

Macroscopic approach to studying the structure of concentrated aqueous LiTFSI solutions

Y. Zhigalenok, S. Abdimomyn, M. Ryabicheva, M. Lepikhin, A. Galeyeva, F. Malchik*

Center of Physical-Chemical Methods of Research and Analysis, Al-Farabi Kazakh National University,
96A, Tole bi str., Almaty, Kazakhstan

ABSTRACT

This work systematically studies the physicochemical properties of aqueous LiTFSI solutions across a wide range of concentrations. The solutions' density, viscosity, electrical conductivity, and water activity were measured, establishing quantitative relationships between macroscopic parameters and structural characteristics of the electrolyte. Analysis of electrical conductivity, incorporating viscosity corrections, demonstrated nearly complete ionic association at high concentrations (above 10 mol/kg), with water activity reaching exceptionally low values (~ 0.15) at maximum solubility. The study revealed nonlinear density changes with increasing concentration, indicating substantial structural reorganization in concentrated solutions. Hydration numbers, calculated using a novel thermodynamic approach combining water activity and conductivity data, showed unexpected solvation behavior: LiTFSI exhibited higher hydration numbers than traditional lithium salts in dilute solutions despite lower TFSI⁻ charge density, attributed to spatial trapping of water molecules by its bulky structure. This pattern inverted at higher concentrations due to increased ionic association and charge screening effects. The calculated parameters aligned well with molecular dynamics simulations, validating our macroscopic approach. The study demonstrated that standard physicochemical measurements can accurately determine electrolyte structural parameters, offering practical advantages for optimizing electrolyte compositions, particularly in systems containing polymer additives and co-solvents where molecular dynamics modeling faces significant challenges.

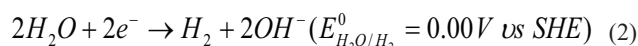
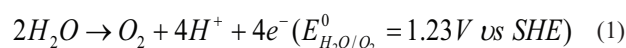
Keywords: lithium-ion batteries, aqueous electrolytes, LiTFSI, physicochemical properties, water activity, hydration numbers, ionic association

1. Introduction

Despite widespread use, modern lithium-ion batteries encountered safety and environmental issues due to their flammable organic electrolytes that release toxic products [1]. This has driven research toward alternative systems, particularly aqueous electrolytes [2]. Water as an electrolyte solvent offers key advantages: high ionic conductivity, low viscosity for effective ion transport [3,4], facilitating effective metal ion transport and is environmentally safe, non-flammable, and cost-effective for large-scale production [5].

However, aqueous electrolytes are limited by their narrow electrochemical stability window (ESW) [5].

ESW, the potential range where the electrolyte is thermodynamically stable without redox reactions [6], is only 1.23 V (thermodynamic value) for water due to its decomposition reactions [7]:



This narrow window creates major obstacles for aqueous electrolytes' practical use. It restricts electrode material selection, as their working potentials must fit within the stability region [8]. Even within these limits, local potential exceedance during cycling may cause parasitic hydrogen or oxygen evolution, leading to electrode corrosion, battery self-discharge, and dangerous gas pressure buildup [6,9].

*Ответственный автор
E-mail: frodo-007@mail.ru

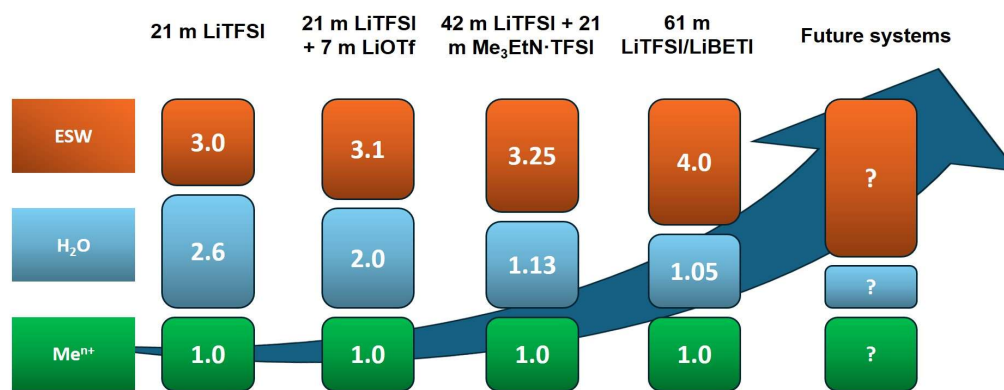


Fig. 1. Scheme illustrating the decrease in $\text{Me}^{n+}/\text{H}_2\text{O}$ ratio with WiSE development.

Aqueous lithium-ion batteries are limited to single cell voltage of 1.35-2 V (practical value), compared to 3.5-4.2 V in traditional organic systems. The development of stable aqueous electrolytes has focused on increasing salt concentration, leading to «Water-in-Salt» electrolytes (WiSE). Initial studies used 5 M LiNO_3 [10] and 13.5 M LiCl , where water molecules form $\text{Li}(\text{H}_2\text{O})_n^+$ complexes ($n \approx 4$), reducing free water susceptible to decomposition [11]. In 2012, Aurbach's group has achieved 1.5 V using WiSE with 2 M Li_2SO_4 , in combination with a Chevrel phase Mo_6S_8 anode and $\text{Li}_x\text{Mn}_2\text{O}_4$ cathode [12].

In 2015, Suo et al. developed a WiSE with 21 mol/kg lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (salt:water ratio 1:2.6) [13]. The fluorinated anion enabled dense SEI formation on the anode, ensuring high voltage stability and extending the electrochemical window to 3.0 V [14].

