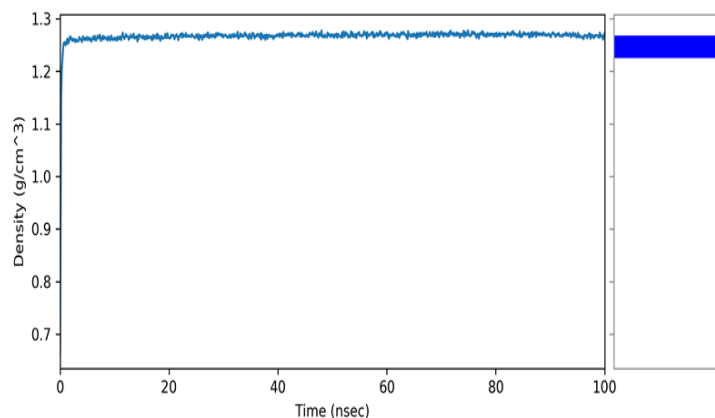


Figure 5. Calculated density of the 1: 1 pure mixture when no solvents were present during the whole simulation time.

IV. Transport Properties

a) Viscosity

Viscosity is determined by the ability of the electrolyte components to move relative to each other. Green–Kubo relations have been applied to calculate the auto-correlation function of off-diagonal pressure tensors. The integral gives shear viscosity as a function of simulation time differences (τ). The final viscosity value is obtained by curve fitting or averaging over a specified range, in the plateau region of the plots.

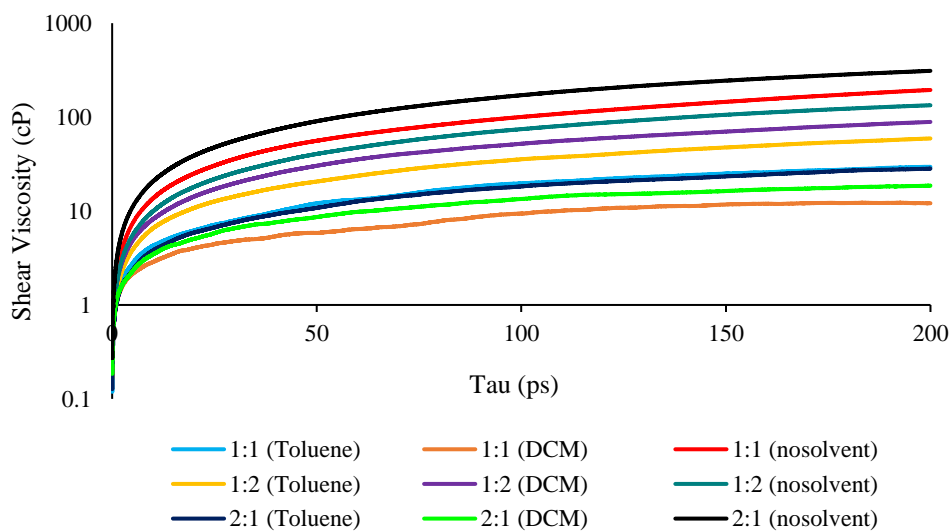


Figure 6. Viscosities of the acidic, neutral and basic systems. The Y axis is in logarithmic scale to show the large range of values of the viscosity in the last 80% of the simulations.

