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The role of potential energy landscape exploration in the development of new electrolyte solutions

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Abstract: The development of new electrolyte solutions with improved characteristics is a key challenge for creating high-performance batteries, fuel cells, supercapacitors, and other electrochemical devices. The study of the potential energy landscape (PEL) plays an important role in this process, providing information about the interactions between solution components at the molecular level. In this work, we review the practice of applying PEL research methods based on classical and quantum-chemical algorithms to analyze the structure, dynamics, and thermodynamic properties of electrolyte solutions. Intermolecular and ion-molecular interactions at the microscopic level, which determine the macroscopic properties of the electrolyte solution, are considered in detail. The importance of identifying stable configurations of ions and their solvates is emphasized. PEL analysis allows for the systematic determination of the most probable structures and complexes formed in solution, which is important for understanding ion transport mechanisms. The study of the PEL allows for the determination of the energy barriers that must be overcome for ion migration, which is related to the conductivity of the electrolyte. The application of PEL research methods in combination with experimental data opens up new possibilities for the rational design of electrolyte solutions with desired physicochemical properties.

Keywords: electrolyte solution; molecular modeling; molecular dynamics; quantum chemistry; potential energy landscape.

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Роль исследования ландшафта потенциальной энергии в разработке новых электролитных растворов

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Аннотация: Разработка новых электролитных растворов с улучшенными характеристиками является ключевой задачей для создания высокоэффективных аккумуляторов, топливных элементов, суперконденсаторов и других электрохимических устройств. Исследование ландшафта потенциальной энергии (ЛПЭ) играет важную роль в этом процессе, предоставляя информацию о взаимодействиях между компонентами раствора на молекулярном уровне. В данной работе рассмотрена практика применения методов исследования ЛПЭ, основанных на классических и квантово-химических алгоритмах, для анализа структуры, динамики и термодинамических свойств электролитных растворов. Подробно рассматриваются межмолекулярные и ион-молекулярные взаимодействия на микроскопическом уровне, определяющие макроскопические свойства электролитного раствора. Подчеркнута важность идентификации стабильных конфигураций ионов и их сольватов. Анализ ЛПЭ позволяет систематически определять наиболее вероятные структуры и комплексы, образующиеся в растворе, что важно для понимания механизмов ионного транспорта. Исследование ЛПЭ позволяет определить энергетические барьеры, которые необходимо преодолеть для миграции ионов, что связано с проводимостью электролита. Применение методов исследования ЛПЭ в сочетании с экспериментальными данными открывает новые возможности для рационального дизайна электролитных растворов с требуемыми физико-химическими свойствами.

Ключевые слова: электролитный раствор; молекулярное моделирование; молекулярная динамика; квантовая химия; ландшафт потенциальной энергии.

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1. Introduction

Due to the rapid growth of household appliances powered by the electrical grid, modern humanity is increasingly in need of additional and more efficient energy sources. This remark applies equally to both primary energy sources and rechargeable devices, among which portable electronics (phones, tablets, laptops) deserve special mention [1–4]. The concept of a potential energy landscape (PEL) is an imaginary multidimensional surface that describes the potential energy of a system depending on the internal coordinates of its components (Fig. 1). It is important to emphasize that, although the instantaneous potential energy of a system is a scalar quantity, the PEL is a multidimensional hypersurface, where the axes represent the coordinates of all particles, and the energy axis represents the corresponding potential energy value for each possible configuration. Thus, studying PEL allows us to analyze the dependence of a system's energy on its geometry, identifying stable states (minima on PEL) and the energy barriers between them, which determines the thermodynamics and kinetics of the processes being studied in electrolytes.

In the context of electrolyte solutions, PEL reflects the interactions between ions, solvent molecules, electrodes, technologically determined additives, and other system components. Systematic analysis of PEL provides valuable information on possible microscopic states of the solution, the mechanisms of solvation and ion transport during charging and discharging, and thermodynamic properties [5, 6]. PEL can use the potential energy of the system, the total energy of the system, or other thermodynamic potentials as energy, depending on the desired interpretation of the concept. Using the total energy of the system allows for the study of electrolyte systems under conditions of finite temperature and pressure.