After 2015, the WiSE concept evolved into «water-in-bisalt» (WIBS), using LiTFSI and LiOTf to bind free water, extending the stability window to 3.1 V [15]. The combination (21m LiTFSI + 7m LiOTf) produces a molten electrolyte with Li^+ concentration of 28 m and cation/water ratio of 1:2 [16]. This allows stable SEI formation, enabling $\text{LiMn}_2\text{O}_4/\text{TiO}_2$ batteries with a voltage of 2.1 V and energy density of 100 Wh/kg.

In 2020, a WIBS electrolyte (42m LiTFSI + 21m $\text{Me}_3\text{EtN-TFSI}$) achieved a total concentration of 63m [17]. $\text{Me}_3\text{EtN-TFSI}$ increased the solubility of LiTFSI and improved SEI formation. At a salt/water ratio of 1.13, it extended the ESW to 3.25 V, enabling $\text{LiMn}_2\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ batteries with 2.5 V and 145 Wh/kg for 150 cycles [17].

From 2015-2020, WiSE evolved significantly, with increasing salt molality expanding ESW (Fig. 1). The concept was extended to NH_4^+ , Na^+ , K^+ and Zn^{2+} systems for various metal-ion batteries [18]. The parallel development of acetate-based

[19,20], modified anion and imidazolium ionic liquid electrolytes [21,22] improved salt solubility. The NaFSA/ElMeImTFSI system now achieves 80 mol/kg molality at ~ 5.0 V ESW [21]. These achievements opened new possibilities for creating safe and stable aqueous electrolytes with high energy efficiency. But can we still call it aqueous-based electrolyte?

In this work, using LiTFSI – one of the most commonly used “water-in-salt” type electrolyte - quantitative correlations between water activity, transport characteristics (viscosity, conductivity), and structural parameters (hydration numbers, degree of ionic association) of the electrolyte have been established for the first time. The identified patterns allow the prediction of the electrochemical behaviour of new compositions based on their macroscopic properties, which significantly simplifies the optimization of electrolyte systems for practical application in batteries.

2. Experimental section

The lithium salt bis-(trifluoromethanesulfonyl)imide(LiTFSI)with 99%purity from ThermoScientific was used in this work. All measurements were conducted at a constant temperature of 25 °C with preliminary thermostating of solutions.

Solution density was measured gravimetrically using a 5 mL Mohr pipette after thermostating at 25 °C for 30 min. Samples were weighed on analytical balances (accuracy 0.0001 g) and the results averaged from three parallel measurements.

Water activity was measured using AQUALAB TDL 2 (Meter Group, ± 0.005 accuracy) with 3 mL samples. The instrument combines dew point determination (chilled mirror sensor) and absorption spectroscopy (TDL), where water absorption is proportional to its activity.

Solution viscosity was measured with SV-1A vibration viscometer (A&D, Japan), based on damping oscillations of plates in liquid. Measurements used 2 mL samples at 25 °C after 15-minute equilibration.

Solution conductivity was measured using a YSI 3200 conductometer with a YSI 3254 cell, calibrated with KCl standard solutions and temperature compensated to 25 °C.

3. Results and discussion

Solution volume increases significantly with salt concentration due to both direct salt addition and ion solvation processes. When ions form solvation shells with water molecules [23], they reorganize the solvent structure, leading to volume changes beyond the simple addition of components [7].

A crucial factor in developing highly concentrated electrolytes is the salt-to-water molar ratio, as it determines solvation shell structure and electrochemical stability. Higher salt ratios lead to saturated lithium-ion solvation shells and fewer free water molecules, suppressing electrochemical decomposition.

Traditional molar concentration (moles per liter of solution) is suboptimal for characterizing these electrolytes because solution volume changes significantly with increasing salt concentration. Since the same molarity can correspond to different salt/water ratios, and volume changes vary by salt type, molar concentration becomes inadequate for comparing different highly concentrated electrolytes or optimizing their composition.

Unlike molar concentration, molal concentration determines the number of moles of solute per kilogram of solvent, making it particularly convenient for characterizing highly concentrated electrolytes. Since the solvent mass (1 kg of water) remains constant regardless of the amount of salt added and solution volume changes, molal concentration directly reflects the ratio between the number of moles of salt and solvent [24,25].

The relationship between molal concentration (m) and the molar salt/water ratio (r) can be expressed by the following equation:

$$r = \frac{n_{salt}}{n_{water}} = \frac{m \cdot M_{water}}{1000} \quad (3)$$

where M_{water} is the molar mass of water (18.015 g/mol), m – the molal concentration of salt [mol/kg], n_{salt} – the amount of salt [mol], n_{water} – the amount of water [mol].

Thus, by multiplying the molal concentration by water's molar mass and dividing by 1000, we directly obtain the molar salt/water ratio.

Molar and molal concentrations are related through solution density (ρ) by the following relationship [24,25]:

$$C = \frac{m \cdot \rho}{1000 + m \cdot M_{salt}} \quad (4)$$

where C is the molar concentration of solution [mol/l], m is the molal concentration of solution [mol/kg], ρ – the density of solution [kg/m³], M_{salt} – the molar mass of salt [g/mol].

Considering the nonlinear relationship between molar and molal concentrations, determined through solution density, experimental investigation of electrolyte density dependence on LiTFSI molal concentration becomes important. These measurements allow not only establishing the nature of density changes with increasing salt concentration but also enable quantitative conversion between different concentration expression methods for practical use. Figure 2 shows the experimentally obtained dependence of LiTFSI aqueous solution density on its molal concentration at room temperature.

As can be seen from the presented relationship (Fig. 2), the solution density increases significantly with increasing LiTFSI concentration; however, this increase is nonlinear. When salt is added to water, the mass of the solution increases linearly – proportionally to the mass of added salt. However, the change in solution volume has a more complex character, determined by intermolecular interactions.

