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RENATO VERÍSSIMO DE OLIVEIRA

ANALYSIS OF THE BEHAVIOR OF Sn^{2+} AND In^{3+} IONS IN DES AND IN WATER:A THEORETICAL APPROACH

FORTALEZA
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Orientador: Prof. Dr. Norberto de Kássio Vieira Monteiro.

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In memory of my grandfather Luiz Veríssimo for the times I accompanied him to the “bodega” as a child; from the Wise King Solomon for showing me that there are ways that in the eyes of men seem good, but their end are ways of death; from the apostle, Paul for teaching me that all things are lawful for me, but not all things are suitable for me; from the prophet Amos for teaching me that two will not walk together unless they agree; of Socrates for telling me that there are universal values; of Jesus Christ for explaining that by repaying evil with evil I will resemble the evil man and of Confucius for saying that silence is the best answer we should give to fools.

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First, I would like to thank my lovely mother for continuing to endure this fateful life, even though it is often complicated for you. Second, I thank you for all the love, affection, education and friendship towards me because, without your unparalleled hug, I don't know how I would bear the finitude of existence. Only your extraordinary inner strength makes me see the human being I need to be! I would also like to congratulate the life of my kind father because his existence is very fundamental to me, and his excellent advice has been very enriching throughout my journey here. Furthermore, I thank my sisters Amanda, Gabriely and Larissa for being an inseparable part of me. My thanks to all my family members who, directly or indirectly, contributed to my personal, professional and intellectual rise.

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I want to dedicate this work to a friend and brother that the UFC provided me and that until now has been incomparable in several ways: a faithful friend, counselor, understandable, willing to help, debater of ideas, extremely dedicated and competent. So to you, my dear friend Joel Leitão, I dedicate this paragraph.

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“If Raphael, returned to life, were to paint a modern School of Athens of physicists, I think he would include Einstein with Galileo, Newton, and Maxwell pointing toward the heavens, while Faraday and Rutherford would point toward the earth.” (Segrè, 1980, p.78).

ABSTRACT

An alternative for replacing conventional organic solvents and ionic liquids, the Deep Eutectic Solvents (DES) emerged, a class of compounds with essential properties in the industry. These solvents have numerous advantages regarding ionic liquids, such as low price, biodegradability, and low toxicity. Furthermore, the DES has many applications in science, for example, organic synthesis, electrodeposition of metals, catalytic process. In this work, the behavior of Sn^{2+} and In^{3+} ions were analyzed in the solvents 1ChCl:2EG (chloride choline and ethylene glycol, DES) and water through computational simulations by molecular dynamics (MD) and Quantum Theory of Atoms in Molecules (QTAIM) calculations. The results showed that the Sn^{2+} and In^{3+} ions strongly interact with the chloride anion in DES. Furthermore, only the Sn^{2+} ion showed interaction with the ethylene glycol molecules in DES, which was not observed for In^{3+}, which led to no interaction with EG. In contrast, the most likely interaction is between cations and oxygen from water in a water solvent. The analysis of Bond Critical Points (BCPs) showed that the strength of these interactions follows the following sequence: In-Ow > In-Cl > Sn-Ow > Sn-Cl. The behavior of both ions in the metallic mixture was invariant in DES and in water when compared to the same isolated ions. Furthermore, it may be observed that the increase in the number of water molecules in the systems containing water did not cause relevant changes.

Keywords: DES; water; Tin; Indium; MD; QTAIM.

RESUMO

Uma alternativa para substituir solventes orgânicos convencionais e líquidos iônicos são os Solventes Eutéticos Profundos (SEP), uma classe de compostos com propriedades essenciais na indústria. Esses solventes apresentam inúmeras vantagens em relação aos líquidos iônicos, como baixo preço, biodegradabilidade e baixa toxicidade. Além disso, os SEP tem muitas aplicações na ciência, por exemplo, síntese orgânica, eletrodeposição de metais, processo catalítico. Neste trabalho, o comportamento dos íons Sn^{2+} e In^{3+} foi analisado nos solventes 1ChCl:2EG (cloreto de colina e etilenoglicol, SEP) e água através de simulações computacionais por dinâmica molecular (DM) e cálculos da Teoria Quântica de Átomos Em Moléculas (TQAEM). Os resultados mostraram que os íons Sn^{2+} e In^{3+} interagem fortemente com o ânion cloreto no DES. Além disso, apenas o íon Sn^{2+} apresentou interação com as moléculas de etilenoglicol no DES, o que não foi observado para o In^{3+}, pois este não apresentou interação com o EG. Em contraste, a interação mais provável é entre cátions e oxigênio da água em solvente água. A análise dos Pontos Críticos de Ligação (PCLs) mostrou que a força dessas interações segue a seguinte sequência: In-Ow > In-Cl > Sn-Ow > Sn-Cl. O comportamento de ambos os íons na mistura metálica foi invariante em SEP e em água quando comparados aos mesmos íons isolados. Além disso, pode-se observar que o aumento do número de moléculas de água nos sistemas contendo água não causou alterações relevantes.

Palavras-chave: DES; água; Estanho; Índio; DM; TQAEM.

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LIST OF ABBREVIATIONS AND ACRONYMS

BCP	Bond Critical Point
B3LYP	Becke-3-Parameter-Lee-Yang-Parr
CCN	Cumulative Coordination Number
ChCl	Choline Chloride
CHELPG	CHarges from ELectrostatic Potentials using a Grid based method
DESs	Deep Eutectic Solvents
DFT	Density Functional Theory
DSC	Differential Scanning Calorimetry
EG	Ethylene Glycol
ELF	Electron Localization Function
GROMACS	GROningen MAchine for Chemical Simulations
HBA	Hydrogen Bond Acceptor
HBD	Hydrogen Bond Donor
ILs	Ionic Liquids
ITO	Indium Tin Oxide
LANL2DZ	Los Alamos National Laboratory 2-double-z
LED	Light Emitting Diode
MD	Molecular Dynamics
M06-2X	Minnesota Functionals, 06 family
NVT	Canonical ensemble
NPT	Isothermal-Isobaric ensemble
OPLS-AA	Optimized Potentials for Liquid Simulations – All Atom
PVC	PolyVinyl Chloride
QTAIM	Quantum Theory of Atoms in Molecules
RDF	Radial Distribution Function
SDF	Spatial Distribution Function
U	Urea
VOCs	Volatile Organic Compounds

SUMMARY

1 INTRODUCTION

Deep Eutectic Solvents (DES) are a class of compounds formed by the junction between a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) species and, as its eutectic name suggests, a DES is a species that has a lower melting point than the melting points of the species through which it was formed in a phase diagram (MIGLIORATI, 2019). Usually, the HBA used as Lewis acid is quaternary ammonium, sulfonic or phosphonic salt of the $Cat^{+}X^{-}$ type, and the Lewis base HBD is, commonly, an electrically neutral molecule and acts as a chelating agent, which here we will denote by Y. Therefore, a DES can be expressed as follows:

$$Cat^{+}X^{-}zY$$

Where $Cat^{+}\ e\ X^{-}$ represents, respectively, the cation (sulfonic, phosphonic or ammonium) and the anion (halide, nitrate, acetate etc.) of the salt acting as HBA. Also, z is the number of Y species that act as HBD.

The DES terminology emerged with the work of Abbott et al., who observed that the resulting product between choline chloride (ChCl, $T_f^{ChCl} = 302\ °C$) and urea (U, $T_f^{U} = 133\ °C$) in a 1:2 ratio (1ChCl:2U, $T_f^{DES} = 12\ °C$) resulted in a mixture with a melting point lower than the melting points of the species when analyzed separately, where T_f^{ChCl}, T_f^{U} and T_f^{DES} represent the melting temperatures of the pure substances and the eutectic mixture, respectively (ABBOTT, 2003; HANSEN *et al.*, 2021).

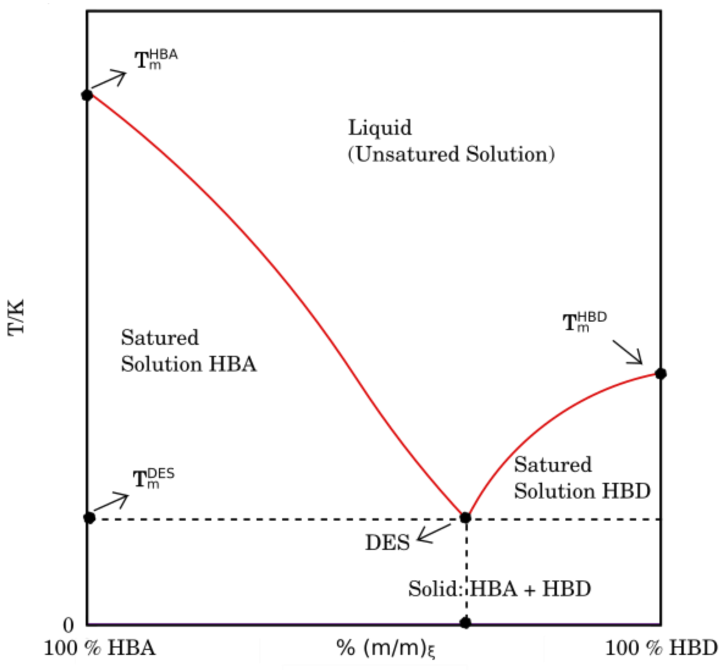
Therefore, if T_f^{HBD} and T_f^{HBA} are the melting temperatures of HBD and HBA, respectively, and T_f^{DES} is the melting temperature of DES formatted by HBA and HBD, then the following inequality is valid:

$$T_f^{DES} < T_f^{\xi}$$

Where ξ denotes the HBA or HBD.

As we can see in the image below, which is a generic phase diagram for the formation of a DES given by the junction between an HBA and an HBD, the formation of DES is characterized by the lowering of the melting temperature of the eutectic mixture, which has a temperature melting temperature lower than the melting temperature of the species through which it was formed. On the ordinate axis, we have the temperature in Kelvin and on the abscissa axis, we have the mass-mass percentage of the species ξ, which symbolizes the HBA or HBD. To obtain the temperature of the DES as a function of the composition and, therefore, of the freezing point, the Differential Scanning Calorimetry (DSC) method is efficient (MORRISON; SUN; NEERVANNAN, 2009).

Phase diagram for a generic DES.



Source: author.

According to Hansen (2021), DES can be categorized as a class of ionic liquids (ILs). This is because they have several similar properties, including high thermal stability, low volatility, low vapor pressure and adjustable polarity. Therefore, such compounds can be a promising alternative to replace Volatile Organic Compounds (VOCs). In addition, DES has some advantages over ILs, such as low price, biodegradability, non-toxicity, adaptable viscosity, high purity, they are ecologically benign and are easy to prepare (DURAND; LECOMTE; VILLENEUVE, 2013; UMAR *et al.*, 2020).

In the present work, choline chloride (ChCl) was used as HBA and ethylene glycol (EG) as HBD because choline is easily accessible, cheap, non-toxic, produced on a large scale, and shown to be environmentally friendly. In addition, choline is one of the B vitamins. Furthermore, it is associated with the formation of acetylcholine, an important neurotransmitter being essential in brain activities and has fundamental importance to the liver. Therefore, the importance of choline for the pharmaceutical and food industries, as well as for science, is indisputable. Regarding the EG, it is easily accessible, as it is widely used in the automotive industry as an antifreeze. It also has several industrial applications in cooling and heating systems and is applied to obtain polyester fibers, thus proving easy obtainment for desired purposes (HANSEN, 2021; RIZWAN-UL-HAQ *et al.*, 2016; ZEISEL, 2012).

As mentioned above, it is pretty clear why we use a DES based on ChCl and EG, given the ease of obtaining such species and the importance of the DES formed by the resulting mixture. In addition to the properties mentioned above, we can highlight the applications of DESs in organic synthesis, biosensors, electrochemistry, nanotechnology, biodiesel transformations and biocatalysis. Furthermore, due to their low toxicity and high biodegradability, most DESs are indispensable for green chemistry (SVIGELJ, 2021; ZHANG et al., 2012; GARCÍA *et al.*, 2015).

In addition to the applications mentioned above, the catalytic activity of DESs has also been known; its vast ability to dissolve a variety of compounds, such as salts, proteins, amino acids, surfactants, etc.; its use as an extraction agent and as a means of separation, its importance in aromatic hydrocarbons and in species in the gaseous state (removal of polluting gases, as well as deposition of gases in metallic pores of chemical interest), its application in bioactive compounds and metals, among others (DURAND; LECOMTE; VILLENEUVE, 2013; UMAR *et al.*, 2020).

Water is considered the universal solvent since most chemical reactions occur in an aqueous medium, for example, acid/base hydrolysis, formation of halohydrins, reduction of carbonyl compounds, oxidation of alkenes/alkynes, etc. Furthermore, this molecule is also environmentally favorable, as it is considered the cleanest solvent in the world and the most abundant, causing profound environmental, economic, and social implications (VOLHARDT and SCHORE, 2004; WEI, 2004).

The metals indium (In) and tin (Sn) have atomic numbers 49 and 50, respectively, and are thus found in the boron group (group 13) and the carbon group (group 14). Both species present singlet multiplicity in the 3+ oxidation states for In and 2+ for Sn. Due to their high scientific, technological and industrial importance, studying these metals in isolation and the form of a mixture is crucial.

In was discovered in 1863 by F. Reich and H. T. Richter in Germany in the laboratories of the Academy of Mines in Freiberg. Due to its applications in innovative technologies, In has attracted academic, governmental and industrial research, as it has high importance in the global technological and economic scenario. Among the chemical properties of this metal, we can highlight malleability, plasticity, ductility, semiconductivity and transparency. Due to these characteristics, In can be applied in solar panels, electroluminescent lamps (LED), indium tin oxide (ITO) thin films, semiconductors, electrodeposition, manufacturing of TV and cell phone screens, metal alloys, coating of surfaces of welding, among others (MONTEIRO *et al.*, 2019; CHUNG and LEE, 2012).

Sn is a polymorphic metal used, mainly for the manufacture of bronze (an alloy of copper and tin) and other metallic alloys, coating of steel sheets, as well as in the manufacture of containers used to store food, as well as in processes of welding, as it has a low melting point. Other applications include coating glass with SnO_2, dental fluoridation with SnF_2, biocidal agents, manufacturing antifouling paints, catalysis, manufacturing cellular panels, computers, electroplating and touch televisions. In addition, there are organotin materials, which emerged in 1849 with the work of Sir E. Frankland, who, through his research on diethylzinc, ended up producing diethyl tin diiodide ($SnEt_2I_2$). Among the main applications of organostannics, we can highlight stabilizers of polyvinyl chloride (PVC) polymer, production of polyurethanes, vulcanization of silicones, preservation of wood and paper, control of bacteria and fungi, as well as in medical applications and organic synthesis (FILGUEIRAS, 1998; LIMA, 2019; WALSH and LOW, 2016).

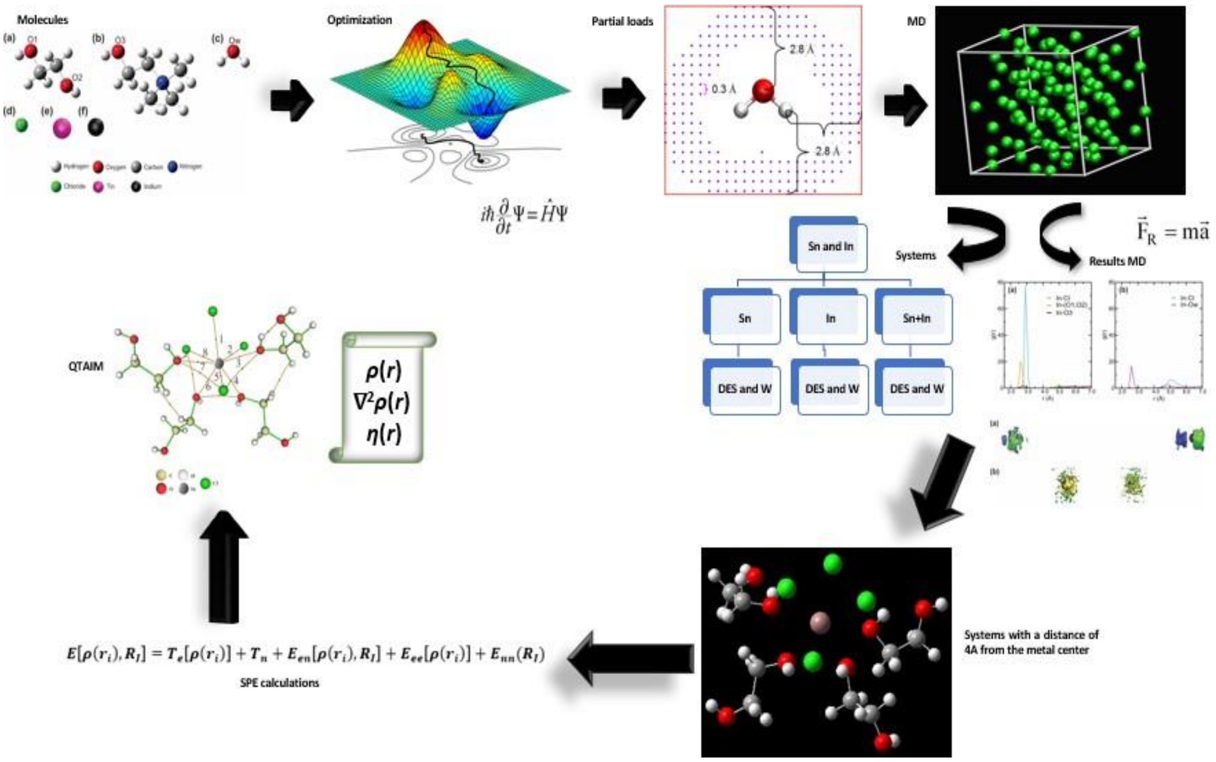
Materials based on InSn (In + Sn) alloys have several applications: nanodevices, nanosensors, nanothermometers, protectors, welding, electronics industry, CO_2 reduction; they are worn resistant and suitable anti-friction agents, in addition to having good physical-mechanics characteristics (ANICAI *et al.*, 2019; JEONG and YEO, 2012; MEDVEDEV, RYBIN and MAKRUSHIN, 2012).