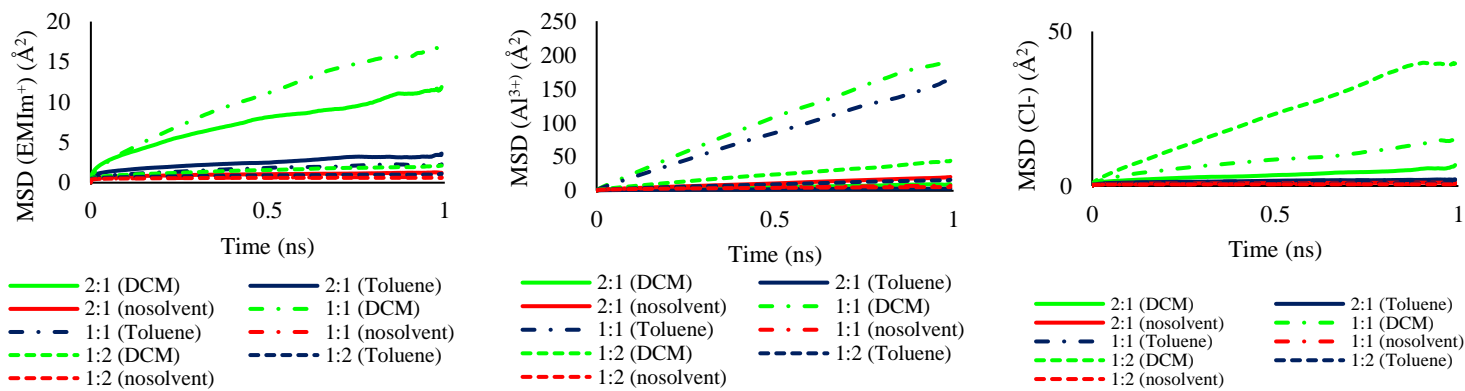


Figure 7. Mean squared displacements of the cations, a) EMIm^+ and b) Al^{3+} , in acidic, neutral and basic systems.

The lack of solvents leads to higher viscosities, decreasing diffusivity. As low viscosity is highly correlated with increased conductivity, solvent addition is indicated.⁴²⁻⁴³

b) Diffusion coefficient

The diffusion coefficient, or diffusivity, is the proportionality constant between the molar flux caused by molecular diffusion and the gradient in the concentration of the species. There are two approaches to calculate the diffusivities: mean squared displacement (MSD) and velocity autocorrelation. The primary way of calculating the diffusion from MD simulations is via mean squared displacements for which the average displacement of particles is measured versus time. For Fickian diffusion, we expect a plot of mean squared displacement versus time to be linear and its slope to be proportional to the diffusion constant. Since diffusivity of the ions is an important factor to be considered while selecting and designing the electrolytes, MSDs of the cations and the Cl^- anion was calculated. From there, and by means of 100 ns MD simulation on the equilibrated systems, the diffusion coefficients of the Al^{3+} , EMIm^+ and Cl^- were measured. The greatest MSD values are obtained (the largest diffusion coefficients) when solvents are present. The solvent interact directly with either through the aromatic cloud in toluene or the lone pair electrons of chlorine in DCM. But these are weak interactions compared with those between AlCl_3 and

EMImCl, where the MSD and diffusivity are decreased. Organic solvents disrupt the AlCl₃-EMImCl interactions, increasing diffusion.

Table 2. Diffusion coefficients (m²/s) of the Al³⁺ and EMIm⁺ in all the systems with different acidities and ratios of the components.

	Component Ratios	Diffusion coefficient (m ² /s)		
		Al ³⁺ (×10 ⁻¹²)	EMIm ⁺ (×10 ⁻¹³)	Cl ⁻ (×10 ⁻¹⁴)
Acidic	2 AlCl ₃ : 1 EMImCl: 5 DCM	13.3	150	726
	2 AlCl ₃ : 1 EMImCl: 3 Toluene	3.82	35.3	189
	2 AlCl ₃ : 1 EMImCl: no solvent	30.3	8.96	76.0
Neutral	1 AlCl ₃ : 1 EMImCl: 3.2 DCM	322	252	2,010
	1 AlCl ₃ : 1 EMImCl: 2 Toluene	228	24.6	196
	1 AlCl ₃ : 1 EMImCl: no solvent	8.17	3.32	24.6
Basic	1 AlCl ₃ : 2 EMImCl: 2.5 DCM	68.1	20.8	6,770
	1 AlCl ₃ : 2EMImCl: 1.5 Toluene	23.6	6.48	43.3
	1 AlCl ₃ : 2EMImCl: no solvent	5.85	1.78	7.33

The solvents, in most cases, enhance the diffusion coefficients of the ions in acidic, neutral and basic systems, with DCM having the stronger effect. These results are comparable to those reported by Salanne *et. al.* who calculated the diffusion coefficient of EMImCl-AlCl₃ to be 1.04×10⁻¹⁰ m²/s,³⁵ and the experimental report of Margulis *et. al* who found the diffusion coefficient of BMIm⁺ in [BMIm][PF6] mixtures was 1.43×10⁻¹¹.⁴⁴

c) Conductivity

Conductivity, the mobility of ions, of an electrolyte plays an important role in batteries. Mobility is related to the electrostatic interactions between the ions of the electrolyte. An electrolyte with high conductivity improves the performance of the battery by affecting the rate of charge/discharge processes. Therefore, along with the transport properties and interactions, one can determine the suitability of the involved IL electrolytes by measuring their conductivities.