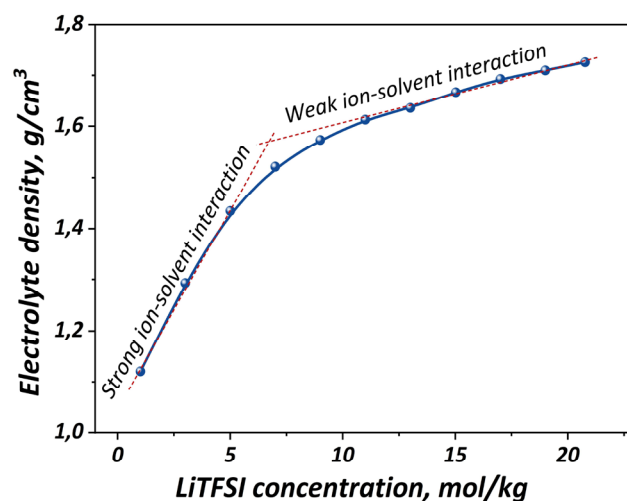


Fig. 2. Dependence of aqueous LiTFSI solution density on molal concentration at 25 °C.

At low concentrations, a sharp density increase occurs as salt ions form compact solvate complexes, effectively filling water structure voids without major disruption. However, at higher concentrations, the density increase becomes more gradual. This change indicates a structural shift where ion pairs and larger aggregates form, interacting more weakly with the solvent and leading to greater volume increases with each salt addition. The system begins to approach ideal solution behavior as specific intermolecular interactions weaken.

Conductivity measurements provide additional confirmation of these structural changes, as conductivity directly reflects charge carrier mobility and concentration in solution. The specific conductivity results for LiTFSI solutions (Fig. 3a) support the formation of ionic associates at high concentrations.

The concentration dependence of LiTFSI aqueous solution specific conductivity demonstrates a characteristic maximum for electrolytes in the medium concentration region. The initial conductivity increase in dilute solutions is due to the increase in charge carriers – lithium and TFSI- ions - in solution. However, with further increase in salt concentration, a decrease in conductivity is observed, which can be explained by the formation of ionic associates that do not participate in charge transfer [25,26].

The degree of salt dissociation (α) can be estimated using Kohlrausch's law from conductivity data. This involves determining the ratio of solution equivalent conductivity (Λ) to limiting equivalent conductivity at infinite dilution (Λ_0) [24,25]:

$$\alpha = \frac{\Lambda_i}{\Lambda_0} \quad (5)$$

where, α is the dissociation degree, Λ_i is the equivalent conductivity of the solution [$\text{S}\cdot\text{m}^2/\text{mol}$], and Λ_0 is the

limiting equivalent conductivity at infinite dilution [$\text{S}\cdot\text{m}^2/\text{mol}$].

In Eq. (5), equivalent conductivity Λ_i is related to specific conductivity (κ) by the relationship:

$$\Lambda_i = \frac{\kappa}{C} \quad (6)$$

where C is the molar concentration of electrolyte [mol/m^3], κ – is specific conductivity of electrolyte [S/m]. The limiting equivalent conductivity Λ_0 can be determined by extrapolating the dependence of Λ_i on $\sqrt{C}$ to zero concentration – shown in Fig. 3b. In our case for LiTFSI solution, the $\Lambda_0 = 6.17 \text{ mS}\cdot\text{m}^2/\text{mol}$.

For correct estimation of salt dissociation degree, it's necessary to consider that ion mobility in solution significantly depends on medium viscosity. This relationship is described by Walden's rule, according to which the product of solution molar conductivity and medium viscosity remains approximately constant:

$$\Lambda_i \cdot \eta = \text{const} \quad (7)$$

where η is the viscosity of solution [$\text{mPa}\cdot\text{s}$].

To separate these effects, measurements of dynamic viscosity of LiTFSI solutions at various concentrations were conducted (Fig. 4a). The obtained dependence demonstrates exponential viscosity grow with increasing salt concentration. Particularly sharp viscosity increase is observed at concentrations above 3 mol/kg, which corresponds to the region of substantial solution conductivity decrease. Such behavior can be explained by forming a developed network of interion interactions in concentrated electrolyte, which significantly hinders particle movement in solution.

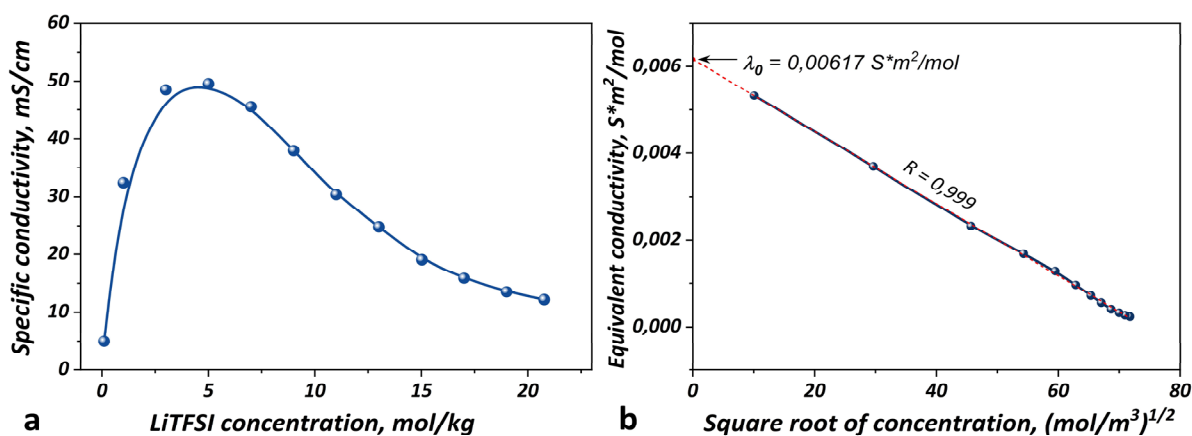


Fig. 3. (a) Dependence of specific conductivity of aqueous LiTFSI solution on molal concentration; (b) Dependence of equivalent conductivity on the square root of molar concentration.