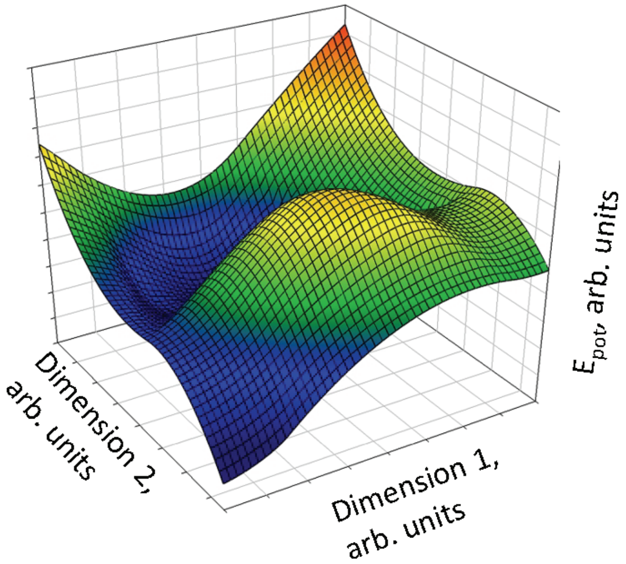


Fig. 1. Model PEL for a small section of an arbitrary electrolyte system

Currently, there is a rapid growth in research in the field of electrochemical devices such as lithium-ion batteries [7–9], sodium-ion batteries [10, 11], magnesium-ion batteries [12], solid-state batteries, fuel cells [13–15], supercapacitors [16–18], and electrolyzers [19–21]. This academic interest is driven by the steadily increasing need to produce efficient and sustainable energy storage and conversion systems [22–25]. In addition to local needs, electrochemical devices naturally play an important role in solving such global problems of civilization as climate change and depletion of fossil fuels. Electrolytes, acting as a medium for ion transport between electrodes, play a key role in the functioning efficiency and durability of these devices. Electrolytes directly affect the most important performance characteristics of electrochemical devices such as efficiency, power, cycle life, operating temperature range, and safety [26, 27]. A particular requirement of modern society is the environmental friendliness, or at least relative environmental friendliness, of the batteries used. The cost of recycling a chemical power source must be included in the overall cost of energy technology developed in today's globalized world. Along with environmental friendliness, the issue of battery safety for the end user is important.

Currently existing electrolytes often do not fully meet the requirements of modern electrochemical devices [27]. For example, organic electrolytes, widely used in lithium-ion batteries, have limited ionic conductivity and proportionally high viscosity, a narrow electrochemical window, high flammability, and toxicity. Highly viscous electrolyte solutions create additional challenges in their development and production. It should be noted that viscosity is inversely proportional to ionic conductivity. The development of chemical power sources with reduced viscosity will automatically increase their electrical conductivity. Ionic conductivity is one of the most important characteristics of an electrolyte, and its high value makes this ion-molecular system technologically competitive [28]. The development of new electrolyte solutions with improved properties, such as high ionic conductivity, a wide electrochemical window, low viscosity, and high thermal and chemical stability, is a critical task for the creation of more efficient, safe, and durable electrochemical devices [28, 29]. Achieving this goal requires a deep understanding of the relationship between the composition, structure, and properties of electrolytes at the molecular level of organization.

Traditional experimental methods, such as measuring conductivity, viscosity, density, and electrochemical stability, provide valuable information on the macroscopic properties of electrolytes. However, they do not always provide a complete understanding of the molecular mechanisms underlying the observed phenomena. In recent years, PEL analysis has become a powerful tool for studying electrolyte solutions and rationally improving their performance. PEL analysis, based on molecular modeling methods such as quantum chemical calculations and classical molecular dynamics, provides detailed information on the interactions between solution components, i.e., ion-molecular and intermolecular electrostatic forces. The latter determine the equilibrium properties of the electrolyte solution [30–33].

Cations, anions, solvent molecules, and molecular additives influence the macroscopic properties of the electrolyte. For example, PEL studies can reveal preferred configurations of ion solvates, energy barriers for ion transport activation, and the influence of temperature and composition on the structure, transport, and macroscopic properties of the electrolyte [34–36].

In this paper, we present a critical review of recent applications of PEL studies based on classical and quantum chemical algorithms to analyze the structure, dynamics, and thermodynamic properties of electrolyte solutions [5, 22, 37, 38].