Therefore, the present work aims to theoretically study the behavior of these species (Sn^{2+} and In^{3+}) in DES and water, either alone or in the form of a mixture, using classical methods and quantum-mechanical methods. Classically, the study was carried out through Molecular Dynamics (MD) and, quantumly, through the Quantum Theory of Atoms in Molecules (QTAIM).

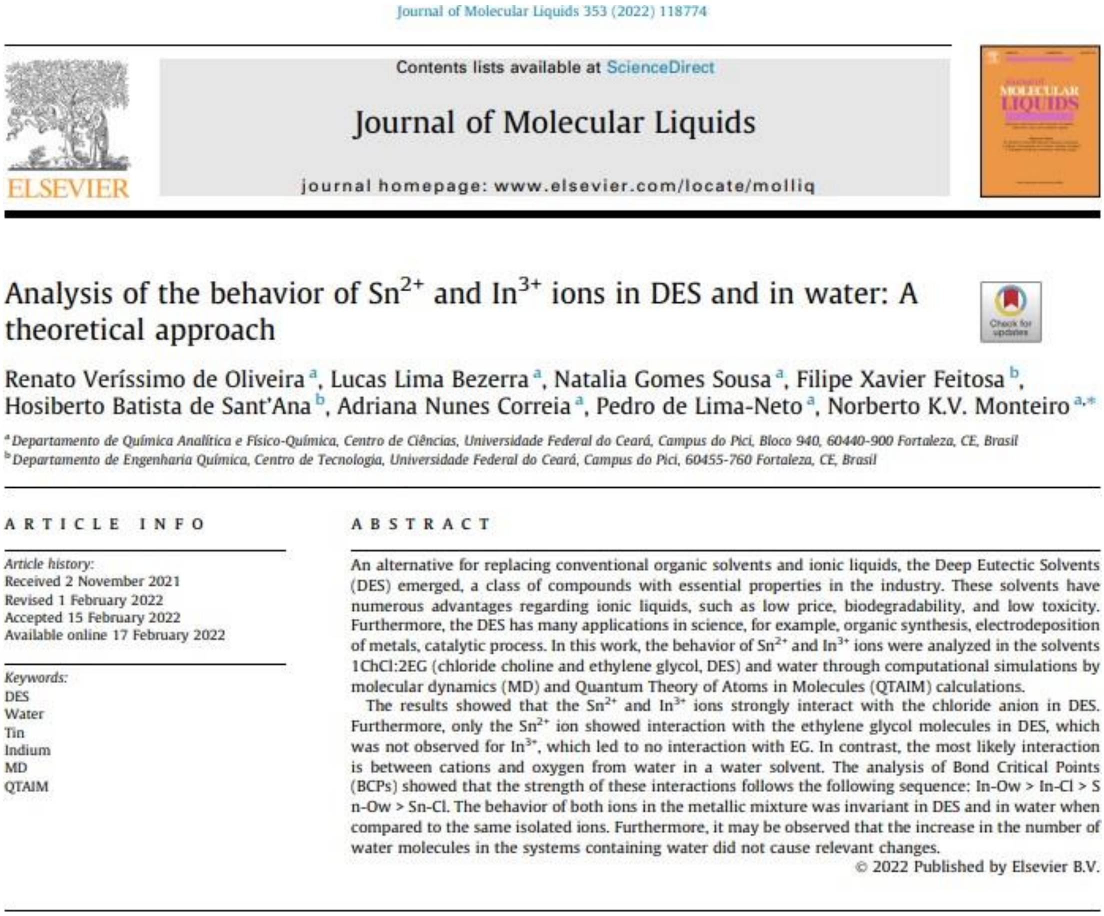
The theoretical approach will analyze the main interactions, which will occur as follows: Radial Distribution Function (RDF or $g(r)$) multiplied by the numerical density of observed atoms ($g(r)\rho$) to analyze the main interactions; Spatial Distribution Function (SDF) to observe the distribution of species around the reference center; Cumulative Coordination Number (CCN) to check the average amount of species around the metallic center and Critical Binding Points (BCPs) to analyze the strength of the interaction through electron density ($\rho(r)$) as well as the Location Function of Electrons (ELF or $\eta(r)$) and observe the character of the interaction through the Laplacian of the electron density ($\nabla^2\rho(r)$). The strength of the interaction and its nature will be studied in a quantum way, while the other analyzes will be carried out classically.

Chapter 1

ANALYSIS OF THE BEHAVIOR OF Sn^{2+} AND In^{3+} IONS IN DES AND IN WATER: A THEORETICAL APPROACH



Computational simulations performed by molecular dynamics (MD) and quantum methods (QTAIM) to analyze the behavior of Sn^{2+} and In^{3+} ions (alone and in the mixture) in deep eutectic solvent (DES) and in water.



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Analysis of the behavior of Sn^{2+} and In^{3+} ions in DES and in water: A theoretical approach

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ABSTRACT

An alternative for replacing conventional organic solvents and ionic liquids, the Deep Eutectic Solvents (DES) emerged, a class of compounds with essential properties in the industry. These solvents have numerous advantages regarding ionic liquids, such as low price, biodegradability, and low toxicity. Furthermore, the DES has many applications in science, for example, organic synthesis, electrodeposition of metals, catalytic process. In this work, the behavior of Sn^{2+} and In^{3+} ions were analyzed in the solvents 1ChCl:2EG (chloride choline and ethylene glycol, DES) and water through computational simulations by molecular dynamics (MD) and Quantum Theory of Atoms in Molecules (QTAIM) calculations.

The results showed that the Sn^{2+} and In^{3+} ions strongly interact with the chloride anion in DES. Furthermore, only the Sn^{2+} ion showed interaction with the ethylene glycol molecules in DES, which was not observed for In^{3+}, which led to no interaction with EG. In contrast, the most likely interaction is between cations and oxygen from water in a water solvent. The analysis of Bond Critical Points (BCPs) showed that the strength of these interactions follows the following sequence: In-Ow > In-Cl > S n-Ow > Sn-Cl. The behavior of both ions in the metallic mixture was invariant in DES and in water when compared to the same isolated ions. Furthermore, it may be observed that the increase in the number of water molecules in the systems containing water did not cause relevant changes.

RESUMO

Uma alternativa para substituir solventes orgânicos convencionais e líquidos iônicos são os solventes eutéticos profundos (DES), uma classe de compostos com propriedades essenciais na indústria. Esses solventes apresentam inúmeras vantagens em relação aos líquidos iônicos, como baixo preço, biodegradabilidade e baixa toxicidade. Além disso, os DES tem muitas aplicações na ciência, por exemplo, síntese orgânica, eletrodeposição de metais, processo catalítico. Neste trabalho, o comportamento dos íons Sn^{2+} e In^{3+} foi analisado nos solventes 1ChCl:2EG (cloreto de colina e etilenoglicol, DES) e água através de simulações computacionais por dinâmica molecular (MD) e cálculos da Teoria Quântica de Átomos em Moléculas (QTAIM). Os resultados mostraram que os íons Sn^{2+} e In^{3+} interagem fortemente com o ânion cloreto no DES. Além disso, apenas o íon Sn^{2+} apresentou interação com as moléculas de etilenoglicol no DES, o que não foi observado para o In^{3+}, pois este não apresentou interação com o EG. Em contraste, a interação mais provável é entre cátions e oxigênio da água em solvente água. A análise dos Pontos Críticos de Ligação (BCPs) mostrou que a força dessas interações segue a seguinte sequência: In-Ow > In-Cl > Sn-Ow > Sn-Cl. O comportamento de ambos os íons na mistura metálica foi invariante em DES e em água quando comparados aos mesmos íons isolados. Além disso, pode-se observar que o aumento do número de moléculas de água nos sistemas contendo água não causou alterações relevantes.

Palavras-chave: DES, Água, Estanho, Índio, MD, QTAIM..

ABSTRACT

An alternative for replacing conventional organic solvents and ionic liquids, the Deep Eutectic Solvents (DES) emerged, a class of compounds with essential properties in the industry. These solvents have numerous advantages regarding ionic liquids, such as low price, biodegradability, and low toxicity. Furthermore, the DES has many applications in science, for example, organic synthesis, electrodeposition of metals, catalytic process. In this work, the behavior of Sn^{2+} and In^{3+} ions were analyzed in the solvents 1ChCl:2EG (chloride choline and ethylene glycol, DES) and water through computational simulations by molecular dynamics (MD) and Quantum Theory of Atoms in Molecules (QTAIM) calculations. The results showed that the Sn^{2+} and In^{3+} ions strongly interact with the chloride anion in DES. Furthermore, only the Sn^{2+} ion showed interaction with the ethylene glycol molecules in DES, which was not observed for In^{3+}, which led to no interaction with EG. In contrast, the most likely interaction is between cations and oxygen from water in a water solvent. The analysis of Bond Critical Points (BCPs) showed that the strength of these interactions follows the following sequence: In-Ow > In-Cl > Sn-Ow > Sn-Cl. The behavior of both ions in the metallic mixture was invariant in DES and in water when compared to the same isolated ions. Furthermore, it may be observed that the increase in the number of water molecules in the systems containing water did not cause relevant changes.

Keywords: DES, Water, Tin, Indium, MD, QTAIM.

1 Introduction

Deep Eutectic Solvents (DES) are mixtures with a lower melting point than isolated components [1]. These solvents are formed by compounds that act as HBA (hydrogen-bond acceptor), usually a quaternary ammonium salt [2], with an HBD (hydrogen-bond donor), usually amines, carboxylic acids, alcohols, polyols, or carbohydrates [3]. DES are considered a new class of ionic liquids (ILs) or their ILs analogs [4].

The main advantages of DES are their high purity, low volatility, and high thermal stability [5]. In addition to these advantages, eutectic solvents have physicochemical properties similar to ILs and advantages over ionic liquid, including Non-toxicity, cheap, easy access, and simple preparation [6], due to hydrogen bond interactions in the right ratio molar [7].

Water is considered the cleanest solvent available and has the least impact on the environment [8]. Moreover, Diels-Alder reactions may be accelerated using water as a solvent instead of organic solvents [9]. Water is also used in the reactions of carbonyl compounds and imines with allyl halides, using indium, tin, and zinc as metallic mediators [9]. The reasons for using this solvent were the applications and the absence of papers describing the behavior of tin and indium ions present in water as a solvent.

The metals tin and indium were chosen for this study due to their various applications in society. Organotin compounds are used as polyvinyl chloride (PVC) stabilizers, industrial biocides, industrial catalysts, surface curing agents [10-13]. The Indium Tin Oxide (ITO) is the material most used in the construction of optoelectronics [14], while the metal indium is used in the manufacture of germanium rectifiers, photoconductors, and thermistors [15].

To understand at the atomic level the behavior of the species of interest (Sn^{2+} and In^{3+} ions) in DES and water, a possible approach is to perform computational simulations using classical mechanics from molecular dynamics (MD) [16], followed by quantum mechanics, through the Bader's Quantum Theory of Atoms in Molecules (QTAIM) [17-19].

The work carried out by V. Migliorati *et al.* on solubilization properties of Hg^{2+} in chloride-based DES showed that the main interaction occurs between the Hg^{2+} cation with the Cl^- anion, in addition to demonstrating that the first solvation layer around the metallic center is due to the presence of chloride, regardless of the applied DES [20]. Therefore, the work mentioned above brings us two fundamental pieces of information for the present study, namely: high coordination capacity of the Cl^- anion (to Hg^{2+}), which constitutes the first solvation layer, and, in addition, the strong interaction between the cation metallic and Cl^-, which even interacts more strongly than the HBD that constitutes the analyzed DES.

In this paper, this study aims to analyze through an approach theoretical the behavior of Sn^{2+} and In^{3+} ions, isolated and in the form of a mixture, in two solvents (DES and water). The theoretical approach will analyze the main interactions, spatial distribution, and bond critical points (BCPs) between the species of interest and the systems components.

2. Computational details

2.1. Optimization of structures and obtaining partial charges

The components (ethylene glycol, choline, and water) shown in Fig. 1 were optimized through Density Functional Theory (DFT) [21-23] using the hybrid functional B3LYP [24-27] and the base set 6-311G+(d,p) [28], from the GAUSSIAN 09 package [29]. Subsequently, the Multiwfn 3.8 *software* [30] was used for obtained the partial charges through of CHELPG method [31] for ethylene glycol ions, and choline ions, and water molecules.

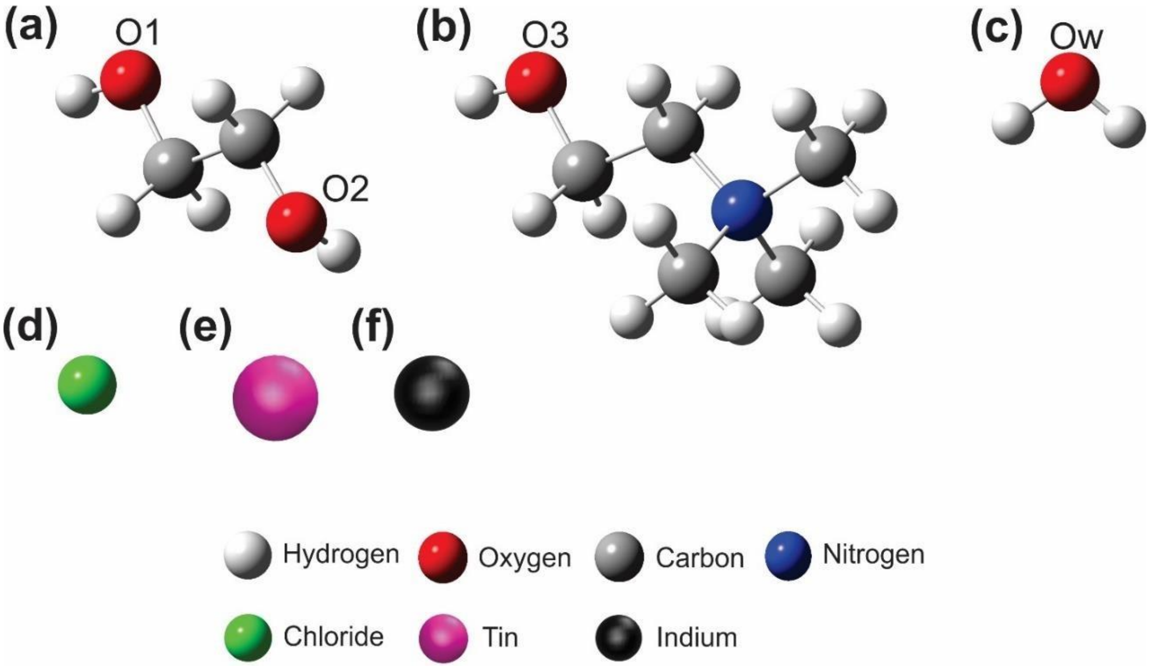

Fig. 1 Geometry of the optimized molecules that were used in MD simulations, (a) ethylene glycol, (b) choline, (c) water, (d) chloride, (e) tin, and (f) indium.

2.2. Molecular dynamics (MD) simulations

The GROMACS (GROningen MAchine for Chemical Simulations) 2019.2 *software* package [32] was used to perform all MD simulations. Nine boxes simulations were created with the cubic format, with dimensions of 8 nm × 8 nm × 8 nm for the systems described in Table 1. These dimensions were used because the volume obtained is sufficient to contain all the ions and molecules of the system and, in addition, larger dimensions would lead to a longer calculation time. OPLSS-AA [33] was the force field used to characterize the simulated systems. However, the partial charges used for the ethylene glycol ions, choline ions, and water molecules were obtained by the CHELPG method [31].

The quantities of each species entered in the simulation box were kept aiming at the systems electroneutrality. In DES, the ratio of EG:Ch followed the balance 2:1 (800:400), and the number of chlorides added in each system will depend on the number of positive charges in the system. As EG is a neutral molecule (EG^0) and choline have a positive unit charge (Ch^{+1}), so to maintain the electroneutrality of a generic metallic cation system (M^{m+}), we need to perform the following procedure:

$$N_{Ch}\ (+1)\ +\ N_{M}\ (m+) = N_{Cl}\ (-1)$$

Where N_{Ch}, N_M and N_{Cl} are the amount of choline, metal and chloride species, respectively. Furthermore, it is worth noting that in an MD, it is necessary to work with thousands of atoms, as this type of calculation is based on statistical mechanics. Therefore, hence the reason to use all these molecules, since the mass of the system will be considerable and the quantum effects may be neglected [16].

In the system containing water, the behavior of Sn^{2+} and In^{3+} ions in two different amounts of water was studied to analyze what would happen with the behavior of these metals when the amount of water in the solution was increased.