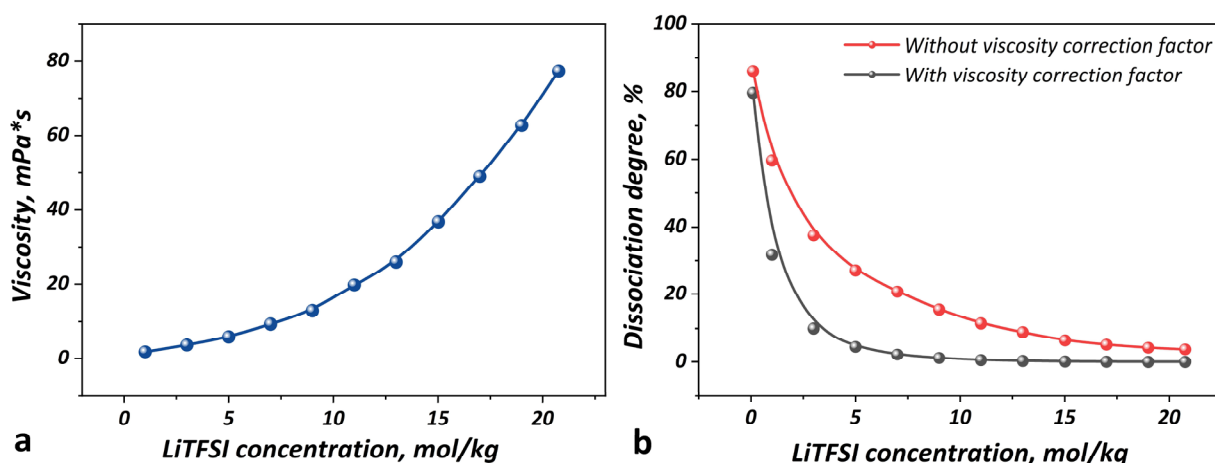


Fig. 4. (a) Dependence of dynamic viscosity of aqueous LiTFSI solution on molal concentration at 25 °C; (b) Dependence of LiTFSI dissociation degree in aqueous solution on molal concentration. Black curve - values corrected for viscosity; red curve - values without viscosity correction.

Considering Walden's rule, for the correct estimation of dissociation degree, it's necessary to introduce a correction for medium viscosity changes. The corrected molar conductivity ($\Lambda_{corrected}$), accounting for viscosity influence, can be calculated using the formula [25]:

$$\Lambda_{corrected} = \Lambda_i(\eta / \eta_0) \quad (8)$$

where η_0 – is pure water viscosity [mPa·s], η is solution viscosity at given salt concentration [mPa·s]. Dissociation degree accounting for viscosity correction is determined as [25]:

$$\alpha = \frac{\Lambda_{corrected}}{\Lambda_0} \quad (9)$$

Figure 4b shows the dependence of the corrected LiTFSI dissociation degree on electrolyte concentration.

As shown in Fig. 4b, incorporating viscosity effects dramatically alters our understanding of ionic association in concentrated solutions. The viscosity-corrected data (black curve) reveals a much steeper decline in dissociation degree with increasing concentration compared to uncorrected values (red curve). This correction reveals that at high concentrations (above 10 mol/kg), ions are almost completely associated, rather than maintaining the significant fraction of free ions suggested by uncorrected data.

The combined analysis of density, conductivity, and viscosity demonstrates that in the high-concentration region typical of «water-in-salt» electrolytes, the solution structure fundamentally changes with the formation of large ionic aggregates.

Water activity quantifies how effectively ions bind solvent molecules and suppress water decomposition reactions. Our previous research [27] has shown that water activity, not total salt concentration, primarily determines aqueous electrolyte electrochemical stability, as decomposition processes involve only unbound water molecules whose concentration is directly reflected by their activity. Figure 5 shows the experimentally obtained dependence of water activity on LiTFSI molal concentration in aqueous solution at room temperature.

As seen from Fig. 5, with increasing LiTFSI concentration, a regular decrease in water activity in solution is observed. It's particularly important to note that at maximum salt solubility (21 mol/kg), water activity reaches an exceptionally low value—around 0.15. Such low water activity means that the vast majority of water molecules are strongly bound in solvate complexes with ions, which is characteristic for «water-in-salt» electrolytes and determines their unique electrochemical properties.

For quantitative understanding of aqueous electrolyte structure and the nature of interactions between its components, determining ion hydration numbers is of key importance. Determining hydration numbers based on electrolyte macroscopic parameters - water activity and dissociation degree - is particularly valuable. Such an approach has several substantial advantages over direct structural research methods. First, it doesn't require complex equipment and can be implemented within standard physicochemical measurements. Second, the obtained values reflect an averaged solvation throughout the solution volume, which is especially important for practical applications. Third, joint use of water activity and dissociation degree data allows

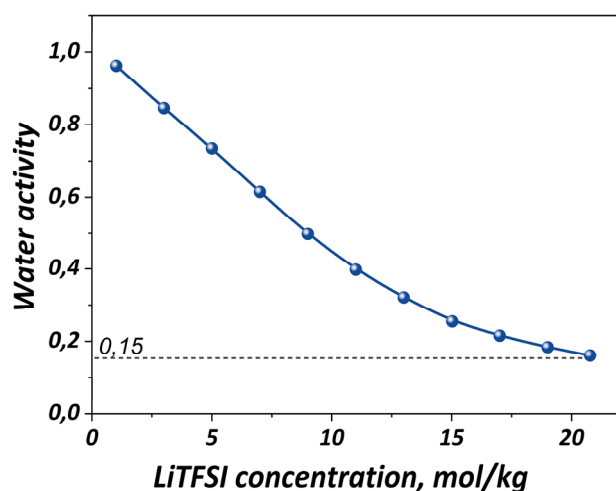


Fig. 5. Dependence of water activity on molal concentration of LiTFSI in aqueous solution at 25 °C.

accounting for different hydration characteristics of free ions and ion pairs, which is critical for a correct description of concentrated solutions.