2. Results and Discussion

Calculations in theoretical chemistry and molecular physics are a powerful tool for studying PEL of electrolyte solutions. They enable modeling interactions between system components at the atomic level and obtaining detailed thermodynamic information about the structure and dynamics of the solution [39–42]. Subsequently, the thermodynamic characteristics of PEL can be translated into the language of electrochemical and physicochemical properties related to the experimentally obtained characteristics [5].

Numerical methods for calculating the potential energy of an ion-electron system from first principles, based on the fundamental laws of quantum mechanics, provide highly accurate results for parameterizing PEL. Unfortunately, they require significant computational resources and cannot be applied to systems of significant size due to the fundamental impossibility of obtaining the analytical solution to the wave equation for multielectron problems. The density functional theory (DFT) method is a less resource-intensive method that is widely used to calculate the electronic structure and properties of molecules, thermodynamic phases, and materials [7, 43–45]. The result of the DFT calculation of an electrolyte system is both the total potential energy and the forces acting on each atom, cation, or anion.

Classical molecular dynamics (MD) uses the classical laws of motion to model the motion of atoms and molecules [46, 47]. Classical MD does not consider electrons as individual interaction centers. Atoms interact with each other via simple potentials [48]. Potential functions are parameterized in advance based on quantum chemical or experimental data. During MD modeling, the potential energy of the system depends only on the distance between each two interacting centers at the current time. This method allows one to study the dynamics of the system and obtain information about its transport properties. For example, within the framework of classical MD modeling, there are methods for calculating the self-diffusion of solvent molecules and the conducting subsystem of the electrolyte, as well as the ionic conductivity and viscosity of a multicomponent electrolyte system as a whole [46, 47, 49, 50].

Ab initio MD combines the principles of quantum mechanics and molecular dynamics, enabling the modeling of chemical reactions and other processes involving changes in electronic structure. An important practical advantage of Ab initio MD is its ability to correctly describe the effects of electron polarization and partial displacement of electron density without preliminary, labor-intensive parameterization of this physical process for different combinations of functional groups [10, 51]. Electronic polarization is an extremely common phenomenon in ion-molecular systems, capable of significantly affecting the structures of solvate complexes and the thermodynamics of the solvation process itself. The magnitude of electron polarization is directly proportional to the difference from zero of the formal charge of the participating cation or anion. While Ab initio MD is capable of producing more realistic simulation results, its cost is orders of magnitude higher than that of classical MD simulation. Therefore, Ab initio MD can only be used for isolated ion clusters and ionic solvates [10].

The Monte Carlo Metropolis method is an alternative to molecular dynamics for studying the motion of a system along PEL [52–55]. This method is used to generate system configurations corresponding to a given probability distribution. The system follows the direction belonging to PEL, which corresponds to a decrease in the potential energy of the system [56]. Unlike MD, the evolution of the system does not require the calculation of energy gradients (forces acting on atoms) and does not use a time step for integrating the equations of motion. The predominant area of application of the method turned out to be equilibrium physicochemical systems [39, 53, 56–59]. Consequently, the most natural application of the Monte Carlo Metropolis method seems to be the possibility of studying thermodynamic properties and phase transitions [6, 60–61].

The kinetic energy injection method allows one to purposefully search for low-energy stationary points by periodic kinetic excitation of the system under study [12, 62, 63]. This method combines equilibrium semi-empirical MD with a stochastic component. While MD modeling progressively leads the system to its minimum potential energies, artificially introduced excitation allows one to avoid lingering in local potential valleys. Thus, the system quickly finds itself in realistic microscopic ion-molecular configurations regardless of the energy of an arbitrarily chosen initial state. It is worth noting that a certain modification of particle momenta does not lead to the formation of unphysical ion-molecular configurations, but at the same time changes the current phase trajectory of the system [10, 64–66]. Thus, kinetic energy injection, compared to the standard MD method, allows the system to visit a larger number of microscopic states of its own phase space (Fig. 2).

Experimental research methods provide important information on the structure and dynamics of electrolyte solutions, which can be used to validate and refine theoretical models. X-ray diffraction allows one to determine the spatial arrangement of atoms and molecules in solution [68]. Neutron diffraction is sensitive to light atoms such as hydrogen, making it useful for investigating the structure of solvents [38]. Nuclear magnetic resonance spectroscopy provides information on the local structure and dynamics of molecules in solution [69]. Raman spectroscopy is used to study the vibrational modes of molecules and obtain information on intermolecular interactions. Electrochemical methods such as cyclic voltammetry, impedance spectroscopy, and others allow one to study the electrochemical properties of solutions and the kinetics of electrode reactions [66].