Table 1 Components and their respective quantities that were used in each system**.**

Systems		
$SnCl_2$ with 1ChCl:2EG / SnDES	**$InCl_3$ with 1ChCl:2EG / InDES**	**$SnCl_2$ and $InCl_3$ with 1ChCl:2EG / InSnDES**
Ethylene glycol (800)	Ethylene glycol (800)	Ethylene glycol (800)
Choline (400)	Choline (400)	Choline (400)
Tin (9)	Indium (9)	Tin (9)
Chloride (418)	Chloride (427)	Indium (9)
		Chloride (445)
$SnCl_2$ with H_2O / SnW1200	**$InCl_3$ with H_2O / InW1200**	**$SnCl_2$ and $InCl_3$ with H_2O / InSnW1200**
Tin (9)	Indium (9)	Tin (9)
Chloride (18)	Chloride (27)	Indium (9)
Water (1200)	Water (1200)	Chloride (45)
		Water (1200)
$SnCl_2$ with H_2O / SnW5580	**$InCl_3$ with H_2O / InW5580**	**$SnCl_2$ and $InCl_3$ with H_2O / InSnW5580**
Tin (9)	Indium (9)	Tin (9)

Chloride (18)	Chloride (27)	Indium (9)
Water (5580)	Water (5580)	Chloride (45)
		Water (5580)

SnDES, InDES and InSnDES represent the Sn, In, and (In + Sn) systems in the eutectic solvent, respectively. SnW1200, InW1200, and InSnW1200 represent the Sn, In, and (In + Sn) systems in 1200 molecules of water, respectively. SnW5580, InW5580, and InSnW5580 represent the Sn, In, and (In + Sn) systems in 5580 water molecules, respectively.

In the minimization step, the steepest descent algorithm [34] was used to optimize the geometries of the systems, with an energy tolerance of 10 kJ mol^{-1} nm^{-1}, 10^{-4} step size, and 100000 for the number of steps. Subsequently, the equilibrium step was performed in 10 ns and divided into two parts. The first one utilized the canonical ensemble (NVT) through the V-rescale method [35] with a temperature of 298 K. The isothermal-isobaric ensemble (NPT) used the Parrinelo-Rahman barostat [36] with 1.0 bar. Finally, the step of MD production was performed for all systems with a time of 500 ns, maintaining the temperature of 298 K and 1.0 bar of pressure, and, in addition, the NPT ensemble was used in this step. The Lennard-Jones parameters used to describe the tin, and indium ions were taken from [37] and [38], respectively.

2.3. Single-point calculations and QTAIM topological properties

After the MD simulations, the equilibrium structures (obtained from the production step) were utilized as starting point for the QTAIM calculations through Multiwfn 3.8 *software* [30], in which in the last frame of the production step obtained in the GROMACS *software*, 4.0 Å spherical cuts were performed in all six systems (SnDES, SnW1200, InDES, InW1200, SnInDES, and SnInW1200), with the metallic cations (Sn^{2+} and In^{3+}) occupying the position (0, 0, 0) in the reference system, solvated by surrounding species (complexes). Then, with the obtained complexes, single-point calculations were performed in the Gaussian 09 package [29] for each complex to get the energy of each system by DFT, since energy is a function of the density, as proposed by the Hohemberg-Kohn theorems. Single-point analyses generated the electron density on Gaussian 09 package [29], with functional M06-2X [39] and basis set LANL2DZ [40] for the Sn^{2+} and In^{3+} ions (where the multiplicities used for both ions was a singlet, as both are d^{10}). In contrast, the basis set 6-31+G(d,p) was used for the atoms C, Cl^-, N, O, and H, respectively. All topological information of electronic density (ρ), Laplacian of electronic density ($\nabla^2\rho$), and Electron Localization Function (ELF, η) were obtained using Multiwfn 3.8 *software* [30].

3. Results and discussion

3.1. Tin in DES and water

3.1.1. SnDES

Fig. 2a shows the Radial Distribution Function (RDF) that uses the density probability [41] of the components present in the SnDES system around the Sn^{2+} ion multiplied by the average number density of observed atoms since it has already been verified that the product $g(r)\rho$ is more suitable when analyzing interactions between different species and that the comparison between only $g(r)$'s can generate misinterpretations [42]. Furthermore, in Fig. 2b, we have the graph for the Cumulative Coordination Number (CCN) of species around the reference center (Sn^{2+}), obtained by integrating the radial distribution function of pairs, the $g(r)$. In the SnDES system (Fig. 2a), the main interaction was between the Sn^{2+} with chloride anion around 2.8 Å and, according to Fig. 2b, we have, on average, 4.2 chlorides complexing Sn^{2+}. This high value of $g(r)\rho$ for this interaction is explained because these ions have oppositely charged and, consequently, a strong electrostatic attraction. The second strongest interaction was Sn-(O1,O2) (Sn^{2+} with the oxygens of ethylene glycol) around 2.4 Å and, according to Fig. 2b, we have, on average, 1.9 ethylene glycol complexing Sn^{2+}. The specie of interest (Sn^{2+}) showed the lowest value of $g(r)\rho$ with oxygen choline (O3), then this interaction will not be discussed. Therefore, we may observe that the numerical density of chlorides around the divalent tin cation has the highest value. In addition, ethylene glycol interacts relatively well with Sn^{2+} since its species density around this cation has considerable importance, as we can see from figures 2a and 2b.

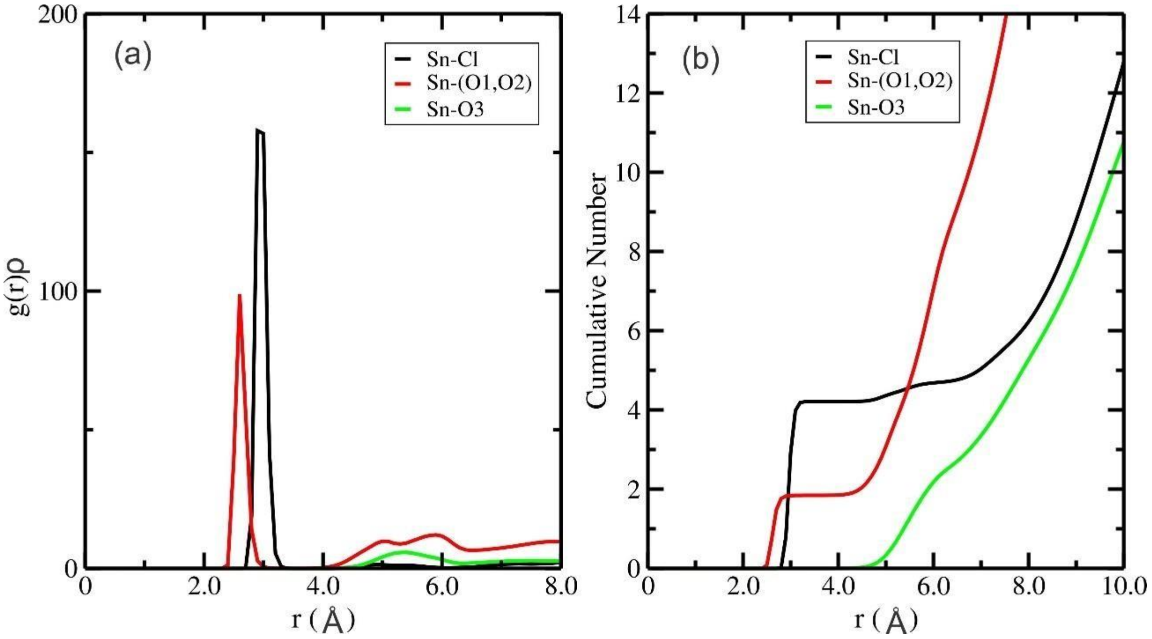

Fig. 2 (a) Radial Distribution Function (RDF or *g*(*r*)) multiplied by the average number density (*ρ*) of the atoms observed around Sn^{2+} ions in the SnDES system, and (b) the cumulative number of counter-ions obtained by integrating *g*(*r*) for this system.

3.1.2 SnW1200 and SnW5580

In the SnW1200, and SnW5580 systems (Fig. 3), the only significant interactions occurred between Sn-Ow (Sn^{2+} with the oxygen atom of water, either with 1200 or 5580 water molecules) around 2.4 Å. According to Fig. 3a, it is possible to observe that the increase in the number of water molecules did not cause any change in the Sn-Ow interaction since the curves (SnW1200 and SnW5580) are perfectly overwritten. Furthermore, we may see that the Sn-Cl interaction is negligible for these two systems. As there are 1200 (or 5580) water molecules for 18 chloride anions, the probability of interaction between divalent ions and oxygen in water becomes infinitely greater (Sn-Ow). The species of interest in Fig. 3a of SnW1200 and SnW5580 systems showed similar behavior; therefore, the SnW5580 system will not be discussed. As we see in Fig. 3b, there are, on average, approximately 8.9 molecules of water complexing the Sn^{2+} ion. Thus, $g(r)\rho$ and CCN show that the average number density of water molecules around the metal under discussion has a high value.

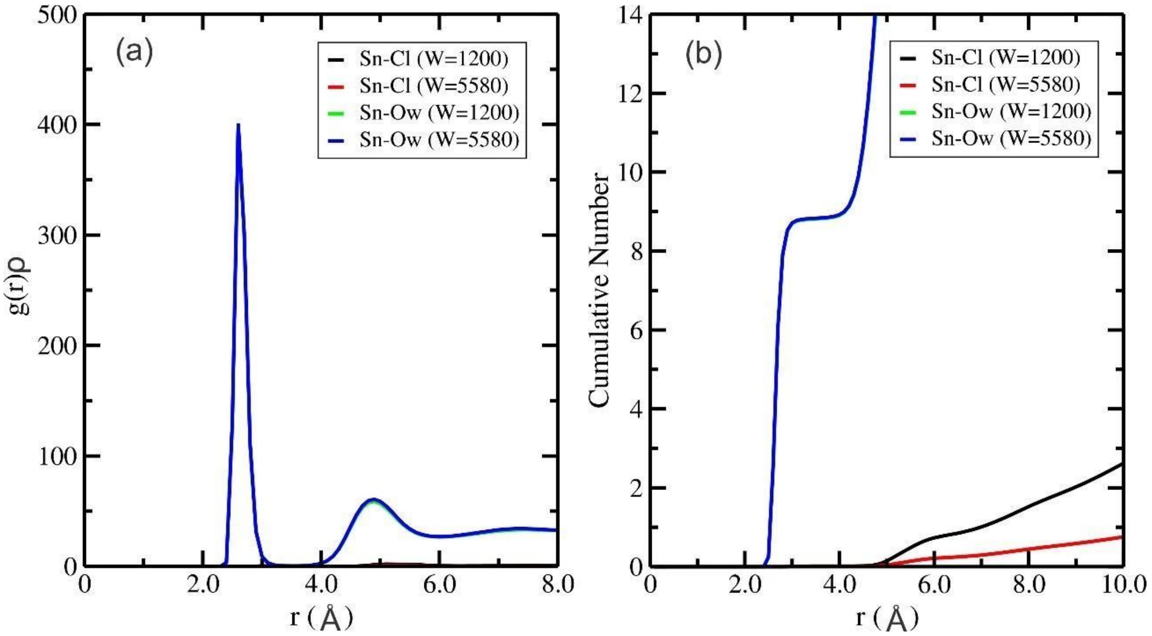

Fig. 3 (a) Radial Distribution Function (RDF or $g(r)$) multiplied by the average number density (ρ) of the atoms observed around Sn^{2+} ions in the SnW (where W=1200 is the system with 1200 water molecules and W=5580 is the system with 5580 water molecules) system and (b) the cumulative number of counter-ions obtained by integrating $g(r)$ for this system.

The Spatial Distribution Function (SDF) shows how the species present in the SnDES and SnW1200 systems are distributed around Sn^{2+} (Figs. 4a and 4b, respectively). In the SnDES system (Fig. 4a), it is possible to observe in the spatial distribution that the probability of interaction Sn-Cl is higher because such species have opposite charges, as explained previously in the topic about RDF (Fig. 2a). We may see in SDF, a larger volume of chloride anions occupy the space around Sn^{2+}, thus confirming the more significant result of $g(r)\rho$ for the Sn-Cl interaction. The second most likely interaction will be Sn-(O1,O2), which has a considerable value of $g(r)\rho$, which may be easily justified by the higher quantity of donor atoms in EG (2 O's) than in Choline (1O). In the SnW1200 system (Fig. 4b), the SDF showed that the Sn^{2+} ions preference to interact with water molecules than the chloride anion, this is explained due to the number of water molecules overcoming the number of chloride anions, as described in the topic above about *g*(*r*)*ρ*.

Thus, it may be observed that the distribution of species in the SnDES System (Fig. 4a) around the Sn^{2+} ion is mainly due to the presence of Cl^-, followed by ethylene glycol molecules in smaller amounts. On the other hand, for the SnW1200 system (Fig. 4b), the ion is coordinated solely by water molecules. Therefore, the SDF analysis for choline (in the SnDES system) will not be performed, as this interaction proved negligible. Similarly, the SDF analysis for the SnW5580 system will not be performed, as the behavior was similar to the SnW1200 system.

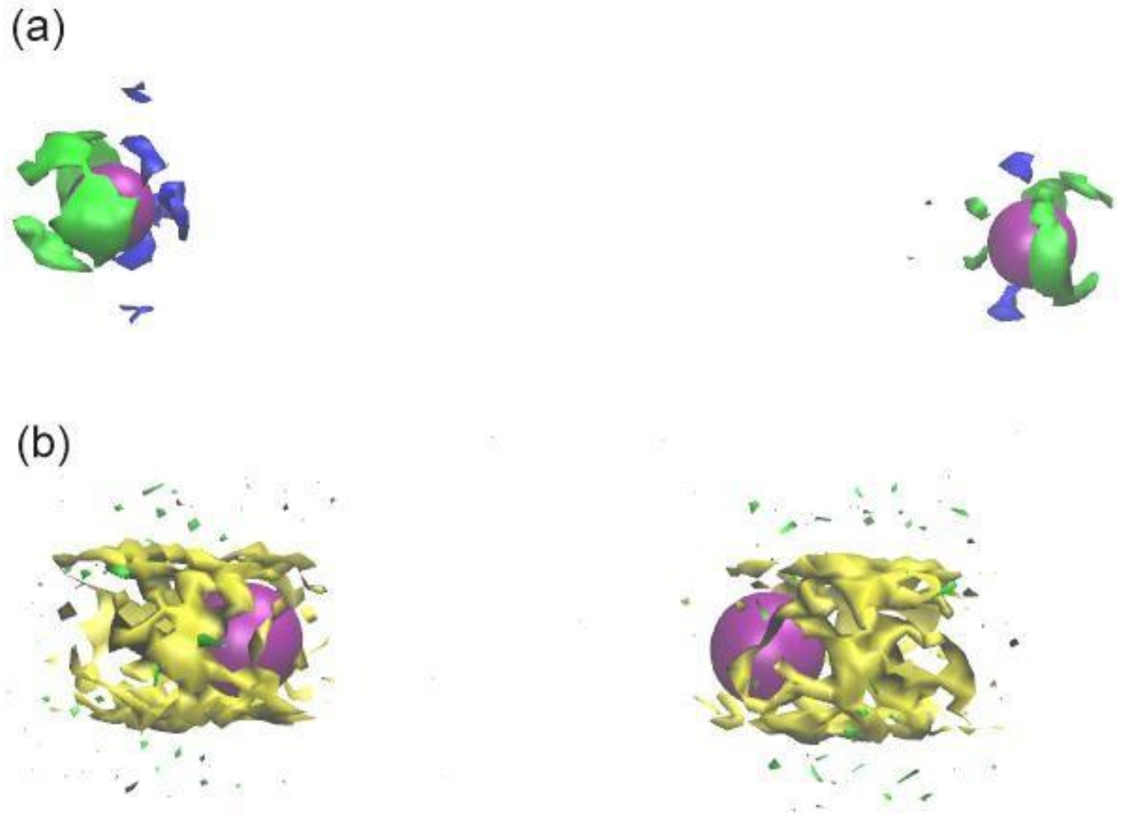

Fig. 4 Spatial Distribution Function (SDF) between Sn^{2+} ion with atoms presents in the system (a) SnDES, and, (b) SnW1200. Sn^{2+} (purple); Chloride (green); Ethylene glycol (blue); Water (yellow). Isovalue using for the system (a) Chloride: 0.00552; Ethylene glycol: 0.011173; (b) Chloride: 0.00029; Water: 0.015377.

Table 2 contains the topological data of selected bond critical points for Sn^{2+} ions on SnDES and SnW1200 systems. The topological data analyzed were electronic density, $\rho(r)$, the Laplacian of the electronic density, $\nabla^2\rho(r)$, and the Electron Localization Function (ELF), $\eta(r)$. For the Sn-Cl interaction and considering the summation of all values of $\rho(r)$ and $\eta(r)$, then: $\Sigma\rho(r)$=1.04E-01 and $\Sigma\eta(r)$=9.14E-01. Similarly, for the Sn-(O1,O2) interaction, it was determined: $\Sigma\rho(r)$=5.87E-02 and $\Sigma\eta(r)$=2.94E-01. Whereas for Sn-Ow interaction, the sum of all $\rho(r)$ and $\eta(r)$ were $\Sigma\rho(r)$=2.43E-01 and $\Sigma\eta(r)$ =1.33E+00, respectively. Therefore, the BCP analysis indicated that the Sn^{2+} and Cl^- ions present greater interaction strength than the Sn-(O1,O2) interaction. However, Sn^{2+} ions showed the highest BCPs with water molecules in the SnW1200 system. Furthermore, it is observed that the strength of the Sn-Ow interaction in the SnW1200 system exceeds the strength of the Sn-Cl interaction in the SnDES system. Therefore, the Sn-Ow interaction is more favorable. As the Laplacian electron density ($\nabla^2\rho(r)$) has a positive value, the graphic concavity ($\rho(r)$ vs. r) is positive, and therefore the curve has a minimum value. Then, it is possible to conclude that the electron density in the BCP is small, so that this density is located in the attractors, characterizing intra or intermolecular interactions [43-44]. Molecular plots with binding pathways and BCPs are illustrated in Fig. 5a for Sn-Cl and Sn-(O1,O2) interactions of the SnDES system, while Sn-Ow interactions are depicted for Fig. 5b of the SnW1200 system.

Table 2 Topological data between the Sn^{2+} ions with SnDES and SnW1200 systems. ELF value, $\eta(r)$, electron density, $\rho(r)$ and Laplacian of electron density, $\nabla^2\rho(r)$ at a bond critical point (BCP) of selected Sn-Cl, Sn-(O1,O2), and Sn-Ow interactions.