The fundamental thermodynamic relationship proposed in work [28] can be used to determine hydration numbers. This equation is based on analysis of solvent molecule distribution between solvation shells and bulk phase, accounting for electrolyte dissociation degree:

$$h = \frac{55.51}{m} - \frac{a_w}{1 - a_w} (1 + \alpha) \quad (10)$$

where h – the hydration number, a_w is the water activity.

The physical meaning of this equation is that it accounts for two main effects: direct binding of water molecules in solvation shells (through activity ratio $a_w/(1-a_w)$) and additional contribution from salt

dissociation (factor $(1+\alpha)$). With complete dissociation ($\alpha = 1$), each formula unit of salt binds twice as many water molecules as in the case of complete association ($\alpha = 0$), which reflects the formation of separate solvation shells around each ion.

Using the previously obtained experimental data on water activity (Fig. 5) and viscosity-corrected dissociation degree (Fig. 4), hydration numbers were calculated for LiTFSI solutions at various concentrations. The calculation was performed using Eq. (14) to obtain quantitative characterization of electrolyte solvation structure across the entire studied concentration range.

Figure 6 shows the concentration dependence of calculated LiTFSI hydration numbers and hydration numbers for LiCl electrolyte, another common “water-in-salt” electrolyte [29–31] for comparison.

The data in Fig. 6 reveals an unexpected pattern in hydration number changes across concentrations for different lithium salts. In dilute solutions, LiTFSI shows higher hydration numbers than LiCl despite TFSI[−] lower charge density. This stems from the TFSI[−] anion’s large spatial dimensions – while its delocalized charge results in weaker electrostatic interactions with water molecules, its bulky structure creates steric hindrances that spatially trap solvent molecules between anions.

At higher concentrations, this pattern inverts, with LiTFSI showing lower hydration numbers than LiCl. This inversion correlates with increased ionic association in concentrated LiTFSI solutions, where large ionic aggregates screen charges and weaken water molecule interactions. The formation of these ionic associates also reduces the number of separately solvated particles in solution.

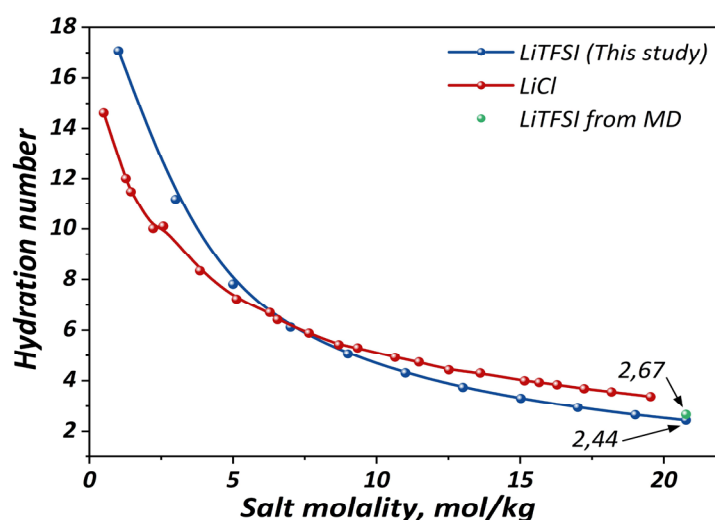


Fig. 6. Concentration dependence of LiTFSI and LiCl hydration numbers in aqueous solutions. Blue points – experimental data for LiTFSI obtained in this work; red points – data for LiCl from work [32]; green point – results of molecular dynamics modeling for LiTFSI from work [33].

The hydration numbers calculated from macroscopic parameters (water activity, conductivity, and viscosity) align well with molecular dynamics modeling results, validating that standard physicochemical measurements can accurately determine electrolyte structural parameters. This approach offers practical advantages for studying complex electrolyte systems with polymer additives and co-solvents, where molecular dynamics modeling faces challenges in constructing accurate force fields.

4. Conclusion

As a result of this research, systematic study of aqueous LiTFSI solutions revealed nonlinear density changes with increasing concentration, indicating substantial structural reorganization. Viscosity-corrected conductivity analysis demonstrated nearly complete ion association and aggregate formation at high concentrations. Water activity and conductivity measurements enabled quantitative characterization of solvation processes, showing that the bulky TFSI⁻ anion yields higher hydration numbers in dilute solutions despite low charge density, with this trend inverting at higher concentrations due to ionic aggregation and charge screening. The effectiveness of this macroscopic approach in studying electrolyte structure opens new possibilities for optimizing electrolyte compositions, with potential applications extending to systems containing polymer additives and co-solvents.

Acknowledgments

This research is funded by the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. AP14871970).