PEL has a fundamental influence on various properties of electrolyte solutions, which determine their effectiveness in various applications. Ionic conductivity is a key parameter of electrolytes, determining the efficiency of charge transfer in electrochemical devices. PEL influences ionic conductivity in the following ways. PEL determines

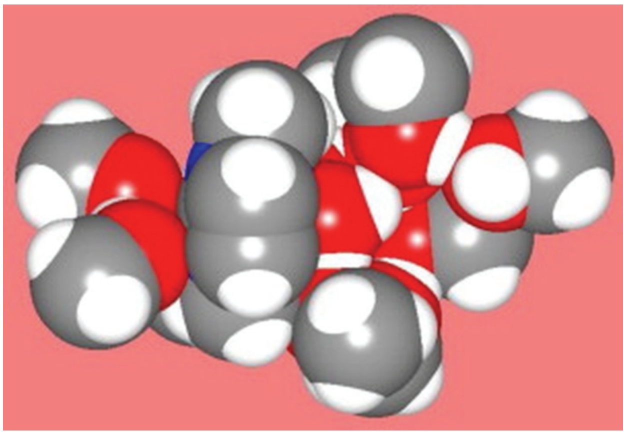


Fig. 2. Solvation shell of the imidazolium cation in a mixture of water and methanol. Reproduced from the author's source [67] with permission from Elsevier. Copyright Elsevier (2024)

the energy barriers that ions must overcome to move in solution. The lower the activation energy, the higher the ionic mobility and, consequently, the conductivity of the electrolyte solution. PEL reflects the coordination of ions by the solvent, which in turn affects their mobility. PEL contains information about the strength of interactions between ions and the formation of ion pairs. The combination of cations and anions in an electrolyte solution is considered undesirable in the context of practical applications, as it leads to a decrease in ionic conductivity. Electrolyte development involves selecting optimal concentrations of all its components to minimize the formation of ionic aggregates. The dependence of ionic conductivity on the mole fraction of ions in the electrolyte contains a maximum corresponding to the desired properties of the system (Fig. 3).

The electrochemical stability of an electrolyte determines its ability to resist decomposition at high voltages, which is critical for the operation of batteries and other devices [71]. The shape of certain PEL regions and specific energy differences in the system describe electrochemical stability. In particular, PEL determines the energy required to decompose solvent molecules or other electrolyte components. Interactions with electrodes can also be reflected in PEL if they were included in the model system during the theoretical study of the landscape. PEL determines the energy of interaction between the electrolyte and the electrodes and provides an estimate of the possibility of the formation of passivation layers or the occurrence of other undesirable reactions [72].

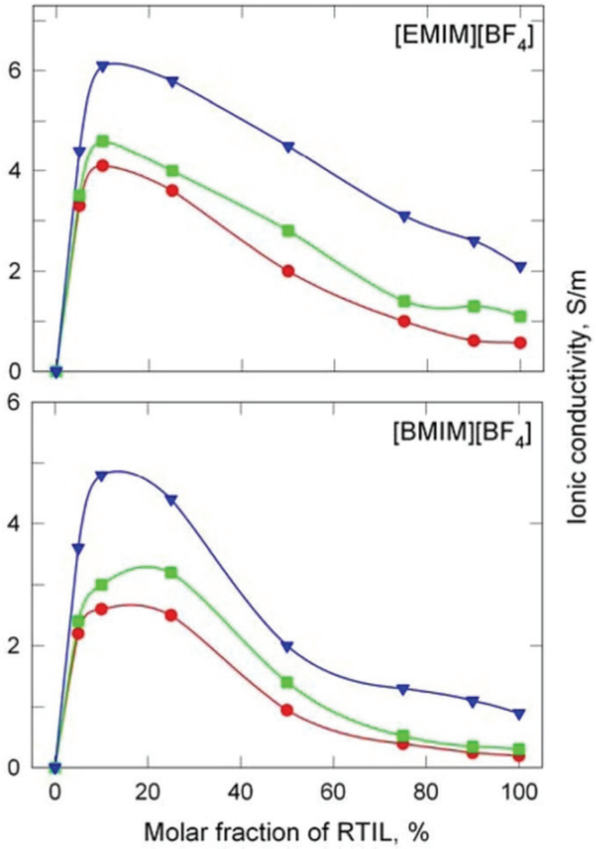


Fig. 3. Calculated maximum conductivity in mixtures of ionic liquids, [EMIM][BF4] and [BMIM][BF4], with acetonitrile at 283 K (red circles), 298 K (green squares), and 323 K (blue triangles). Reproduced from the author’s source [70] with permission from the American Chemical Society. Copyright ACS (2024)