Interaction	**BCP**	$\boldsymbol{\rho(r)}$	$\boldsymbol{\nabla^2\rho(r)}$	$\boldsymbol{\eta(r)}$	**System**
Sn-Cl	P_3	2.31E-02	5.02E-02	2.11E-01	SnDES
	P_4	1.94E-02	4.59E-02	1.46E-01	
	P_5	3.38E-02	7.32E-02	3.24E-01	
	P_6	2.78E-02	6.24E-02	2.33E-01	
$\sum$	4	1.04E-01		9.14E-01	
Sn-(O1,O2)	P_1	2.70E-02	7.61E-02	1.35E-01	
	P_2	3.17E-02	9.39E-02	1.59E-01	
$\sum$	2	5.87E-02		2.94E-01	
Sn-Ow	P_1	2.69E-02	7.23E-02	1.60E-01	SnW1200
	P_2	3.11E-02	9.34E-02	1.70E-01	
	P_3	2.53E-02	7.29E-02	1.39E-01	
	P_4	2.34E-02	6.40E-02	1.25E-01	
	P_5	2.90E-02	8.64E-02	1.57E-01	
	P_6	2.69E-02	7.73E-02	1.41E-01	
	P_7	2.72E-02	7.89E-02	1.46E-01	
	P_8	2.49E-02	6.74E-02	1.41E-01	
	P_9	2.86E-02	8.12E-02	1.54E-01	
$\sum$	9	2.43E-01		1.33E+00	

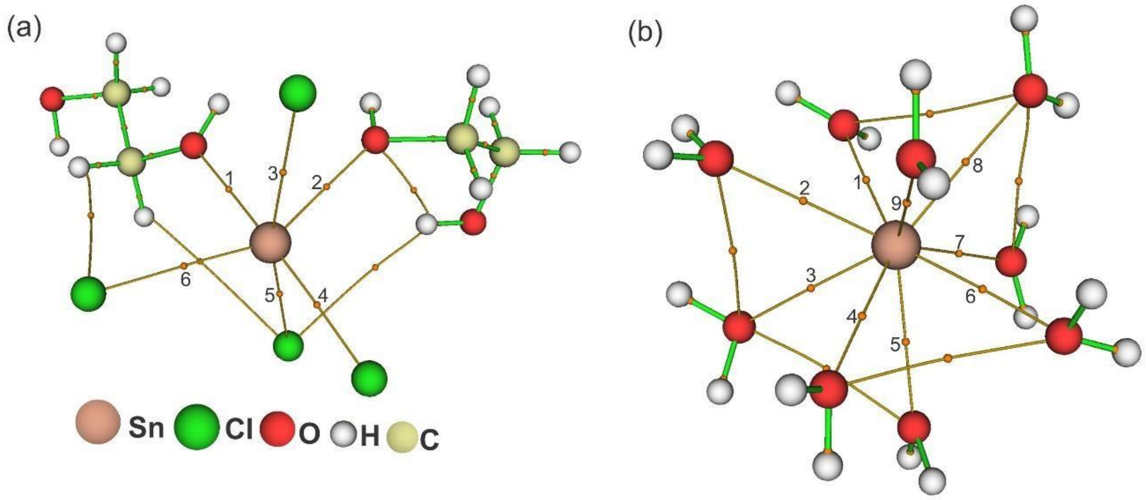

Fig. 5 Molecular graphs with intermolecular interactions and BCP of the Sn^{2+} ion with the system (a) SnDES, and (b) SnW1200.

3.2. Indium in DES and water

3.2.1. InDES

The $g(r)\rho$ results of the InDES system (Fig. 6a) indicate that the main interaction was between In^{3+} ion with Cl^{-} around 2.04 Å. Similar to what happened with the interaction between oppositely charged ions (Sn^{2+} and Cl^{-}) in the SnDES system (Fig. 2a), which has the highest $g(r)\rho$ value, in this case, the explanation is the same. Because they have opposite charges, the In-Cl interaction will occur more efficiently, as it is electrostatically more favorable. Unlike the Sn^{2+} ion that interacted relatively well with the ethylene glycol molecule (see topic 3.1.1), the In^{3+} ion practically did not interact with this molecule, as it showed a meager value of $g(r)\rho$. Likewise, the same occurred for the interaction with the choline oxygen (In-O3), which presented a very negligible value of $g(r)\rho$.

According to Fig. 6b, it is possible to observe that there are, on average, approximately 3.9 chloride ions complexing In^{3+}. Therefore, we may conclude from Figs. 6a and 6b that for the InDES system, the only substantial interaction occurs between In^{3+} and Cl^{-}. However, the other interactions (In-(O1,O2) and In-O3) are negligible, as we analyze the graphs of *g*(*r*)*ρ* and CCN.

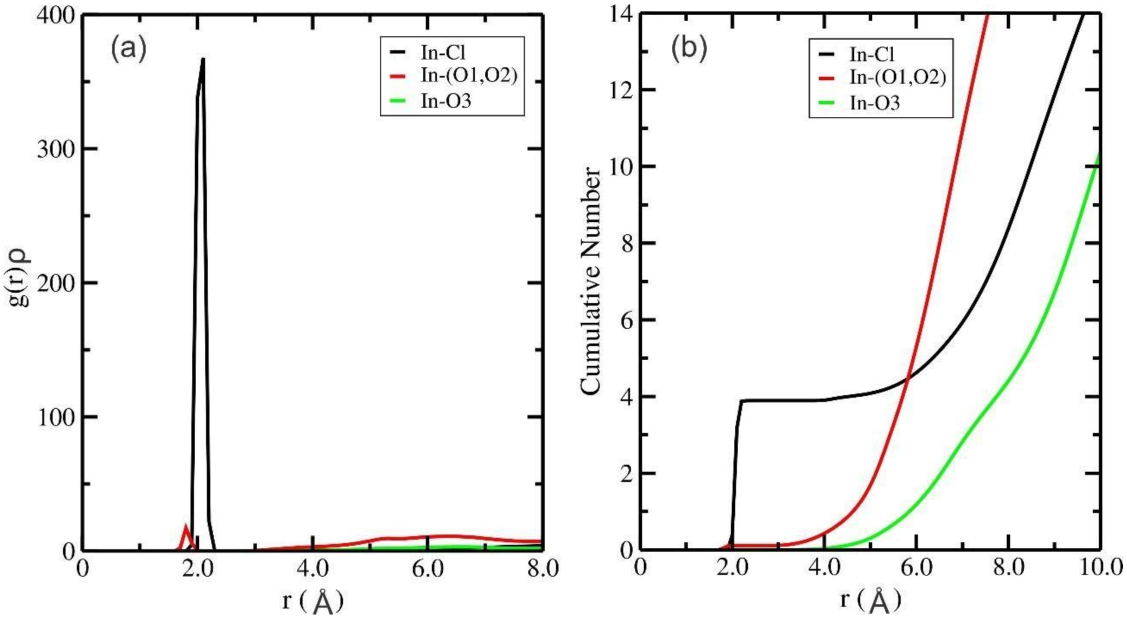

Fig. 6 (a) Radial Distribution Function (RDF or *g*(*r*)) multiplied by the average number density (*ρ*) of the atoms observed around In^{3+} ions in the InDES system, and (b) the cumulative number of counter-ions obtained by integrating *g*(*r*) for this system.

3.2.2. InW1200 and InW5580

Fig. 7a showed the *g*(*r*)*ρ* of In^{3+} ion with InW1200 and InW5580 systems, where interactions in the system with 1200 water molecules are denoted by In-X (W=1200), where X=Cl or X=Ow. Comparatively, the representation is the same for the system with 5580 water molecules, changing only W=1200 by W=5580.

As seen in Fig. 7a, the behavior of In^{3+} when increasing the number of water molecules practically did not change, although there is an increase in *g*(*r*)*ρ* (665 for W=1200 and 818 for W=5580) for the interaction In-Ow. However, the In-Cl interaction presented very low *g*(*r*)*ρ* when compared to the In-Ow interaction. The first solvation layer between the In^{3+} ion and the water oxygen (Ow) started to occur at approximately 1.6 Å. Notably, the similarity concerning the Sn-Ow (Fig. 3) interaction and, consequently, the explanation will be the same. Since there are 1200 (or 5580) water molecules to 27 chloride anions, it is reasonable that the probability of interaction between the trivalent cations In^{3+} and the water oxygen atoms is higher.

As we can see in Fig. 7b (CCN), there are, on average, approximately 5.2 water molecules solvating the In^{3+} ion and 0.69 chlorides interacting with In^{3+} in the system with 1200 water molecules. However, for the system with 5580 water molecules, there are, on average, 5.76 water molecules solvating the In^{3+} ion and 0.26 chlorides interacting with In^{3+}. Therefore, there is a slight substitution of chlorides by water molecules. However, this amount is negligible and will not be considered in the present work. The InW5580 system will not be discussed because the behavior was similar to the InW1200 system.

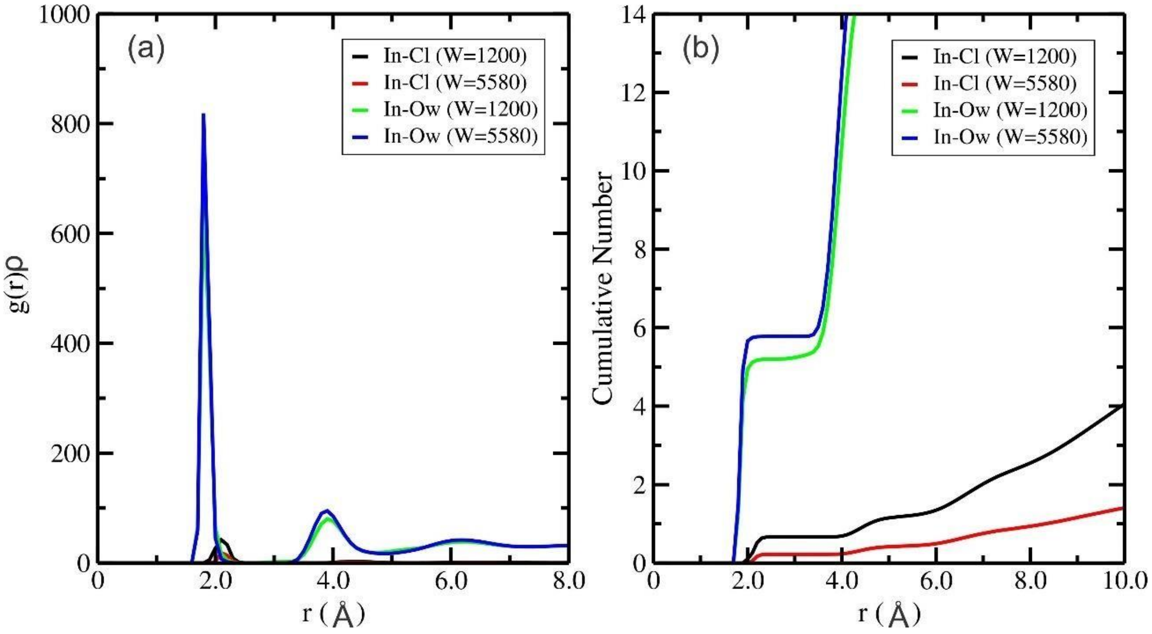

Fig. 7 (a) Radial Distribution Function (RDF or $g(r)$) multiplied by the average numerical density (ρ) of the atoms observed around In^{3+} ions in the SnW (where W=1200 is the system with 1200 water molecules and W=5580 is the system with 5580 water molecules) system, and (b) the cumulative number of counter-ions obtained by integrating $g(r)$ for this system.

Fig. 8 showed the spatial distribution function (SDF) of In^{3+} ion with InDES and InW1200 systems (Figs. 8a and 8b, respectively). As we may see in Fig. 8a, the distribution of Cl^{-} ions around the In^{3+} ion is dominant, so there are practically no ethylene glycol molecules around the metallic center. Confirming the result obtained by $g(r)\rho$ previously, it is possible to observe that in DES, the main interaction occurred between In-Cl. As seen in Fig. 8b (InW1200), in a water solvent, it may note an inversion, where the main interaction occurs between In-Ow followed by In-Cl, because the quantity of water molecules significantly overcomes the number of chloride anions, as aforementioned for the discussion of Fig. 7a. Due to its low value of $g(r)\rho$, the In-O3 interaction will not be discussed in this section. Furthermore, the In-Ow interaction (W=5580) will not be discussed here, as the behavior was shown to be similar to the In-Ow system (W=1200), as discussed above.

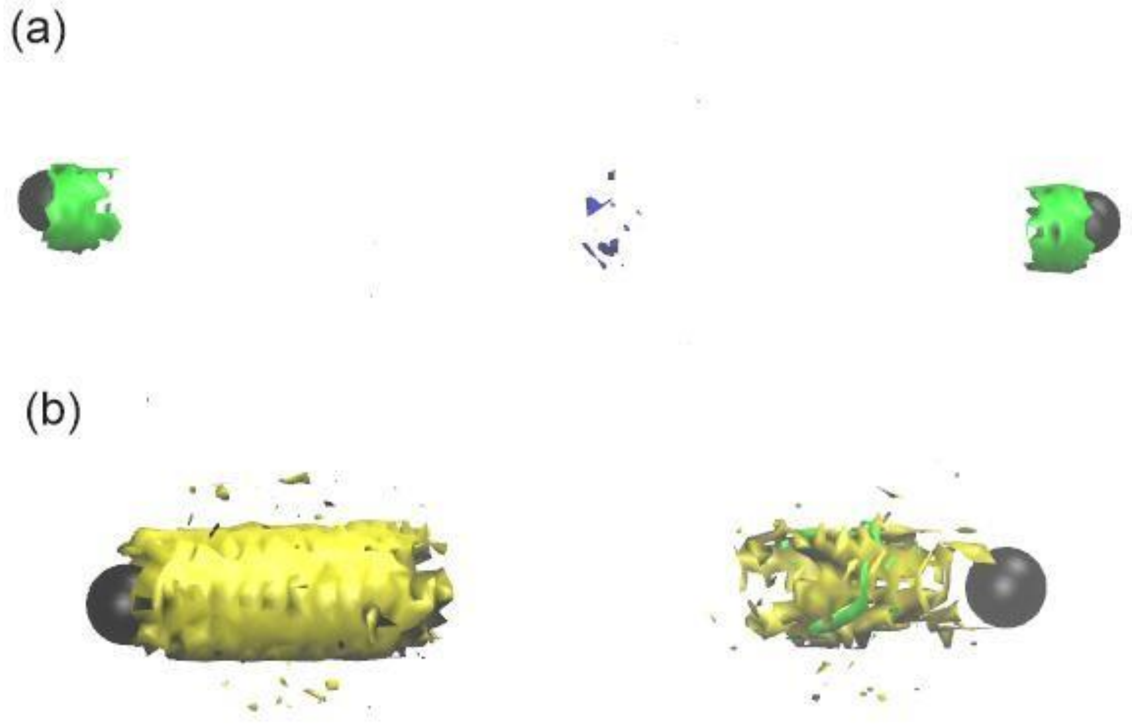

Fig. 8 Spatial Distribution Function (SDF) between the In^{3+} ion with atoms present in the systems (a) InDES and (b) InW1200. In^{3+} (black); Chloride (green); Ethylene glycol (blue); Water (yellow). Isovalue using for the system (a) Chloride: 0.00479; Ethylene glycol: 0.008429; (b) Chloride: 0.001111; Water: 0.014652.

According to Table 3: For the In-Cl interaction, the sum of all $\rho(r)$ and $\eta(r)$ values was obtained: $\Sigma\rho(r)$=5.86E-01 and $\Sigma\eta(r)$=3.45E+00, respectively. Thus, for the InDES system, the In^{3+} ion presented BCPs (4), only with the Cl^- ion. Furthermore, for the In-Ow interaction, the sum of all values of $\rho(r)$ and $\eta(r)$ were $\Sigma\rho(r)$=6.61E-01 and $\Sigma\eta(r)$=3.89E+00, with a total of 5 BCPs. However, for the InW1200 system, a BCP corresponding to the In-Cl interaction was formed, which presents $\rho(r)$=1.38E-01 and $\eta(r)$=8.75E-01. Therefore, the In^{3+} ion had a higher probability (Fig. 9a) of interaction ($\rho(r)$) and a higher ELF value with the chloride anion in DES, thus contributing to a stronger interaction between these species. However, in water solvent, the In-Ow interaction is stronger due to the higher $\Sigma\rho(r)$ and $\Sigma\eta(r)$ value. As $\Sigma\rho(r)$ and ELF for the In-Cl interaction is significant, we can conclude that the electron density of Cl^{-} ions around In^{3+} is pronounced and strong, a result confirmed by $g(r)\rho$ (Fig. 6a) and SDF (Fig. 7a).

For $\nabla^2\rho(r)>0$, indicate that the electron density is locally depleted, characterizing intra or intermolecular interactions [45-46]. Fig. 8a shows the molecular graphs with bond paths and BCPs for In-Cl for the InDES system, while Fig. 8b shows the In-Ow bond paths for the InW1200.

Table 3 Topological data of In^{3+} ions with InDES and InW1200 systems. ELF value, $\eta(r)$, electron density, $\rho(r)$ and Laplacian of electron density, $\nabla^2\rho(r)$ at a bond critical point (BCP) of selected In-Cl and In-Ow interactions.