References

- [1]. Quintans De Souza G. A comparison between aqueous and organic electrolytes for lithium ion batteries // *Chemical Engineering, School of Engineering Sciences in Chemistry, Biotechnology and Health (CBH)*. – 2021. – Vol. SECOND CYC. – P. 1-34.
- [2]. Chao D., Zhou W., Xie F., Ye C., Li H., Jaroniec M., Qiao S.-Z. Roadmap for advanced aqueous batteries: From design of materials to applications // *Science Advances*. – 2024. – Vol. 6(21). – P. 4098.
- [3]. Kim H., Hong J., Park K.-Y., Kim H., Kim S.-W., Kang K. Aqueous Rechargeable Li and Na Ion Batteries // *Chemical Reviews*. – 2014. – Vol. 114(23). – P. 11788-11827.
- [4]. Pasta M., Wessells C.D., Huggins R.A., Cui Y. A high-rate and long cycle life aqueous electrolyte battery for grid-scale energy storage // *Nature Communications*. – 2012. – Vol. 3(1). – P. 1149.
- [5]. Ahn H., Kim D., Lee M., Nam K.W. Challenges and possibilities for aqueous battery systems // *Communications Materials*. – 2023. – Vol. 4(1). – P. 37.
- [6]. Borodin O. Challenges with prediction of battery electrolyte electrochemical stability window and guiding the electrode – electrolyte stabilization // *Current Opinion in Electrochemistry*. – 2019. – Vol. 13. – P. 86-93.
- [7]. Zhao Y., Hu X., Stucky G.D., Boettcher S.W. Thermodynamic, Kinetic, and Transport Contributions to Hydrogen Evolution Activity and Electrolyte-Stability Windows for Water-in-Salt Electrolytes // *Journal of the American Chemical Society*. – 2024. – Vol. 146(5). – P. 3438-3448.
- [8]. Xue L., Zhang Q., Huang Y., Zhu H., Xu L., Guo S., Zhu X., Liu H., Huang Y., Huang J., Lu L., Zhang S., Gu L., Liu Q., Zhu J., Xia H. Stabilizing Layered Structure in Aqueous Electrolyte via Dynamic Water Intercalation/Deintercalation // *Advanced Materials*. – 2022. – Vol. 34(13). – P. 2108541.
- [9]. Yang W., Yang Y., Yang H., Zhou H. Regulating Water Activity for Rechargeable Zinc-Ion Batteries: Progress and Perspective // *ACS Energy Letters*. – 2022. – Vol. 7(8). – P. 2515-2530.
- [10]. Li W., Dahn J.R., Wainwright D.S. Rechargeable Lithium Batteries with Aqueous Electrolytes // *Science*. – 1994. – Vol. 264(5162). – P. 1115-1118.
- [11]. Deutscher R.L., Florence T.M., Woods R. Investigations on an aqueous lithium secondary cell // *Journal of Power Sources*. – 1995. – Vol. 55(1). – P. 41-46.
- [12]. Levi M.D., Shilina Y., Salitra G., Aurbach D., Guyot E., Seghir S., Lecuire J.M., Boulanger C. Ultrafast anode for high voltage aqueous Li-ion batteries // *Journal of Solid State Electrochemistry*. – 2012. – Vol. 16(11). – P. 3443-3448.
- [13]. Suo L., Borodin O., Gao T., Olguin M., Ho J., Fan X., Luo C., Wang C., Xu K. “Water-in-salt” electrolyte enables high-voltage aqueous lithium-ion chemistries // *Science*. – 2015. – Vol. 350(6263). – P. 938-943.
- [14]. Han J., Zhang H., Varzi A., Passerini S. Fluorine-Free Water-in-Salt Electrolyte for Green and Low-Cost Aqueous Sodium-Ion Batteries // *ChemSusChem*. – 2018. – Vol. 11(21). – P. 3704-3707.
- [15]. Yamada Y., Usui K., Sodeyama K., Ko S., Tateyama Y., Yamada A. Hydrate-melt electrolytes for high-energy-density aqueous batteries // *Nature Energy*. – 2016. – Vol. 1(10). – P. 16129.