Electrolyte viscosity affects the transport properties and the operating efficiency of electrochemical devices [73, 74]. Viscosity is associated with energy gradients observed in PEL. Intermolecular interactions that determine PEL characterize the strength of interactions between solvent molecules and ions, which affects the viscosity of the solution.

PEL reflects the possible microscopic states of the electrolyte solution at different temperatures and pressures. The structure of an electrolyte solution, among other things, implies the formation of clusters or other ordered structures, which can also dramatically affect viscosity.

Therefore, information on PEL can be used for the rational design of new electrolyte solutions with improved characteristics. PEL analysis enables the selection of the most suitable solvent that ensures optimal ion solvation and minimal activation energy for ion transport. PEL allows for the quantitative assessment of the strength of interactions between ions and the selection of a salt that minimizes ion association and ensures high ionic conductivity. PEL also allows for the study of the influence of additives on the structure and properties of an electrolyte, such as viscosity, electrochemical stability, and electrode wettability [75].

For the past two decades, ionic liquids have been considered a promising basis for liquid electrolyte systems. The low volatility of these compounds eliminates electrolyte loss at any stage of production and operation of a chemical power source. Some ionic liquids exhibit only minor toxicity to humans and animals or are generally considered harmless. The wide range of liquid states, especially at low temperatures, opens up new frontiers for the application of such electrolytes. Because ionic liquids do not contain molecules, their use as electrolytes enables previously unheard-of concentrations of cations and anions in the system. However, a current problem is the high viscosity and, consequently, the mediocre electrical conductivity of these chemical compounds. To stimulate ion transport in electrolytes, optimal mixtures of ionic and molecular liquids are being developed, for example, those containing acetonitrile, methanol, or propylene carbonate [76]. PEL enables the study of the structure and properties of ionic liquids, as well as the above-described mixtures, which remain promising electrolytes for various electrochemical applications [70].

Beyond the scope of electrolyte solutions, the versatility of PEL as a source of information on a wide range of chemical and physicochemical properties of a prototype system should be noted. Similar to the cases described above, studying PEL allows us to investigate the mechanisms of ion transport in solid and polymer electrolytes and develop new materials with higher ionic conductivity. This goal can potentially be achieved by suppressing undesirable atom-atom interactions. Naturally, such modification of the electrolyte system also requires synthetic efforts on the part of the electrochemical laboratory.

Ion migration in liquid electrolyte solutions is a complex physical process that requires overcoming certain energy barriers. These barriers arise from the interaction of the migrating ion with surrounding atoms or molecules. For ion migration in an electrolyte, several significant energy barriers of varying heights must be overcome. The specific values of the activation barriers within ion transport depend on the nature of the solvent and the electrostatic charge of the ion. For example, it is well known that the solvation of cations in the vast majority of cases is described by higher potential energies than the solvation of anions [77].

Using PEL, it is possible to calculate the activation energy for an ion to leave its solvation shell. Ions in an electrolyte are surrounded by solvent molecules, forming a solvation shell. For an ion to begin moving, it must break these bonds, which requires energy. Next, it must overcome an energy barrier to move the ion through the electrolyte. Ion movement in the electrolyte is hindered by interactions with other ions and solvent molecules. The ion must overcome electrostatic attraction and repulsion forces, as well as van der Waals forces. An energy barrier also accompanies the ion's entry into its new solvation shell. When the ion reaches its destination, it must form new bonds with solvent molecules to create a new solvation shell. A correctly calculated PEL contains complete thermodynamic information characterizing the processes described above [78].

The following factors influence the heights of energy barriers. The type of solvent and solutes initially determines the energy barriers. For example, solvent viscosity affects the energy required for ion movement. The higher the ion concentration, the stronger the interaction between them, which increases energy barriers. Increasing temperature increases the kinetic energy of ions, which helps them overcome energy barriers. An external electric field can lower the energy barriers to ion movement in a given direction.