Interaction	**BCP**	$\boldsymbol{\rho(r)}$	$\boldsymbol{\nabla^2\rho(r)}$	$\boldsymbol{\eta(r)}$	**Systems**
In-Cl	P_1	1.52E-01	5.70E-01	8.67E-01	InDES
	P_2	1.68E-01	6.28E-01	8.74E-01	
	P_3	1.26E-01	4.70E-01	8.50E-01	
	P_4	1.40E-01	5.27E-01	8.61E-01	
$\sum$	4	5.86E-01		3.45E+00	
	P_2	1.50E-01	9.35E-01	8.23E-01	InW1200
	P_3	1.76E-01	1.10E+00	8.45E-01	
	P_4	6.43E-02	3.52E-01	5.93E-01	
	P_5	1.21E-01	7.38E-01	7.98E-01	

In-Ow	P_6	1.48E-01	9.17E-01	8.30E-01	
∑	5	6.61E-01		3.89E+00	
In-Cl	P_1	1.38E-01	5.10E-01	8.75E-01	

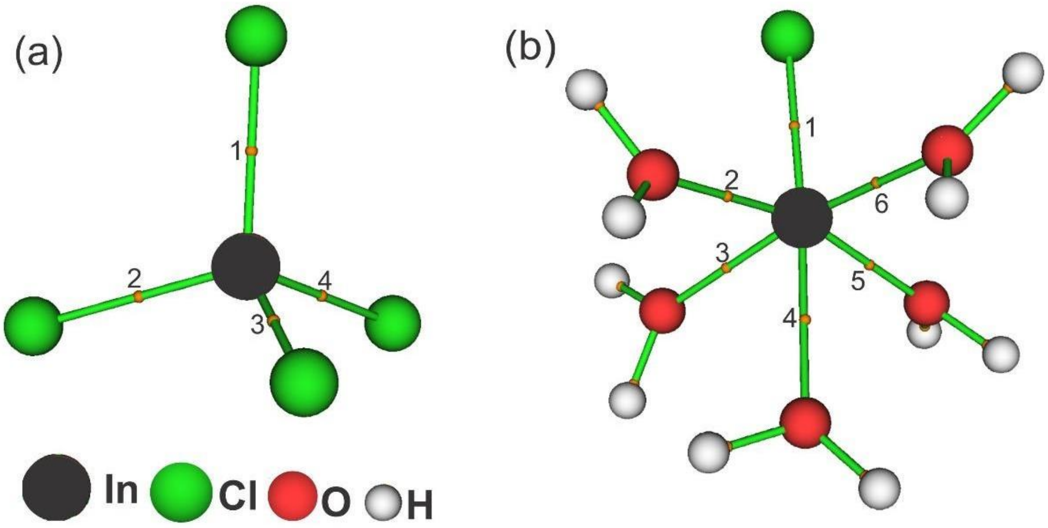

Fig. 9 Molecular graphs with intermolecular interactions and BCP of In^{3+} ion with the system (a) InDES and (b) InW1200.

3.3. Indium and Tin in the form of a mixture in DES and water

3.3.1. InSnDES

In Fig. 10a, we may see those main interactions between In^{3+} ions and anion chlorides around 1.86 Å. The second strongest interaction occurs between Sn^{2+} and Cl^- around 2.71 Å. The $g(r)\rho$ results indicate that the In-Cl interaction is more probable than the Sn-Cl interaction because it presented a higher $g(r)\rho$ value. This result can be explained because indium is a trivalent cation while tin is a divalent cation. This justification is reasonable since the force field expression used in MD consists of Coulomb's Law to nonbonded interactions [47-48]. The other interactions, Sn-(O1,O2) and In-(O1,O2), are localized in 2.38 Å and 1.67 Å, respectively. The interaction of interest Sn^{2+} and In^{3+} with oxygen choline (O3) will not be discussed because of the lowest $g(r)\rho$ values. Therefore, the presence of both ions in the InSnDES system did not cause significant changes in the interactions previously seen for each isolated ion.

As shown in Fig. 10b, there are, on average, approximately 3.6 Cl^- ions complexing the In^{3+} ion and 0.5 ethylene glycol molecules interacting with the In^{3+} ion. Furthermore, we can observe that 4.28 Cl^- ions complex the Sn^{2+} cation, while 1.68 ethylene glycol molecules interact with the Sn^{2+} ion. Therefore, we conclude that the behavior of both metals did not vary significantly in the mixture when analyzed in DES. The reason why o $g(r)\rho$ (see Fig. 10a) is much more significant for the In-Cl interaction than for the Sn-Cl interaction is, most likely, because o $g(r)$ for the In-Cl interaction is higher, given that the 3+ charge of the Indium atom favors it. However, CCN (see Fig. 10b) shows that the amount (~4) of Cl^- complexing both metals is approximately equal.

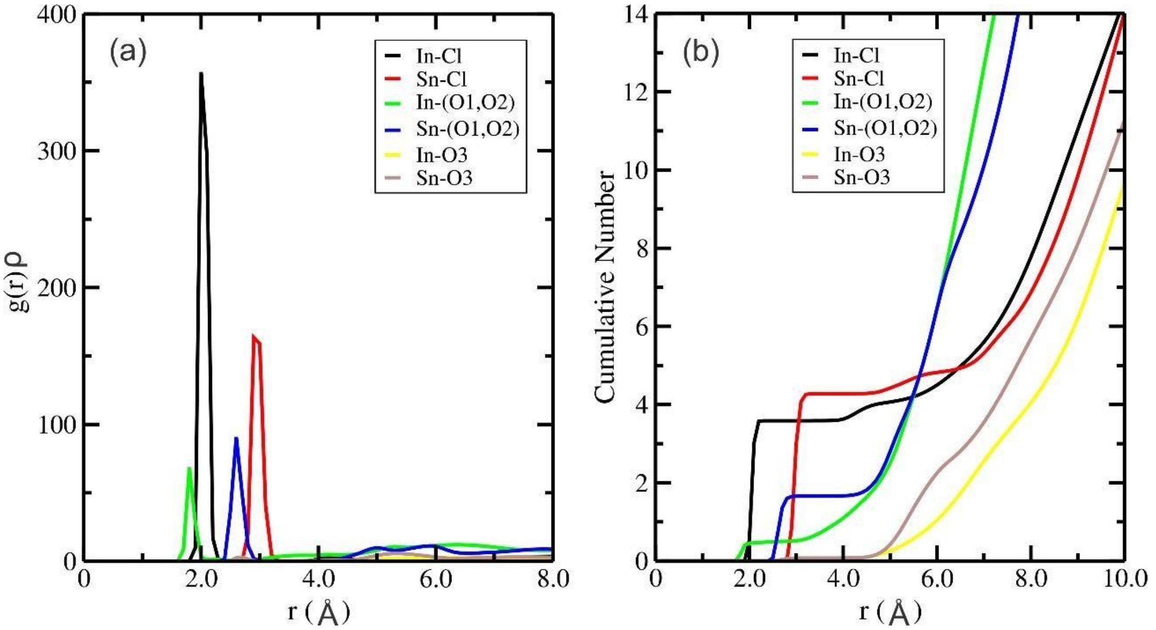

Fig. 10 (a) Radial Distribution Function (RDF or $g(r)$) multiplied by the average numerical density (ρ) of the atoms observed around In^{3+} and Sn^{2+} ions in the InSnDES system and (b) the cumulative number of counter-ions obtained by integrating $g(r)$ for this system.

3.3.2. InSnW1200 and InSnW5580

The g(r)ρ's results for InSnW1200 and InSnW5580 (Fig. 11a) systems showed that the main interaction was between In^{3+} with oxygen water (Ow) around 1.58 Å. As we can see, the increase in the number of water molecules caused a substantial increase in $g(r)\rho$ for the In-Ow interaction, which can be explained by the fact that In^{3+} has a smaller ionic radius than Sn^{2+}, allowing it to a more significant solvation layer when more binders are added to the medium. Sn-Ow was the second strongest interaction around 2.37 Å, and both curves for interactions with 1200 and 5580 water molecules overlapped perfectly, showing that the mixture did not change the behavior of Sn^{2+} in water at all. The other interactions (Sn-Cl and In-Cl) will not be discussed here, as it presented an insignificant value of $g(r)\rho$ when compared to other interactions.

According to the graph in Fig. 11b, approximately 4.7 and 6.0 water molecules are solvating the In^{3+} ion for the InW1200 and InW5580 systems, respectively. Therefore, it was not a considerable increase in the CCN, considering that the water molecules practically quintupled (5580=4.65x1200). Furthermore, the presence of 1.1 Cl^- ions are observed in the InW1200 system and its absence in the InW5580 system, which is explained by the fact that it is being replaced by a water molecule. For the SnW1200 and SnW5580 systems, the Sn^{2+} ion is solvated by approximately 8.87 water molecules, and both curves overlap for the two amounts of water analyzed here. Therefore, more water molecules are solvating Sn^{2+} than In^{3+}, which justifies a greater distance. The behavior of Sn^{2+} and In^{3+} ions was similar for the two systems (Fig. 11a); thus, the system InSnW5580 will not be discussed.

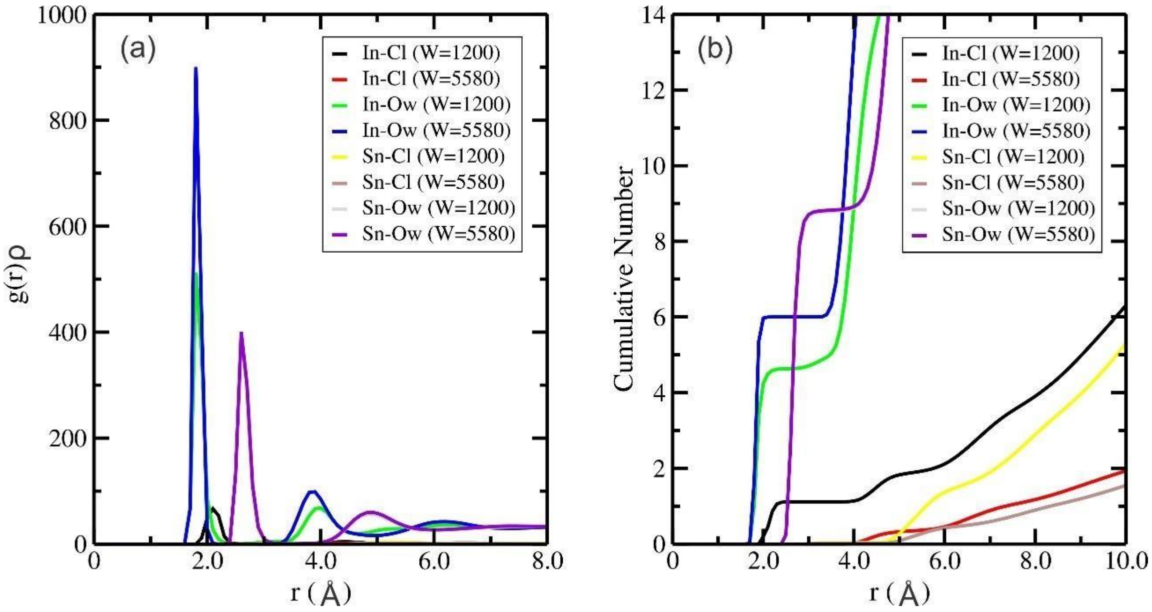

Fig. 11 (a) Radial Distribution Function (RDF or *g*(*r*)) multiplied by the average numerical density (*ρ*) of the atoms observed around In^{3+} and Sn^{2+} ions in the InSnW (where W=1200 is the system with 1200 water molecules and W=5580 is the system with 5580 water molecules) system, and (b) the cumulative number of counter-ions obtained by integrating *g*(*r*) for this system.

Fig. 12a shows how the main interactions [Sn-Cl, Sn-(O1,O2), In-Cl, and In-(O1,O2] are distributed in the InSnDESS system by SDF analysis. In this case, the following interaction order is observed for ionic species: In-Cl > Sn-Cl, thus supporting the data obtained by *g*(*r*)*ρ*. However, the number of Cl^- ions next to the In^{3+} ion does not perfectly complex this ion, so the molecules that actually complex the In^{3+} ions are practically the same amount of species that complex the Sn^{2+} ion. In addition, it is possible to observe that the EG spatial distribution around In^{3+} is smaller than Sn^{2+}. On the other hand, for the InSnW1200 system (Fig. 12b), the water molecules were evenly distributed around the Sn^{2+} ion for a greater distance (see topic 3.2.2), while for the In^{3+} ion, the distribution of water molecules was not it was well distributed for a shorter length; this may be associated with the presence of both ions of interest in the system. Furthermore, as shown in Fig. 12b, the Sn^{2+} atom is better located than the In^{3+} concerning counter-ions.

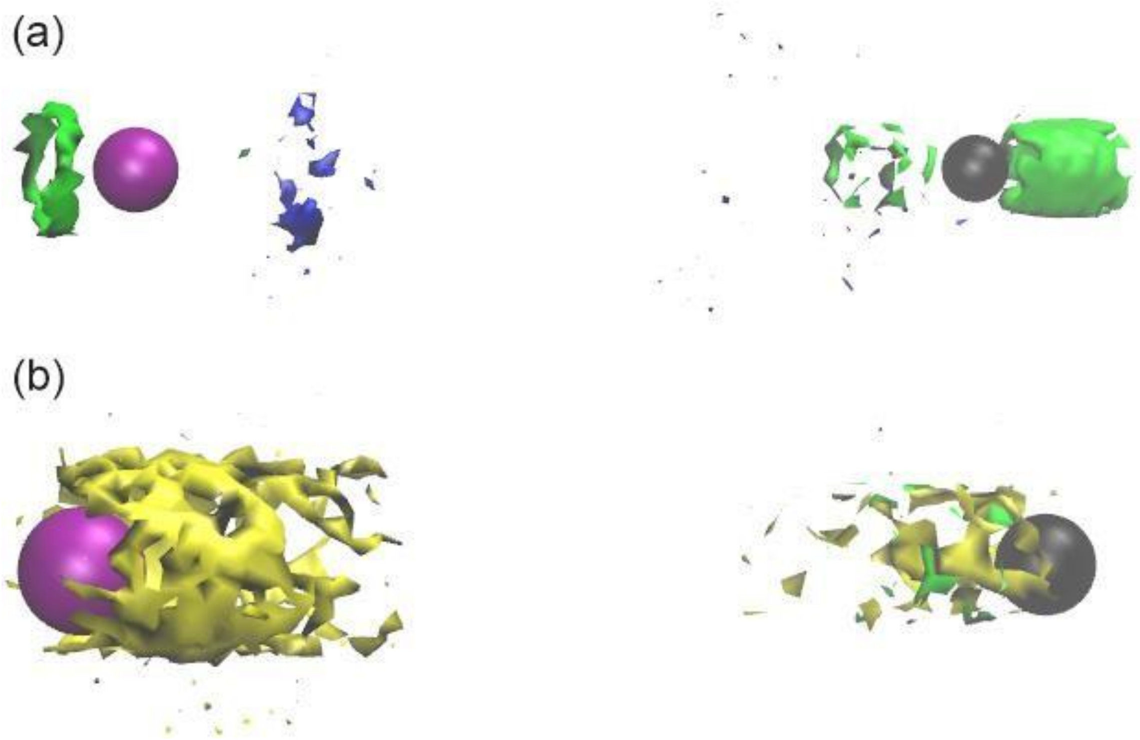

Fig. 12 Spatial Distribution Function (SDF) between the Sn^{2+} and In^{3+} ions with atoms present in the systems (a) InSnDES and (b) InSnW1200. Sn^{2+} (purple); In^{3+} (black); Chloride (green); Ethylene glycol (blue); Water (yellow). Isovalue using for the system (a) Chloride: 0.002952; Ethylene glycol: 0.008255; (b) Chloride: 0.001116; Water: 0.014909.

Considering the InSnDES system, for the Sn-Cl interactions, the sum of all values of $\rho(r)$ and $\eta(r)$ were $\Sigma\rho(r)$=1.08E-01, $\Sigma\eta(r)$=8.97E-01, while for Sn-(O1,O2) the interactions were $\Sigma\rho(r)$=5.33E-02, $\Sigma\eta(r)$=2.78E-01 (Table 4). Furthermore, the sum of all $\rho(r)$ and $\eta(r)$ values obtained for the In-Cl interactions was $\Sigma\rho(r)$=5.67E-01 and $\Sigma\eta(r)$=3.44E+00. Therefore, the presence of both ions (Sn^{2+} and In^{3+}) in the InSnDES system practically did not vary the value of $\Sigma\rho(r)$ and $\Sigma\eta(r)$ for the Sn-Cl and Sn-(O1,O2) interactions when compared with the values of the same interactions for the isolated Sn^{2+} ion (Table 2). Furthermore, a similar behavior was observed for the In-Cl interactions. Regarding the InSnW1200 system (Table 5), for the Sn-Ow interactions, the sum of all values of $\rho(r)$ and $\eta(r)$ were $\Sigma\rho(r)$=2.47E-01 and $\Sigma\eta(r)$=1.38E+00, while for In-Ow interactions were $\Sigma\rho(r)$=6.99E-01 and $\Sigma\eta(r)$=4.05E+00.

Therefore, it is possible to verify that the behavior of the interactions Sn-Cl, Sn-(O1,O2), Sn-Ow, In-Cl, and In-Ow showed to be invariant when analyzed in the form of a mixture if compared with the studied systems in isolation. For all interactions observed, the $\nabla^2\rho(r)>0$, it indicates that the system has intra or intermolecular interactions due to locally depleting electronic density [45-46].

Fig. 13a illustrated the molecular graphs with bond paths and BCPs for Sn-Cl, Sn-(O1,O2) and In-Cl interactions for the system InSnDES, while Fig. 13b illustrated for the Sn-Ow and In-Ow interactions for system SnInW1200.

Table 4 Topological data of Sn^{2+} and In^{3+} ions with InSnDES system. ELF value, $\eta(r)$, electron density, $\rho(r)$ and Laplacian of electron density, $\nabla^2\rho(r)$ at a bond critical point (BCP) of selected Sn-Cl, Sn-(O1,O2), In-Cl, In-(O1,O2) interactions.