- [16]. Suo L., Borodin O., Sun W., Fan X., Yang C., Wang F., Gao T., Ma Z., Schroeder M., Cresce A. Von, Russell S.M., Armand M., Angell A., Xu K., Wang C. High-Voltage Aqueous Lithium-Ion Battery Enabled by “Water-in-Bisalt” Electrolyte // *Zuschriften*. – 2016. – Vol. 85287. – P. 7252-7257.
- [17]. Chen L., Zhang J., Li Q., Vatamanu J., Ji X., Pollard T.P., Cui C., Hou S., Chen J., Yang C., Ma L., Ding M.S., Garaga M., Greenbaum S., Lee H.-S., Borodin O., Xu K., Wang C. A 63 m Superconcentrated Aqueous Electrolyte for High-Energy Li-Ion Batteries // *ACS Energy Letters*. – 2020. – Vol. 5(3). – P. 968-974.
- [18]. Zhang H., Liu X., Li H., Hasa I., Passerini S. Challenges and Strategies for High-Energy Aqueous Electrolyte Rechargeable Batteries // *Angew Chem Int Ed* – 2021. – Vol. 60(2). – P. 598-616.
- [19]. Jiang L., Lu Y.-C. Building a Long-Lifespan Aqueous K-Ion Battery Operating at -35 °C // *ACS Energy Letters*. – 2024. – Vol. 9(3). – P. 985-991.
- [20]. Lukatskaya M.R., Feldblyum J.I., Mackanic D.G., Lissel F., Michels D.L., Cui Y., Bao Z. Concentrated mixed cation acetate “water-in-salt” solutions as green and low-cost high voltage electrolytes for aqueous batteries // *Energy Environ. Sci.* – 2018. – Vol. 11(10). – P. 2876-2883.
- [21]. Monti D., Jónsson E., Palacín M.R., Johansson P. Ionic liquid based electrolytes for sodium-ion batteries: Na⁺ solvation and ionic conductivity // *J Power Sources*. – 2014. – Vol. 245. – P. 630-636.
- [22]. Dhatarwal H.S., Kashyap H.K. Heterogeneity and Nanostructure of Superconcentrated LiTFSI–EmimTFSI Hybrid Aqueous Electrolytes: Beyond the 21 m Limit of Water-in-Salt Electrolyte // *The Journal of Physical Chemistry B*. – 2022. – Vol. 126(28). – P. 5291-5304.
- [23]. Ugata Y., Shigenobu K., Tatara R., Ueno K., Watanabe M., Dokko K. Solvate electrolytes for Li and Na batteries: Structures, transport properties, and electrochemistry // *Physical Chemistry Chemical Physics*. – 2021. – Vol. 23(38). – P. 21419-21436.
- [24]. Damaskin B.B., Petrii O.A., Tsirlina G.A. *Electrochemistry* (In Russian). 2nd ed., revised and updated. – Moscow: Khimiya, KolosS, 2006. – 672 p.
- [25]. Izmailov N.A. *Electrochemistry of solutions* 3rd edition (corrected) (In Russian), 1976. – 488 p.
- [26]. Farhat D., Lemordant D., Jacquemin J., Ghamouss F. Alternative Electrolytes for Li-Ion Batteries Using Glutaronitrile and 2-methylglutaronitrile with Lithium Bis(trifluoromethanesulfonyl) Imide // *Journal of The Electrochemical Society*. – 2019. – Vol. 166. – P. A3487-A3495.
- [27]. Zhigalenok Y., Abdimomyn S., Levi M., Shpigel N., Ryabicheva M., Lepikhin M., Galeeva A., Malchik F. Water activity: the key to unlocking high-voltage aqueous electrolytes? // *Journal of Materials Chemistry A*. – 2024. – Vol. 12. – P. 33855-33869.
- [28]. Bakeev M.I. *Hydration and Physicochemical Properties of Electrolyte Solutions* (In Russian). – Alma-Ata: Nauka Kaz SSR, 1978. – 244 p.
- [29]. Malchik F., Maldybayev K., Kan T., Kokhmetova S., Chae M.S., Kurbatov A., Galeeva A., Kaupbay O., Nimkar A., Bergman G., Levi N., Zhang H., Jin Q., Lin Z., Shpigel N., Mandler D. Boosting the capacity of MXene electrodes in neutral aqueous electrolytes // *Cell Reports Physical Science*. – 2023. – Vol. 4(7). – P. 101507.
- [30]. Malchik F., Maldybayev K., Kan T., Kokhmetova S., Kurbatov A., Galeeva A., Tubul N., Shpigel N., Djenizian T. Application of a conversion electrode based on decomposition derivatives of Ag₄[Fe(CN)₆] for aqueous electrolyte batteries // *RSC Advances*. – 2022. – Vol. 12(16). – P. 9862-9867.
- [31]. Bunpheng A., Sakulae P., Hirunpinyopas W., Nueangnoraj K., Luanwuthi S., Iamprasertkun P. Revisiting the properties of lithium chloride as “water-in-salt” electrolyte for pouch cell electrochemical capacitors // *Journal of Electroanalytical Chemistry*. – 2023. – Vol. 944. – P. 117645.
- [32]. Wahab A., Mahiuddin S. Isentropic compressibility and viscosity of aqueous and methanolic lithium chloride solutions // *Canadian Journal of Chemistry*. – 2011. – Vol. 80. – P. 175-182.
- [33]. Borodin O., Suo L., Gobet M., Ren X., Wang F., Faraone A., Peng J., Olguin M., Schroeder M., Ding M.S., Gobrogge E., von Wald Cresce A., Munoz S., Dura J.A., Greenbaum S., Wang C., Xu K. Liquid Structure with Nano-Heterogeneity Promotes Cationic Transport in Concentrated Electrolytes // *ACS Nano*. – 2017. – Vol. 11(10). – P. 10462-10471.

References

- [1]. Quintans De Souza G (2021) *Chemical Engineering, School of Engineering Sciences in Chemistry, Biotechnology and Health (CBH) SECOND CYC*:1-34.
- [2]. Chao D, Zhou W, Xie F, Ye C, Li H, Jaroniec M, Qiao S-Z (2024) *Sci Adv* 6(21):4098. <https://doi.org/10.1126/sciadv.aba4098>
- [3]. Kim H, Hong J, Park K-Y, Kim H, Kim S-W, Kang K (2014) *Chem Rev* 114(23):11788-11827. <https://doi.org/10.1021/cr500232y>