The magnitude of the energy barriers in PEL at the microscopic level determines the macroscopic characteristics of the electrolyte. The lower the energy barriers, the higher the ion mobility and, consequently, the ionic conductivity of the electrolyte. Energy barriers affect the rate of ion diffusion in the electrolyte and the dynamics of charging and discharging [78]. Understanding the energy barriers to ion migration is key to the development of new electrolytes with improved characteristics, for example, for use in batteries, fuel cells, and other electrochemical devices.

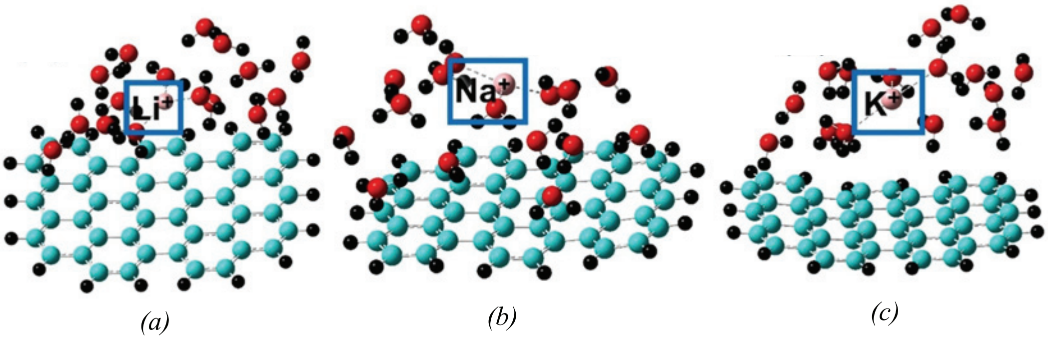
PEL allows for the modeling of processes occurring in batteries [79], such as ion intercalation, the formation of passivation layers, and electrolyte degradation. Furthermore, PEL enables the modeling of charge and mass transfer processes in fuel cells and the optimization of their design. Finally, PEL enables the modeling of charge storage processes in supercapacitors and the development of new high-capacity materials [78].

Research into PEL has enabled the development of new electrolytes with high ionic conductivity and electrochemical stability, leading to batteries with increased efficiency, capacity, reduced production costs, and extended service life. Similar research into supercapacitors has enabled the increase of their capacity and charging rates [80, 81].

Lithium-sulfur batteries have a high theoretical capacity, but their practical application is limited by several issues, such as the dissolution of lithium polysulfides and the low electrical conductivity of sulfur. Research into PEL allows us to understand the mechanisms of these processes and develop electrolytes that minimize polysulfide dissolution and increase sulfur conductivity. For example, the use of electrolytes with a high salt content or the addition of special additives can significantly improve the performance of lithium-sulfur batteries [82]. Sodium-ion batteries are considered a promising alternative to lithium-ion batteries due to their lower cost and greater availability of sodium. However, sodium ions are larger in size and mass than lithium ions, resulting in reduced ionic conductivity and deterioration of electrode reaction kinetics. Studying PEL allows for optimization of electrolyte compositions for sodium-ion batteries, for example, by selecting solvents with high permittivity and low viscosity, as well as by adding salts with high solubility and low activation energy for sodium ion transport [10, 51]. Modeling PEL allows for inclusion of the electrode in the analysis and an energetic description of the electrolyte behavior in a charged device (Fig. 4).

Studying the influence of temperature and pressure on PEL helps understand how electrolyte properties change under various operating conditions. Taking into account the shape of PEL in an applied electric field allows us to understand charge transfer mechanisms in electrolytes and optimize the operation of electrochemical devices [83]. Electrolyte–electrode surface interactions are important for understanding the mechanisms of electrode reactions. Thus, it is possible to propose new, improved materials with improved electrochemical properties.

The development of theoretical methods for studying PEL opens new possibilities for the development of electrolyte solutions with improved characteristics [84–85]. A comparative analysis of modern approaches (Table 1) demonstrates their complementarity.