Interaction	**BCP**	$\boldsymbol{\rho(r)}$	$\boldsymbol{\nabla^2\rho(r)}$	$\boldsymbol{\eta(r)}$	**System**
Sn-Cl	P_3	2.85E-02	6.69E-02	2.07E-01	InSnDES
	P_4	2.49E-02	5.65E-02	2.01E-01	
	P_5	2.88E-02	6.52E-02	2.40E-01	
	P_6	2.59E-02	5.59E-02	2.48E-01	
$\sum$	4	1.08E-01		8.97E-01	
Sn-(O1,O2)	P_1	2.51E-02	6.90E-02	1.29E-01	
	P_2	2.83E-02	8.25E-02	1.49E-01	
$\sum$	2	5.33E-02		2.78E-01	
In-Cl	P_1	1.23E-01	4.60E-01	8.48E-01	
	P_2	1.64E-01	6.12E-01	8.72E-01	
	P_3	1.30E-01	4.86E-01	8.55E-01	
	P_4	1.50E-01	5.64E-01	8.67E-01	
$\sum$	4	5.67E-01		3.44E+00	

Table 5 Topological data of Sn^{2+} and In^{3+} ions with SnInW1200 system. ELF value, $\eta(r)$, electron density, $\rho(r)$ and Laplacian of electron density, $\nabla^2\rho(r)$ at a bond critical point (BCP) of selected Sn-Ow and In-Ow interactions.

Interaction	**BCP**	$\boldsymbol{\rho(r)}$	$\boldsymbol{\nabla^2\rho(r)}$	$\boldsymbol{\eta(r)}$	**System**
Sn-Ow	P_1	3.16E-02	9.35E-02	1.89E-01	InSnW1200
	P_2	3.23E-02	9.12E-02	1.87E-01	
	P_3	3.58E-02	1.12E-01	2.08E-01	
	P_4	2.60E-02	6.73E-02	1.56E-01	
	P_5	2.98E-02	8.79E-02	1.66E-01	
	P_6	2.92E-02	8.51E-02	1.65E-01	
	P_7	2.54E-02	7.11E-02	1.35E-01	
	P_8	1.72E-02	4.77E-02	8.11E-02	
	P_9	1.93E-02	5.35E-02	9.54E-02	
Total	9	2.47E-01		1.38E+00	
In-Ow	P_1	1.57E-01	9.82E-01	8.30E-01	
	P_2	9.75E-02	5.86E-01	7.35E-01	
	P_3	1.33E-01	8.17E-01	8.16E-01	
	P_4	1.59E-01	9.93E-01	8.34E-01	
	P_5	1.52E-01	9.42E-01	8.35E-01	
Total	5	6.99E-01		4.05E+00	
In-Cl	P_6	1.22E-01	4.45E-01	8.65E-01	

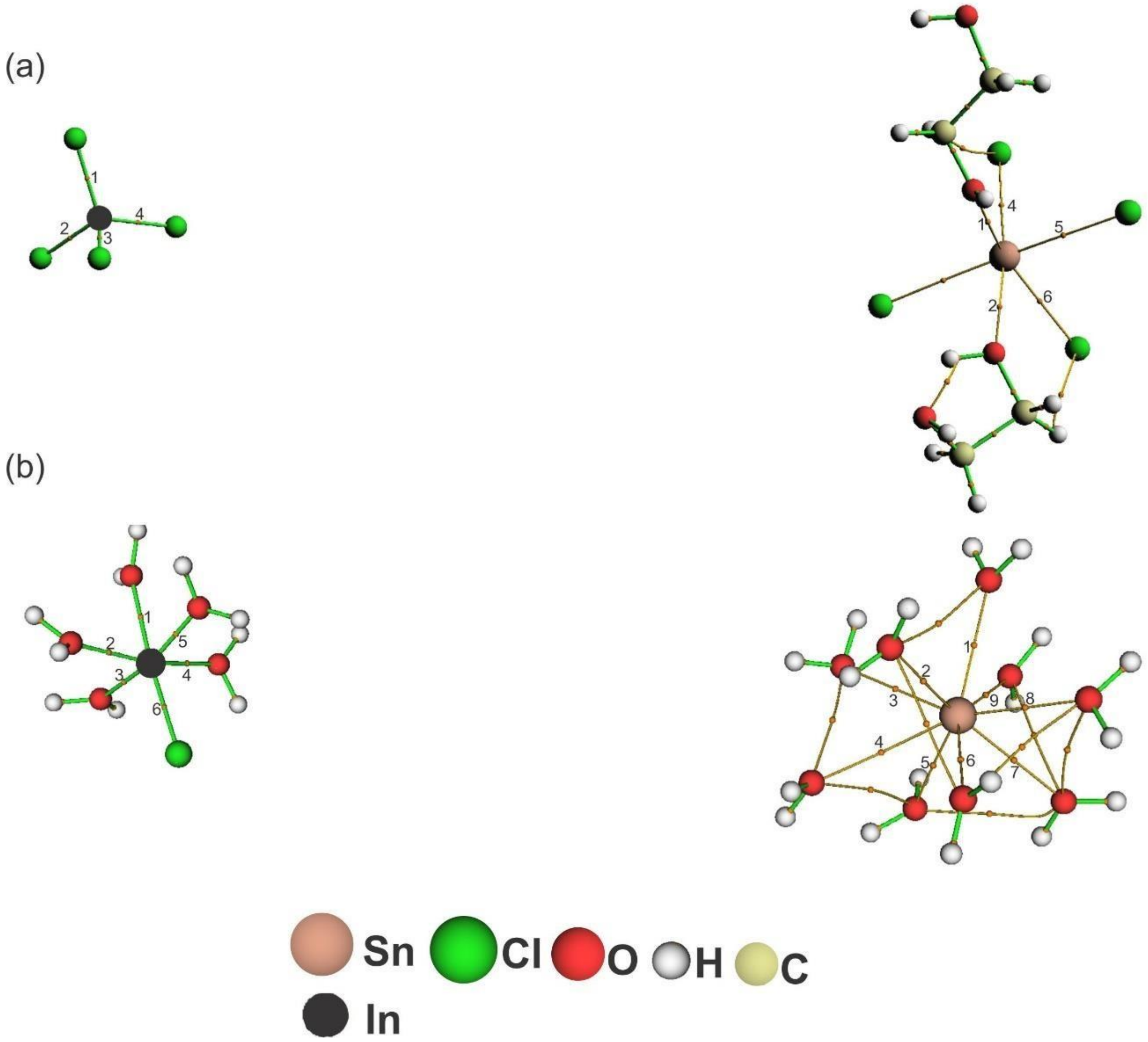

Fig. 13 Molecular graphs with intermolecular interactions and BCP of the Sn^{2+} and In^{3+} ions with the (a) InSnDES, and (b) InSnW1200 systems.

4. Conclusions

The simulations performed for the Sn^{2+} and In^{3+} ions isolated in the SnDES and InDES systems showed a high probability of the ions of interest to interact with the chloride anion in terms of $g(r)\rho$, followed by the ethylene glycol molecules, only for the SnDES system, because In^{3+} showed no interaction with the ethylene glycol molecule. In the mixture form (InSnDES), the behavior of the interactions remained the same. In the SnW1200, SnW5580, InW1200, and InW5580 systems, the isolated ions Sn^{2+} and In^{3+} prefer interacting with water molecules in the first solvation layer. In contrast, interactions with Cl^- ions had no significant $g(r)\rho$. In the form of a metallic mixture, the behavior of the InSnW1200 system did not vary significantly. Furthermore, the increase in the number of water molecules did not cause significant changes in the trends of the ions, either alone or in the form of a mixture.

According to QTAIM calculations, the strength of interactions (related to the values of $\rho(r)$ and $\eta(r)$) showed the following trend: In-Ow > In-Cl (DES) > Sn-Ow > Sn- Cl (DES), where the representation (DES) denotes that the metal-chloride interaction takes place in a deep eutectic solvent.

Theoretical calculations for Sn^{2+} and In^{3+} in metallic mixture showed that both ions in the same system did not significantly alter the $g(r)\rho$ and CCN plots, regardless of the solvents used. The QTAIM calculations performed for the InSnDES and InSnW1200 systems showed that the ELF values remained for the Sn-Cl, Sn-(O1,O2), and Sn-Ow interactions in the metallic mixture in the isolated ions of interest. Likewise, this fact was observed for the In^{3+} ion. Furthermore, the increase in the amount of water (1200 to 5580 molecules) did not bring significant changes in the behavior of Sn^{2+} and In^{3+}, isolated or in the form of a metallic mixture.

Declaration of Competing Interest

The authors declare that they have no known competing finan- cial interests or personal relationships that could have appeared to influence the work reported in this paper.

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3 CONCLUSIONS

Based on the results obtained by MD ($g(r)\rho$, CCN and SDF), we can conclude that in DES, the main interaction occurs between the metal ions and the chloride anion (Sn^{2+} and In^{3+} with Cl^{-}), either alone or in the form of a mixture. Furthermore, only the Sn^{2+} ion showed to interact with the EG oxygens, which was not observed for the In^{3+} ion, isolated or in the form of a mixture. The results of QTAIM ($\rho(r)$ and $\eta(r)$) corroborate the conclusions obtained by Molecular Dynamics.

For aqueous systems, In^{3+} and Sn^{2+} species interacted well with water oxygen (Sn-Ow and In-Ow), either alone or in the form of a mixture. Furthermore, increasing the amount of water in the system containing Sn^{2+} did not cause a change in the value of the interaction. However, the increase in the number of water molecules slightly altered the profile of the In-Ow interaction, even if negligibly, either alone or in the form of a mixture.

Therefore, the behavior of the metal ions Sn^{2+} and In^{3+} was studied separately and as a mixture in two solvents (water and DES) through MD and QTAIM. Although the behavior of ions in two amounts of water has been analyzed, investigating the behavior of these cations in more amounts of water is a goal for the future. Furthermore, analyzing the behavior of interactions with increasing temperature is desired and calculating transport properties. Furthermore, studying what happens with the change of HBD is something planned for the future.

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APPENDIX A – AUTOR'S CURRICULAR DATA

05/07/2022 Curriculum System of Curriculum Lattes (Renato Veríssimo de Oliveira)

Renato Veríssimo de Oliveira

Endereço para acessar este CV: http://lattes.cnpq.br/3566534967018492
ID Lattes: **3566534967018492**
Última atualização do currículo em 28/06/2022

Possui experiência em Modelagem Molecular, utilizando-se para isto de métodos quanto-mecânicos via Química Computacional para cálculos de propriedades físico-químicas de interesse, a depender do sistema em estudo. Ultimamente, tem trabalhado, sobretudo, com Dinâmica Molecular (MD), Teoria Quântica de Átomos em Moléculas (QTAIM) e Teoria do Funcional da Densidade (DFT). Foi medalhista em Química Orgânica (ouro) e Físico-Química (bronze) pela III OCESQ (2019), bem como menção honrosa em Química Geral e na classificação geral. E, ainda, menção honrosa em Química Geral, Química Orgânica, Físico-Química e na classificação geral pela II OCESQ (2018). Possui domínio em cálculo diferencial e integral, matemática elementar e funções transcendentais. Além do fascínio por matemática pura e aplicada, também tem interesse e conhecimento em química orgânica, inorgânica e físico-química. Em química orgânica, tem especial interesse em estereoisomeria das moléculas, assim como em mecanismos de reações orgânicas; em química inorgânica, seu foco é a teoria quântica e simetria dos compostos e, em físico-química, tem grande afinidade por termodinâmica, cinética química, eletroquímica e termodinâmica estatística. Ultimamente, tem se dedicado ao estudo da Química Quântica (mais especificamente, Química Computacional), pois está fazendo uma pós-graduação em Química Teórica. Possui experiência no ensino de Química, pois atuou por dois anos como monitor das disciplinas de Química Orgânica Teórica I, II e Química Geral (esta última, por apenas um semestre), onde tirava dúvidas, resolvia exercícios e explicava o conteúdo, quando os alunos necessitavam. Além disso, fez parte de um reforço escolar, em que ajudava alunos de ensino fundamental e médio, máxime, em sua maioria, de escolas particulares. Nas horas livres, dedica-se aos clássicos da Literatura (Dostoiévski, Nietzsche, Schopenhauer, Montaigne, Maquiavel, ...), da Arte (Van Gogh, Michelangelo, da Vinci, Picasso, ...) e da Música (Bach, Beethoven, Mozart, Chopin, Liszt, Schubert, Tchaicovsky, Vivaldi, Paganini, Mendelssohn, Rachmaninov, Strauss II, Stravinsky, Scriabin, Schumann, Brahms ...). **(Texto informado pelo autor)**

Identificação

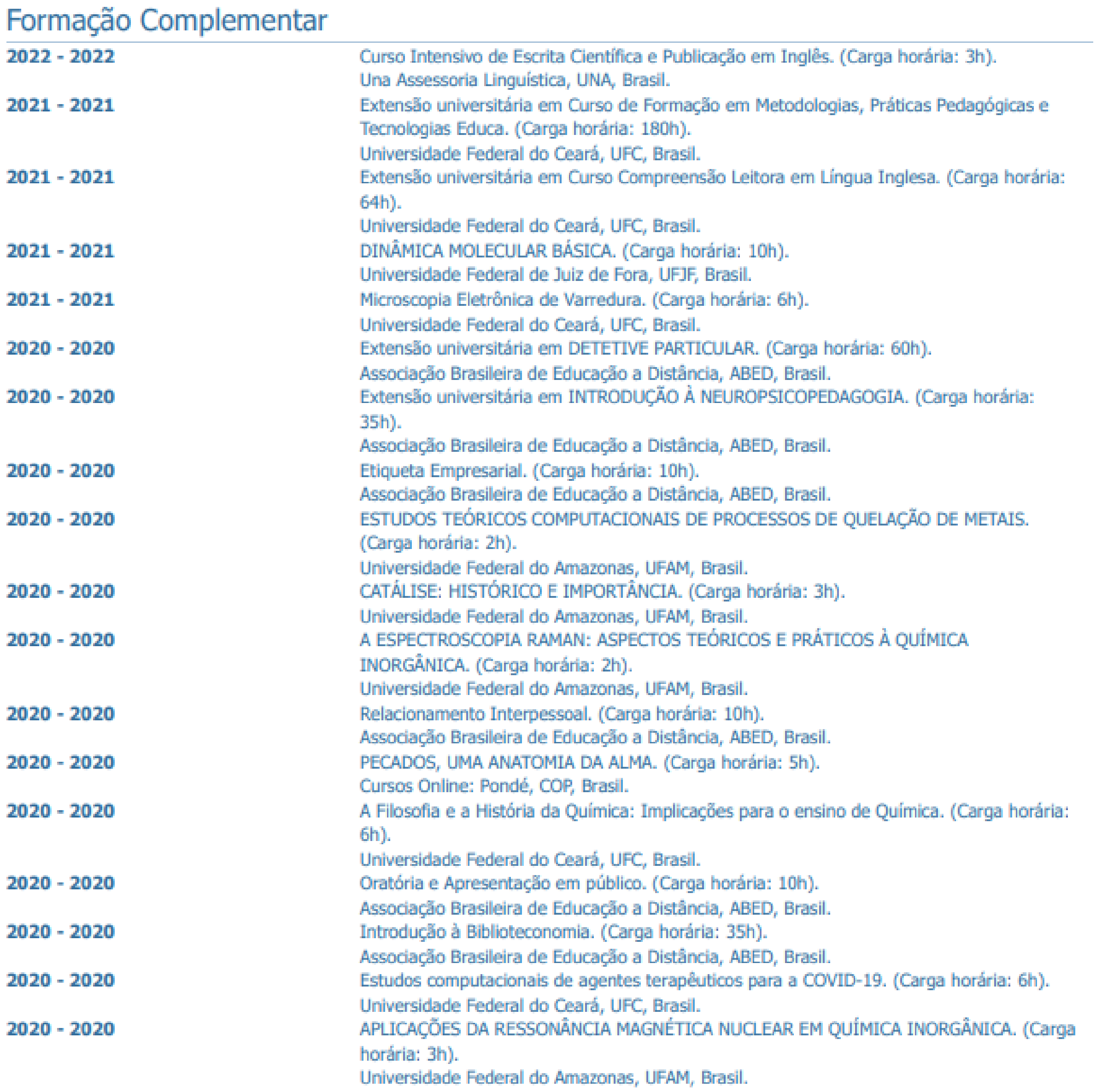
Nome	Renato Veríssimo de Oliveira
Nome em citações bibliográficas	OLIVEIRA, R. V.;VERÍSSIMO DE OLIVEIRA, RENATO
Lattes iD	http://lattes.cnpq.br/3566534967018492
Orcid iD	? https://orcid.org/0000-0003-0620-3178

Endereço

Endereço Profissional	Universidade Federal do Ceará, Centro de Ciências. Avenida Humberto Monte - de 2391 ao fim - lado ímpar Pici 60440593 - Fortaleza, CE - Brasil Telefone: (85) 33669370

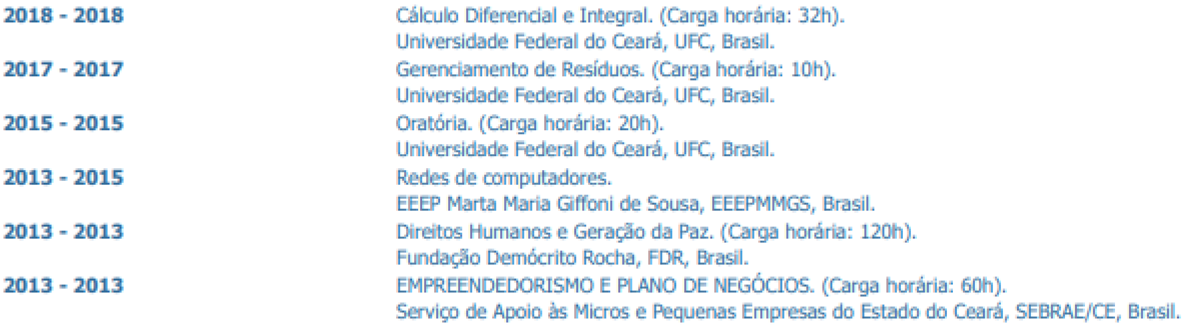
Formação acadêmica/titulação

2020	Mestrado em andamento em QUÍMICA. Universidade Federal do Ceará, UFC, Brasil. Título: Métodos de Química Teórica aplicados a simulações de mecanismos reacionais no meio interestelar (em desenvolvimento). Orientador: Pedro de Lima Neto. Coorientador: Norberto de Kassio Vieira Monteiro. Bolsista do(a): Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, CAPES, Brasil. Palavras-chave: Química Teórica; Astroquímica; Química Computacional.
2015 - 2019	Graduação em Química. Universidade Federal do Ceará, UFC, Brasil. Título: Uma proposta interdisciplinar entre Química e Matemática para abordagem do conteúdo de gases. Orientador: Jair Mafezoli.
2012 - 2014	Ensino Médio (2º grau). EEEP Marta Maria Giffoni de Sousa, EEEPMMGS, Brasil.