A crude upper bound estimate for the molar conductivity of the system can be derived from the Nernst-Einstein equation⁴⁴⁻⁴⁸:

$$\Lambda_{N-E} = N_A e^2 / k_B T (D[EMIm^+] + D[Cl^-]) \quad (6)$$

where N_A is Avogadro's number, e is the electron charge, k_B is the Boltzmann constant and D is the corresponding diffusion coefficient of the ions. The molar conductivities of the electrolytes were calculated (Table 3).

Table 3. Molar conductivities ($S\ m^2/mol$) of the systems with different acidities and ratios of the components.

	Component Ratios	$\Lambda_{N-E} (\times 10^{-5}) (S\ m^2/mol)$
Acidic	2 $AlCl_3$: 1 EMImCl: 5 DCM	8.2
	2 $AlCl_3$: 1 EMImCl: 3 Toluene	2.0
	2 $AlCl_3$: 1 EMImCl: no solvent	0.6
Neutral	1 $AlCl_3$: 1 EMImCl: 3.2 DCM	16.7
	1 $AlCl_3$: 1 EMImCl: 2 Toluene	1.6
	1 $AlCl_3$: 1 EMImCl: no solvent	0.2
Basic	1 $AlCl_3$: 2 EMImCl: 2.5 DCM	25.7
	1 $AlCl_3$: 2 EMImCl: 1.5T oluene	0.4
	1 $AlCl_3$: 2 EMImCl: no solvent	0.1

Adding organic solvents improves the molar conductivities in all cases. This can be attributed to the strong coulombic interaction between cations and anions of the aluminum ion salt in the absence of solvents which significantly decreases solubility and electrolyte ionic conductivity. DCM enhanced the molar conductivities significantly more than toluene in all conditions. This was expected, as in general, conductivity and viscosity should be inversely proportional. For the most viscous mixtures, in the absence of organic solvents, conductivity and diffusivity tend to be smallest. Previously reported results on similar ionic liquid mixtures without solvent present show the diffusion coefficients of $\Lambda_{N-E} = 9.45 \times 10^{-5} S\ m^2/mol$ which is comparable to our calculated values.⁴⁴

Discussion

The calculated densities were comparable to those measured experimentally when available (*i.e.* for the solvent free systems). This suggests that this computational model is sufficient to simulate the actual electrolyte environment. For the systems with lower viscosities like those contained DCM and toluene, the density turned out to be higher compared to pure electrolytes. The effects of the organic solvents on the transport properties, *i.e.*, viscosity, diffusivity and conductivity of

the AIBs electrolytes have been investigated using molecular dynamics simulations. DCM and toluene decrease the viscosities and improve the diffusion coefficients of the ions in AlCl_3 -EMImCl mixtures under all three acidic, neutral and basic conditions, and DCM acts more effectively than toluene. These two solvents enhance the molar conductivities in all acidities observed in this study. Not using a solvent additive is predicted to be detrimental for electrolyte performance.

Solvents effectively improve the formation of the two important anionic species in the intercalation process in Al batteries, $\text{AlCl}_3 \cdots \text{Cl}$ (AlCl_4^-) and $\text{AlCl}_4^- \cdots \text{AlCl}_4^-$ (Al_2Cl_7^-) especially in acidic mixtures. This is also the only valid pH system for an effective Al battery, so it is promising that we see this effect in this case.

Conclusions

The systems with lower viscosity and higher diffusion coefficient and conductivity would be appropriate for further investigation as electrolytes in Al batteries. Furthermore, as AlCl_4^- and Al_2Cl_7^- are essential for the (de)intercalation process, the radial distribution function analysis shows that they should be more easily formed in acidic mixtures in the presence of solvents. This data all correlates well with the sparse experimental evidence available. The identified conditions are likely not optimal; other solvents, or slight changes to concentration might be advantageous, but this approach provides useful data for guiding the investigation into next generation batteries to move into the post-lithium future.

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