(a) *(b)* *(c)*

Fig. 4. Low-energy ion-molecular configurations of lithium, sodium, and potassium ions on the surface of a negatively charged graphene electrode. Dashed lines indicate the water molecules closest to the ions. Reproduced from the author's source [51] with permission from Elsevier. Copyright Elsevier (2024)

Table 1. Comparative assessment of the methods for studying PEL presented in this paper and their application

Method	Essence of the method	Potential opportunities	Disadvantages
Quantum-chemical calculations (DFT) [7, 12, 43-45]	Solution of quantum mechanical equations to calculate the electronic structure and total energy of a system	High accuracy, study of chemical reactions, bond breaking / formation, electron polarization, parametrization of force fields for classical methods	Extremely high computational costs. Inapplicable to large systems (>1000 atoms) and long processes
Classical Molecular Dynamics (MD) [22, 46-47, 49]	Simulation of atomic motion based on classical Newton's laws using predefined force fields	Simulation of large systems (millions of atoms) over nanoseconds and microseconds. Calculation of transport properties: ionic conductivity, viscosity, and self-diffusion coefficients	Accuracy depends entirely on the quality of the force field parameterization. It does not take into account chemical reactions or electron polarization (without special polarizable fields)
Ab initio molecular dynamics (AIMD) [10, 23, 51]	A combination of quantum chemical calculations (usually DFT) and molecular dynamics. Forces are calculated on the fly from first principles	The most accurate modeling, taking into account the electronic structure. Correct description of reactions, polarization, and charge transfer. It does not require parameterization of force fields	The most resource-intensive method. Limited to very small systems (hundreds of atoms) and picosecond time scales

Continued Table 1

Method	Essence of the method	Potential opportunities	Disadvantages
Monte Carlo (Metropolis) Method [6, 52–55]	A stochastic method for generating system configurations according to a given distribution (e.g., canonical NVT)	Efficient calculation of equilibrium thermodynamic properties (free energies, phase diagrams). It does not require calculation of forces (energy gradients)	It does not provide information on the dynamics and kinetics of processes (no concept of time). Not applicable for direct calculation of transport properties
Kinetic Energy Injection Method [12, 62, 63]	A modification of MD in which the system periodically receives kinetic excitation to escape from local PEL minima	It effectively searches for the global energy minimum and low-energy configurations. It allows one to avoid "stuckness" and more fully explore the phase space	It introduces a non-physical stochastic element. It requires careful selection of injection parameters to avoid artifacts and non-physical states
Experimental methods (for validation) [38, 66, 69]	X-ray and neutron diffraction, NMR, Raman spectroscopy, and electrochemical methods	Provide direct data on the structure, dynamics, and macroscopic properties of real systems. Critically important for testing and refining theoretical models	They provide averaged information, often without atomic detail. They do not allow one to directly "see" PEL, but only its consequences

Advances in methods for calculating the potential energy of a system can enable the study of electrolyte systems with more complex compositions and provide more information about PEL. The combination of theoretical calculations and experimental data will provide a more symbiotic understanding of PEL and use this information for the rational design of new electrolytes. Finally, the application of machine learning methods to PEL analysis will accelerate the development of new electrolytes and optimize their properties [83].

3. Conclusion

This paper analyzed a significant number of the most recent literature sources, covering both comprehensive studies of electrolyte solutions using molecular modeling methods to describe PEL, and auxiliary computer calculations to confirm experimental results.

Based on this critical analysis, we believe it is appropriate to draw the following conclusions. Studying PEL is a powerful tool for analyzing and predicting the properties of electrolyte solutions. The use of research methods based on classical and quantum chemical approaches allows us to obtain unique physical information. First, it seems possible to study in detail the intermolecular and ion-molecular interactions that determine the macroscopic properties of an electrolyte solution. Ionic conductivity, viscosity, and density can be calculated using analytical relationships based on statistical processing of the system's phase trajectory. Second, it is easy to identify stable configurations of ions and solvates that influence the equilibrium state of the electrolyte and the mechanisms of ion transport within it. Third, the resulting thermodynamic properties of the simulated system and the energies of paired ion-molecule interactions allow us to estimate barriers to ion migration, which is directly related to electrolyte conductivity.

Thus, the combination of PEL research methods with experimental data opens new prospects for the targeted design of electrolyte solutions with specified characteristics, which is crucial for the development of highly efficient electrochemical devices.

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V.V. Chaban is a visiting professor and international consultant at Yerevan State University.

5. Conflict of interest

The authors declare no conflict of interest.

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