Formação Complementar

2022 - 2022	Curso Intensivo de Escrita Científica e Publicação em Inglês. (Carga horária: 3h). Una Assessoria Linguística, UNA, Brasil.
2021 - 2021	Extensão universitária em Curso de Formação em Metodologias, Práticas Pedagógicas e Tecnologias Educa. (Carga horária: 180h). Universidade Federal do Ceará, UFC, Brasil.
2021 - 2021	Extensão universitária em Curso Compreensão Leitora em Língua Inglesa. (Carga horária: 64h). Universidade Federal do Ceará, UFC, Brasil.
2021 - 2021	DINÂMICA MOLECULAR BÁSICA. (Carga horária: 10h). Universidade Federal de Juiz de Fora, UFJF, Brasil.
2021 - 2021	Microscopia Eletrônica de Varredura. (Carga horária: 6h). Universidade Federal do Ceará, UFC, Brasil.
2020 - 2020	Extensão universitária em DETETIVE PARTICULAR. (Carga horária: 60h). Associação Brasileira de Educação a Distância, ABED, Brasil.
2020 - 2020	Extensão universitária em INTRODUÇÃO À NEUROPSICOPEDAGOGIA. (Carga horária: 35h). Associação Brasileira de Educação a Distância, ABED, Brasil.
2020 - 2020	Etiqueta Empresarial. (Carga horária: 10h). Associação Brasileira de Educação a Distância, ABED, Brasil.
2020 - 2020	ESTUDOS TEÓRICOS COMPUTACIONAIS DE PROCESSOS DE QUELAÇÃO DE METAIS. (Carga horária: 2h). Universidade Federal do Amazonas, UFAM, Brasil.
2020 - 2020	CATÁLISE: HISTÓRICO E IMPORTÂNCIA. (Carga horária: 3h). Universidade Federal do Amazonas, UFAM, Brasil.
2020 - 2020	A ESPECTROSCOPIA RAMAN: ASPECTOS TEÓRICOS E PRÁTICOS À QUÍMICA INORGÂNICA. (Carga horária: 2h). Universidade Federal do Amazonas, UFAM, Brasil.
2020 - 2020	Relacionamento Interpessoal. (Carga horária: 10h). Associação Brasileira de Educação a Distância, ABED, Brasil.
2020 - 2020	PECADOS, UMA ANATOMIA DA ALMA. (Carga horária: 5h). Cursos Online: Pondé, COP, Brasil.
2020 - 2020	A Filosofia e a História da Química: Implicações para o ensino de Química. (Carga horária: 6h). Universidade Federal do Ceará, UFC, Brasil.
2020 - 2020	Oratória e Apresentação em público. (Carga horária: 10h). Associação Brasileira de Educação a Distância, ABED, Brasil.
2020 - 2020	Introdução à Biblioteconomia. (Carga horária: 35h). Associação Brasileira de Educação a Distância, ABED, Brasil.
2020 - 2020	Estudos computacionais de agentes terapêuticos para a COVID-19. (Carga horária: 6h). Universidade Federal do Ceará, UFC, Brasil.
2020 - 2020	APLICAÇÕES DA RESSONÂNCIA MAGNÉTICA NUCLEAR EM QUÍMICA INORGÂNICA. (Carga horária: 3h). Universidade Federal do Amazonas, UFAM, Brasil.



2018 - 2018	Cálculo Diferencial e Integral. (Carga horária: 32h). Universidade Federal do Ceará, UFC, Brasil.
2017 - 2017	Gerenciamento de Resíduos. (Carga horária: 10h). Universidade Federal do Ceará, UFC, Brasil.
2015 - 2015	Oratória. (Carga horária: 20h). Universidade Federal do Ceará, UFC, Brasil.
2013 - 2015	Redes de computadores. EEEP Marta Maria Giffoni de Sousa, EEEPMMGS, Brasil.
2013 - 2013	Direitos Humanos e Geração da Paz. (Carga horária: 120h). Fundação Demócrito Rocha, FDR, Brasil.
2013 - 2013	EMPREENDEDORISMO E PLANO DE NEGÓCIOS. (Carga horária: 60h). Serviço de Apoio às Micros e Pequenas Empresas do Estado do Ceará, SEBRAE/CE, Brasil.

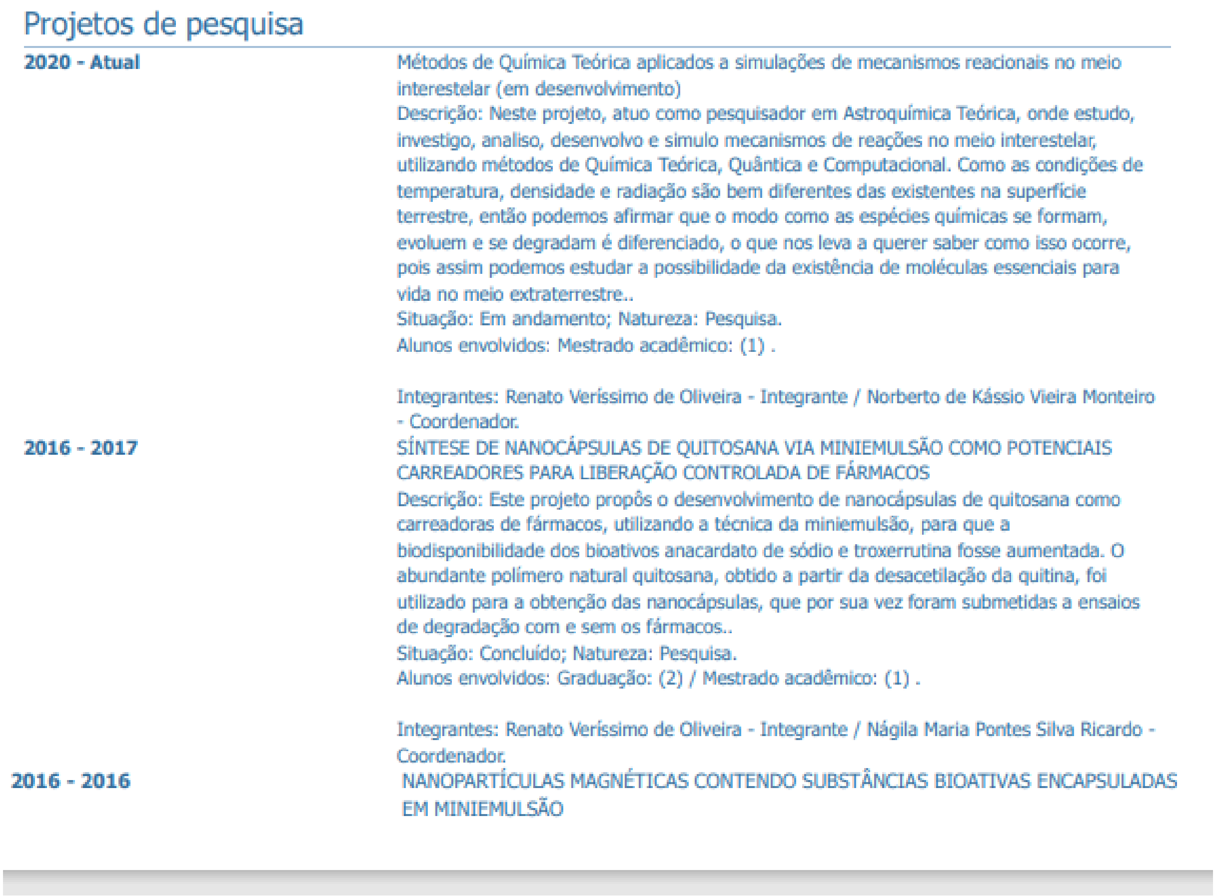
Atuação Profissional

Universidade Federal do Ceará, UFC, Brasil.

Vínculo institucional	
2019 - 2019	Vínculo: Bolsista, Enquadramento Funcional: Monitor de Química Orgânica Teórica II e QG, Carga horária: 12
Outras informações	Neste período, acompanhei uma turma de Química Orgânica Teórica II para Química, uma turma de Química Geral e Orgânica para Biologia e uma turma de Química Orgânica Teórica II para Farmácia.
Vínculo institucional	
2018 - 2018	Vínculo: Bolsista, Enquadramento Funcional: Monitor de Química Orgânica Teórica II, Carga horária: 12
Outras informações	Neste período, atuei como monitor de Química Orgânica Teórica II, principalmente para turmas do curso de Farmácia. Essa disciplina, puramente mecanística, exige uma bagagem de conhecimentos em Química Orgânica Teórica I, como: reconhecimento de grupos funcionais, estereoquímica, representação de seta e meia-seta, projeções de Newman e Fischer, análise conformacional etc. O primeiro assunto abordado são as reações de alcenos (adição eletrofílica), alcinos (adição eletrofílica) e aromáticos (Substituição Eletrofílica e Nucleofílica Aromática); depois substituição nucleofílica de primeira (SN1) e segunda ordem (SN2), bem como eliminação de primeira (E1) e segunda ordem (E2); em seguida, é ministrado as reações de álcoois, fenóis e éteres (bem como epóxidos) e, posteriormente, estuda-se as reações de adição nucleofílica a compostos carbonílicos (aldeídos e cetonas) e finalmente, as reações de ácidos carboxílicos e derivados (ésteres, cloretos de ácido, nitrila, anidridos e amidas).

Reforço Escolar Caixinha de Letras, RECL, Brasil.

Vínculo institucional	
2016 - 2017	Vínculo: Monitor/Auxíliar estudantil, Enquadramento Funcional: Monitor em reforço escolar para EF e EM, Carga horária: 16
Outras informações	Aqui, participei como ajudante em um reforço escolar para estudantes de ensino fundamental (EF) e ensino médio (EM), tirando dúvidas sobre Química, Física e Matemática, onde grande parte dos participantes eram estudantes de escolas particulares de Fortaleza.



Projetos de pesquisa

2020 - Atual

Métodos de Química Teórica aplicados a simulações de mecanismos reacionais no meio interestelar (em desenvolvimento)
Descrição: Neste projeto, atuo como pesquisador em Astroquímica Teórica, onde estudo, investigo, analiso, desenvolvo e simulo mecanismos de reações no meio interestelar, utilizando métodos de Química Teórica, Quântica e Computacional. Como as condições de temperatura, densidade e radiação são bem diferentes das existentes na superfície terrestre, então podemos afirmar que o modo como as espécies químicas se formam, evoluem e se degradam é diferenciado, o que nos leva a querer saber como isso ocorre, pois assim podemos estudar a possibilidade da existência de moléculas essenciais para vida no meio extraterrestre..
Situação: Em andamento; Natureza: Pesquisa.
Alunos envolvidos: Mestrado acadêmico: (1) .

Integrantes: Renato Veríssimo de Oliveira - Integrante / Norberto de Kássio Vieira Monteiro - Coordenador.

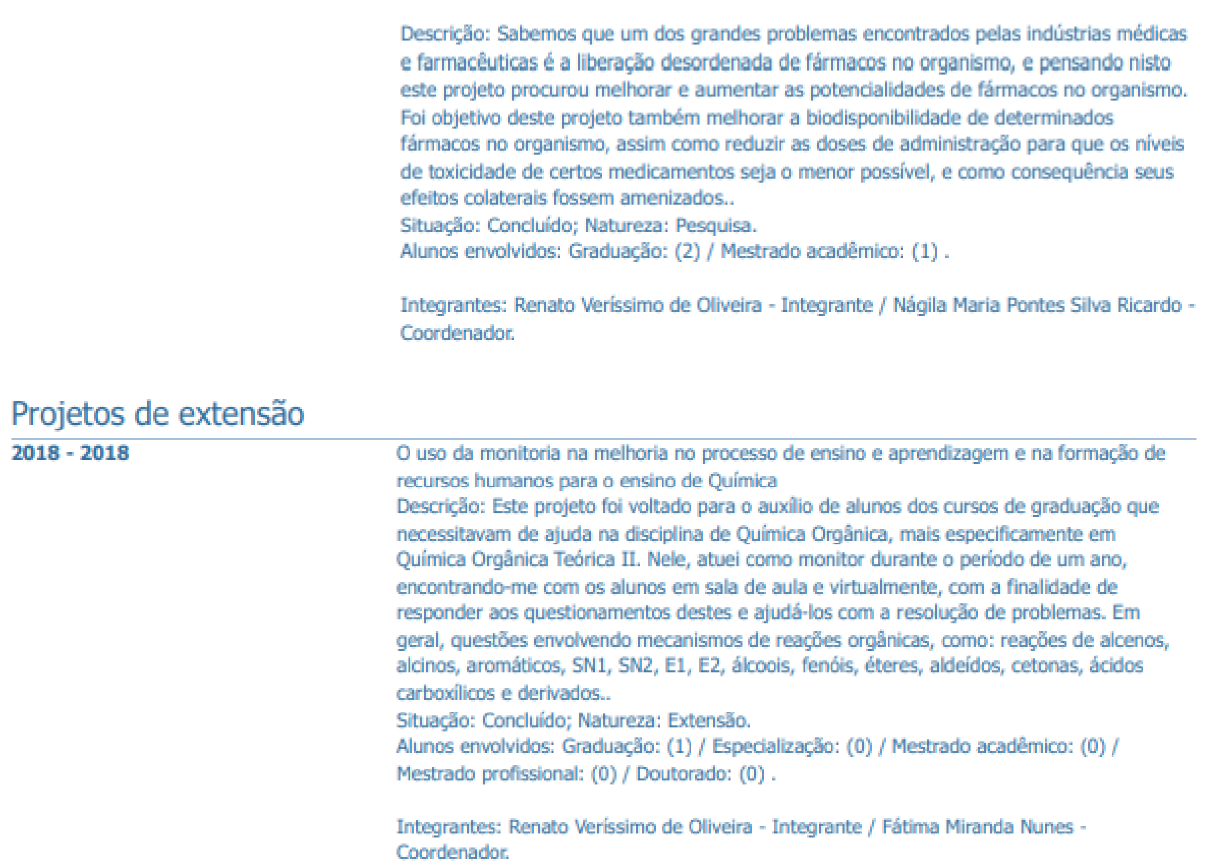
2016 - 2017

SÍNTESE DE NANOCÁPSULAS DE QUITOSANA VIA MINIEMULSÃO COMO POTENCIAIS CARREADORES PARA LIBERAÇÃO CONTROLADA DE FÁRMACOS
Descrição: Este projeto propôs o desenvolvimento de nanocápsulas de quitosana como carreadoras de fármacos, utilizando a técnica da miniemulsão, para que a biodisponibilidade dos bioativos anacardato de sódio e troxerrutina fosse aumentada. O abundante polímero natural quitosana, obtido a partir da desacetilação da quitina, foi utilizado para a obtenção das nanocápsulas, que por sua vez foram submetidas a ensaios de degradação com e sem os fármacos..
Situação: Concluído; Natureza: Pesquisa.
Alunos envolvidos: Graduação: (2) / Mestrado acadêmico: (1) .

Integrantes: Renato Veríssimo de Oliveira - Integrante / Nágila Maria Pontes Silva Ricardo - Coordenador.

2016 - 2016

NANOPARTÍCULAS MAGNÉTICAS CONTENDO SUBSTÂNCIAS BIOATIVAS ENCAPSULADAS EM MINIEMULSÃO



Descrição: Sabemos que um dos grandes problemas encontrados pelas indústrias médicas e farmacêuticas é a liberação desordenada de fármacos no organismo, e pensando nisto este projeto procurou melhorar e aumentar as potencialidades de fármacos no organismo. Foi objetivo deste projeto também melhorar a biodisponibilidade de determinados fármacos no organismo, assim como reduzir as doses de administração para que os níveis de toxicidade de certos medicamentos seja o menor possível, e como consequência seus efeitos colaterais fossem amenizados..
Situação: Concluído; Natureza: Pesquisa.
Alunos envolvidos: Graduação: (2) / Mestrado acadêmico: (1) .

Integrantes: Renato Veríssimo de Oliveira - Integrante / Nágila Maria Pontes Silva Ricardo - Coordenador.

Projetos de extensão

2018 - 2018

O uso da monitoria na melhoria no processo de ensino e aprendizagem e na formação de recursos humanos para o ensino de Química
Descrição: Este projeto foi voltado para o auxílio de alunos dos cursos de graduação que necessitavam de ajuda na disciplina de Química Orgânica, mais especificamente em Química Orgânica Teórica II. Nele, atuei como monitor durante o período de um ano, encontrando-me com os alunos em sala de aula e virtualmente, com a finalidade de responder aos questionamentos destes e ajudá-los com a resolução de problemas. Em geral, questões envolvendo mecanismos de reações orgânicas, como: reações de alcenos, alcinos, aromáticos, SN1, SN2, E1, E2, álcoois, fenóis, éteres, aldeídos, cetonas, ácidos carboxílicos e derivados..
Situação: Concluído; Natureza: Extensão.
Alunos envolvidos: Graduação: (1) / Especialização: (0) / Mestrado acadêmico: (0) / Mestrado profissional: (0) / Doutorado: (0) .

Integrantes: Renato Veríssimo de Oliveira - Integrante / Fátima Miranda Nunes - Coordenador.

Outros Projetos

2019 - Atual	Desenvolvimento de ações que visem a diminuição da retenção e evasão discente no curso de bacharelado em Química Descrição: Nesse projeto, realizo três coisas principais: acompanhamento semanal dos discentes; auxílio ao professor no desenvolvimento de atividades e reuniões com o docente. A disciplina em que acompanho os estudantes é Química Orgânica Teórica II, pois já tenho uma base muito boa nessa área e isso facilita o processo de ensino-aprendizagem turma-monitor.. Situação: Em andamento; Natureza: Outra. Alunos envolvidos: Graduação: (1) . Integrantes: Renato Veríssimo de Oliveira - Integrante / Fátima Miranda Nunes - Coordenador.

Áreas de atuação

1.	Grande área: Ciências Exatas e da Terra / Área: Química / Subárea: Físico-Química Teórica.
2.	Grande área: Ciências Exatas e da Terra / Área: Química / Subárea: Astroquímica Teórica.
3.	Grande área: Ciências Exatas e da Terra / Área: Química / Subárea: Química Quântica.
4.	Grande área: Ciências Exatas e da Terra / Área: Química / Subárea: Química Computacional.
5.	Grande área: Ciências Exatas e da Terra / Área: Química / Subárea: Química Orgânica.
6.	Grande área: Ciências Exatas e da Terra / Área: Química / Subárea: Cálculo diferencial e integral.

Idiomas

Espanhol	Compreende Bem, Fala Razoavelmente, Lê Bem, Escreve Pouco.
Inglês	Compreende Razoavelmente, Fala Pouco, Lê Razoavelmente, Escreve Pouco.
Francês	Compreende Razoavelmente, Fala Pouco, Lê Razoavelmente, Escreve Pouco.
Português	Compreende Bem, Fala Bem, Lê Bem, Escreve Bem.

Prêmios e títulos

2019	Menção honrosa na classificação geral da Olimpíada Cearense do Ensino Superior de Química, III OCESQ, UNIVERSIDADE FEDERAL DO CEARÁ.
2019	Menção honrosa na modalidade Química Geral da Olimpíada Cearense do Ensino Superior de Química, III OCESQ, UNIVERSIDADE FEDERAL DO CEARÁ.
2019	Primeiro colocado na modalidade Química Orgânica da Olimpíada Cearense do Ensino Superior de Química, III OCESQ, UNIVERSIDADE FEDERAL DO CEARÁ.
2019	Terceiro colocado na modalidade Físico-Química da Olimpíada Cearense do Ensino Superior de Química, III OCESQ, UNIVERSIDADE FEDERAL DO CEARÁ.
2018	Menção honrosa na classificação geral da Olimpíada Cearense do Ensino Superior de Química, II OCESQ, UNIVERSIDADE FEDERAL DO CEARÁ.
2018	Menção honrosa na modalidade Físico-Química da Olimpíada Cearense do Ensino Superior de Química, II OCESQ, UNIVERSIDADE FEDERAL DO CEARÁ.
2018	Menção honrosa na modalidade Química Geral da Olimpíada Cearense do Ensino Superior de Química, II OCESQ, UNIVERSIDADE FEDERAL DO CEARÁ.
2018	Menção honrosa na modalidade Química Orgânica da Olimpíada Cearense do Ensino Superior de Química, II OCESQ, UNIVERSIDADE FEDERAL DO CEARÁ.
2012	Primeiro colocado no soletrando, EEIEF - Escola de Educação Infantil e Ensino Fundamental Dom José.

Produções

Produção bibliográfica

Artigos completos publicados em periódicos

Ordenar por

Ordem Cronológica

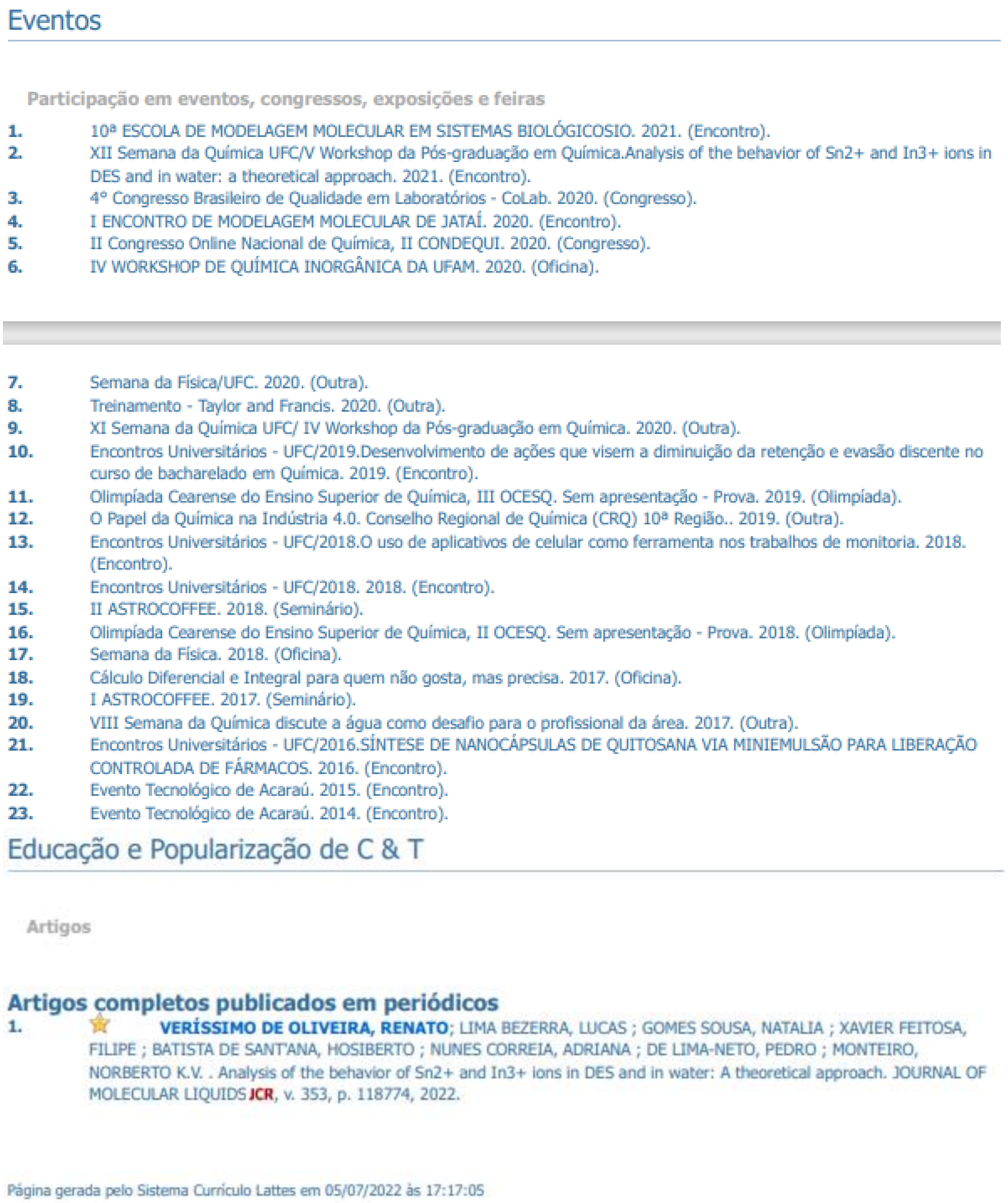
1. **VERÍSSIMO DE OLIVEIRA, RENATO**; LIMA BEZERRA, LUCAS ; GOMES SOUSA, NATALIA ; XAVIER FEITOSA, FILIPE ; BATISTA DE SANT'ANA, HOSIBERTO ; NUNES CORREIA, ADRIANA ; DE LIMA-NETO, PEDRO ; MONTEIRO, NORBERTO K.V. . Analysis of the behavior of Sn2+ and In3+ ions in DES and in water: A theoretical approach. JOURNAL OF MOLECULAR LIQUIDS **JCR**, v. 353, p. 118774, 2022.

Bancas

Participação em bancas de trabalhos de conclusão

Trabalhos de conclusão de curso de graduação

1. VIDAL, R. M. B.; **VERÍSSIMO DE OLIVEIRA, RENATO**; FERREIRA, E. N.. Participação em banca de João Paulo Oliveira de Alcântara.SEQUÊNCIA DIDÁTICA INVESTIGATIVA SOBRE FAKE SCIENCE DE SUBSTÂNCIAS ÁCIDAS E BÁSICAS COM ESTUDANTES DO ENSINO MÉDIO. 2022. Trabalho de Conclusão de Curso (Graduação em Licenciatura em Química) - Universidade Federal do Ceará.
2. FERREIRA, O. P.; QUEIROZ, F. S.; **OLIVEIRA, R. V.**. Participação em banca de Macário Vitório Mota Rodrigues.Uma proposta multidisciplinar entre Física e Química para a abordagem do conteúdo de Eletroquímica. 2020. Trabalho de Conclusão de Curso (Graduação em Química) - Universidade Federal do Ceará.



Eventos

Participação em eventos, congressos, exposições e feiras

1. 10ª ESCOLA DE MODELAGEM MOLECULAR EM SISTEMAS BIOLÓGICOSIO. 2021. (Encontro).
2. XII Semana da Química UFC/V Workshop da Pós-graduação em Química.Analysis of the behavior of Sn2+ and In3+ ions in DES and in water: a theoretical approach. 2021. (Encontro).
3. 4° Congresso Brasileiro de Qualidade em Laboratórios - CoLab. 2020. (Congresso).
4. I ENCONTRO DE MODELAGEM MOLECULAR DE JATAÍ. 2020. (Encontro).
5. II Congresso Online Nacional de Química, II CONDEQUI. 2020. (Congresso).
6. IV WORKSHOP DE QUÍMICA INORGÂNICA DA UFAM. 2020. (Oficina).
7. Semana da Física/UFC. 2020. (Outra).
8. Treinamento - Taylor and Francis. 2020. (Outra).
9. XI Semana da Química UFC/ IV Workshop da Pós-graduação em Química. 2020. (Outra).
10. Encontros Universitários - UFC/2019.Desenvolvimento de ações que visem a diminuição da retenção e evasão discente no curso de bacharelado em Química. 2019. (Encontro).
11. Olimpíada Cearense do Ensino Superior de Química, III OCESQ. Sem apresentação - Prova. 2019. (Olimpíada).
12. O Papel da Química na Indústria 4.0. Conselho Regional de Química (CRQ) 10ª Região.. 2019. (Outra).
13. Encontros Universitários - UFC/2018.O uso de aplicativos de celular como ferramenta nos trabalhos de monitoria. 2018. (Encontro).
14. Encontros Universitários - UFC/2018. 2018. (Encontro).
15. II ASTROCOFFEE. 2018. (Seminário).
16. Olimpíada Cearense do Ensino Superior de Química, II OCESQ. Sem apresentação - Prova. 2018. (Olimpíada).
17. Semana da Física. 2018. (Oficina).
18. Cálculo Diferencial e Integral para quem não gosta, mas precisa. 2017. (Oficina).
19. I ASTROCOFFEE. 2017. (Seminário).
20. VIII Semana da Química discute a água como desafio para o profissional da área. 2017. (Outra).
21. Encontros Universitários - UFC/2016.SÍNTESE DE NANOCÁPSULAS DE QUITOSANA VIA MINIEMULSÃO PARA LIBERAÇÃO CONTROLADA DE FÁRMACOS. 2016. (Encontro).
22. Evento Tecnológico de Acaraú. 2015. (Encontro).
23. Evento Tecnológico de Acaraú. 2014. (Encontro).

Educação e Popularização de C & T

Artigos

Artigos completos publicados em periódicos

1. ☆ **VERÍSSIMO DE OLIVEIRA, RENATO**; LIMA BEZERRA, LUCAS ; GOMES SOUSA, NATALIA ; XAVIER FEITOSA, FILIPE ; BATISTA DE SANT'ANA, HOSIBERTO ; NUNES CORREIA, ADRIANA ; DE LIMA-NETO, PEDRO ; MONTEIRO, NORBERTO K.V. . Analysis of the behavior of Sn2+ and In3+ ions in DES and in water: A theoretical approach. JOURNAL OF MOLECULAR LIQUIDS **JCR**, v. 353, p. 118774, 2022.

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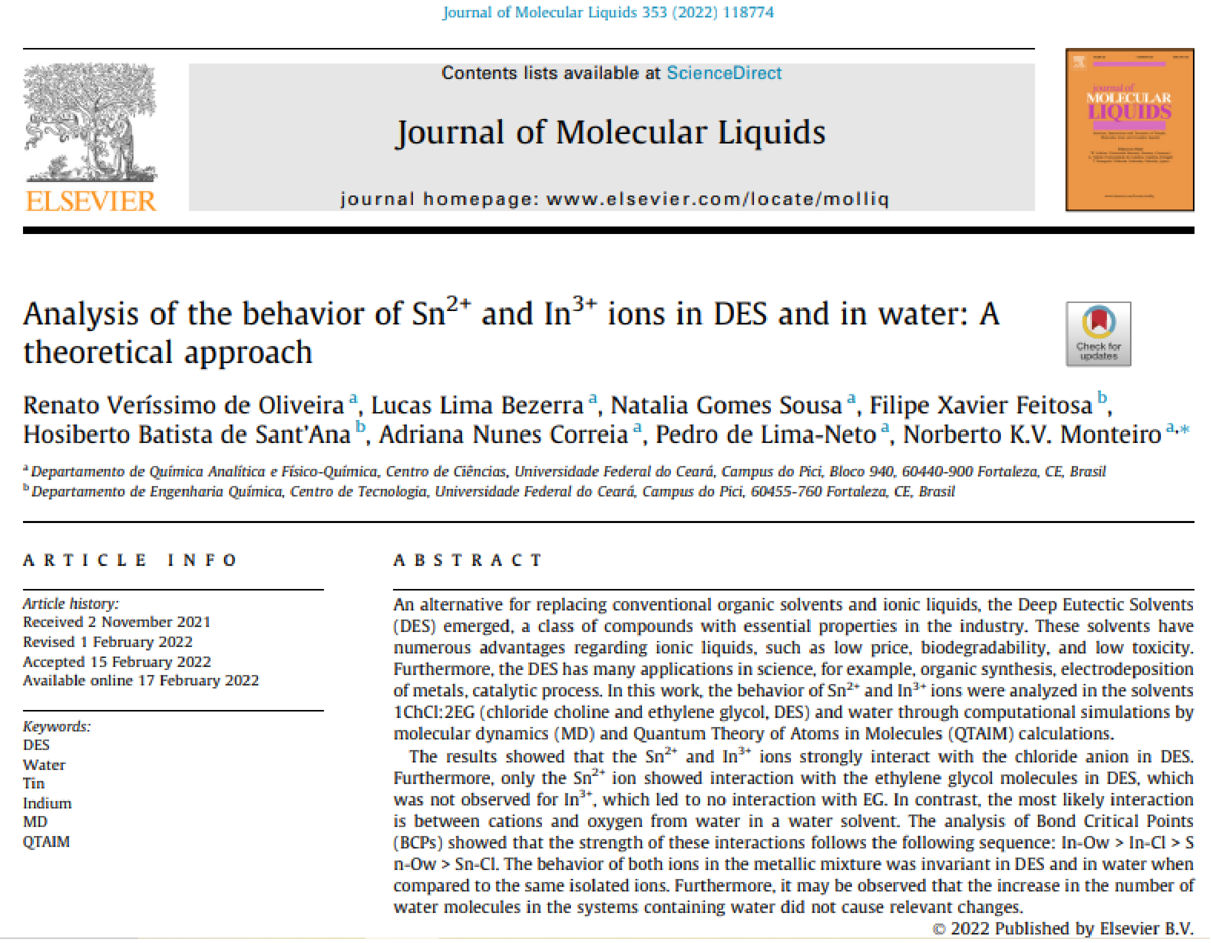

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Analysis of the behavior of Sn^{2+} and In^{3+} ions in DES and in water: A theoretical approach

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ABSTRACT

An alternative for replacing conventional organic solvents and ionic liquids, the Deep Eutectic Solvents (DES) emerged, a class of compounds with essential properties in the industry. These solvents have numerous advantages regarding ionic liquids, such as low price, biodegradability, and low toxicity. Furthermore, the DES has many applications in science, for example, organic synthesis, electrodeposition of metals, catalytic process. In this work, the behavior of Sn^{2+} and In^{3+} ions were analyzed in the solvents 1ChCl:2EG (chloride choline and ethylene glycol, DES) and water through computational simulations by molecular dynamics (MD) and Quantum Theory of Atoms in Molecules (QTAIM) calculations.

The results showed that the Sn^{2+} and In^{3+} ions strongly interact with the chloride anion in DES. Furthermore, only the Sn^{2+} ion showed interaction with the ethylene glycol molecules in DES, which was not observed for In^{3+}, which led to no interaction with EG. In contrast, the most likely interaction is between cations and oxygen from water in a water solvent. The analysis of Bond Critical Points (BCPs) showed that the strength of these interactions follows the following sequence: In-Ow > In-Cl > Sn-Ow > Sn-Cl. The behavior of both ions in the metallic mixture was invariant in DES and in water when compared to the same isolated ions. Furthermore, it may be observed that the increase in the number of water molecules in the systems containing water did not cause relevant changes.