- [4]. Pasta M, Wessells CD, Huggins RA, Cui Y (2012) *Nat Commun* 3(1):1149. <https://doi.org/10.1038/ncomms2139>
- [5]. Ahn H, Kim D, Lee M, Nam KW (2023) *Commun Mater* 4(1):37. <https://doi.org/10.1038/s43246-023-00367-2>
- [6]. Borodin O (2019) *Curr Opin Electrochem* 13:86-93. <https://doi.org/10.1016/j.coelec.2018.10.015>
- [7]. Zhao Y, Hu X, Stucky GD, Boettcher SW (2024) *JACS* 146(5):3438-3448. <https://doi.org/10.1021/jacs.3c12980>
- [8]. Xue L, Zhang Q, Huang Y, Zhu H, Xu L, Guo S, Zhu X, Liu H, Huang Y, Huang J, Lu L, Zhang S, Gu L, Liu Q, Zhu J, Xia H (2022) *Adv Mater* 34(13):2108541. <https://doi.org/10.1002/adma.202108541>
- [9]. Yang W, Yang Y, Yang H, Zhou H (2022) *ACS Energy Lett* 7(8):2515-2530. <https://doi.org/10.1021/acsenenergylett.2c01152>
- [10]. Li W, Dahn JR, Wainwright DS (1994) *Science* 264(5162):1115-1118. <https://doi.org/10.1126/science.264.5162.1115>
- [11]. Deutscher RL, Florence TM, Woods R (1995) *J Power Sources* 55(1):41-46. [https://doi.org/10.1016/0378-7753\(94\)02166-Z](https://doi.org/10.1016/0378-7753(94)02166-Z)
- [12]. Levi MD, Shilina Y, Salitra G, Aurbach D, Guyot E, Seghir S, Lecuire JM, Boulanger C (2012) *J Solid State Electrochem* 16(11):3443-3448. <https://doi.org/10.1007/s10008-012-1841-1>
- [13]. Suo L, Borodin O, Gao T, Olguin M, Ho J, Fan X, Luo C, Wang C, Xu K (2015) *Science* 350(6263):938-943. <https://doi.org/10.1126/science.aab1595>
- [14]. Han J, Zhang H, Varzi A, Passerini S (2018) *Chem Sus Chem* 11(21): 3704-3707. <https://doi.org/10.1002/cssc.201801930>
- [15]. Yamada Y, Usui K, Sodeyama K, Ko S, Tateyama Y, Yamada A (2016) *Nat Energy* 1(10): 16129. <https://doi.org/10.1038/nenergy.2016.129>
- [16]. Suo L, Borodin O, Sun W, Fan X, Yang C, Wang F, Gao T, Ma Z, Schroeder M, Cresce A Von, Russell SM, Armand M, Angell A, Xu K, Wang C (2016) *Zuschriften* 85287: 7252-7257. <https://doi.org/10.1002/ange.201602397>
- [17]. Chen L, Zhang J, Li Q, Vatamanu J, Ji X, Pollard TP, Cui C, Hou S, Chen J, Yang C, Ma L, Ding MS, Garaga M, Greenbaum S, Lee H-S, Borodin O, Xu K, Wang C (2020) *ACS Energy Lett* 5(3):968-974. <https://doi.org/10.1021/acsenenergylett.0c00348>
- [18]. Zhang H, Liu X, Li H, Hasa I, Passerini S (2021) *Angew Chem Int Ed* 60(2):598-616. <https://doi.org/10.1002/anie.202004433>
- [19]. Jiang L, Lu Y-C (2024) *ACS Energy Lett* 9(3):985-991. <https://doi.org/10.1021/acsenenergylett.4c00098>
- [20]. Lukatskaya MR, Feldblyum JI, Mackanic DG, Lissel F, Michels DL, Cui Y, Bao Z (2018) *Energy Environ Sci* 11(10):2876-2883. <https://doi.org/10.1039/C8EE00833G>
- [21]. Monti D, Jónsson E, Palacín MR, Johansson P (2014) *J Power Sources* 245:630-636. <https://doi.org/10.1016/j.jpowsour.2013.06.153>
- [22]. Dhatarwal HS, Kashyap HK (2022) *J Phys Chem B* 126(28):5291-5304. <https://doi.org/10.1021/acs.jpccb.2c02822>
- [23]. Ugata Y, Shigenobu K, Tatara R, Ueno K, Watanabe M, Dokko K (2021) *Phys Chem Chem Phys* 23(38):21419-21436. <https://doi.org/10.1039/D1CP02946K>
- [24]. Damaskin BB, Petrii OA, Tsirlina GA *Electrochemistry* (2006). 2nd ed., revised and updated. Khimiya, Moscow. P. 672.
- [25]. Izmailov NA (1976) *Electrochemistry of solutions* 3rd edition (corrected). P. 488. (In Russian)
- [26]. Farhat D, Lemordant D, Jacquemin J, Ghamouss F (2019) *J Electrochem Soc* 166:A3487-A3495. <https://doi.org/10.1149/2.1261914jes>
- [27]. Zhigalenok Y, Abdimomyn S, Levi M, Shpigel N, Ryabicheva M, Lepikhin M, Galeyeva A, Malchik F (2024) *J Mater Chem* 12:33855-33869. <https://doi.org/10.1039/D4TA06655C>
- [28]. Bakeev MI (1978) *Hydration and Physicochemical Properties of Electrolyte Solutions*. Nauka, Alma-Ata, Kaz SSR. P. 244 p.
- [29]. Malchik F, Maldybayev K, Kan T, Kokhmetova S, Chae MS, Kurbatov A, Galeyeva A, Kaupbay O, Nimkar A, Bergman G, Levi N, Zhang H, Jin Q, Lin Z, Shpigel N, Mandler D (2023) *Cell Rep* 4(7):101507. <https://doi.org/10.1016/j.xcrp.2023.101507>
- [30]. Malchik F, Maldybayev K, Kan T, Kokhmetova S, Kurbatov A, Galeyeva A, Tubul N, Shpigel N, Djenizian T (2022) *RSC Adv* 12(16):9862-9867. <https://doi.org/10.1039/D2RA00617K>
- [31]. Bunpheng A, Sakulaue P, Hirunpinyopas W, Nueangnoraj K, Luanwuthi S, Iamprasertkun P (2023) *J Electroanal Chem* 944:117645. <https://doi.org/10.1016/j.jelechem.2023.117645>
- [32]. Wahab A (2011) *Can J Chem* 80:175-182. <https://doi.org/10.1139/v02-007>
- [33]. Borodin O, Suo L, Gobet M, Ren X, Wang F, Faraone A, Peng J, Olguin M, Schroeder M, Ding MS, Gobrogge E, von Wald Cresce A, Munoz S, Dura JA, Greenbaum S, Wang C, Xu K (2017) *ACS Nano* 11(10):10462-10471. <https://doi.org/10.1021/acsnano.7b05664>

Макроскопический подход к изучению структуры концентрированных водных растворов LiTFSI

Я. Жигаленок, С. Абдимомын, М. Рябичева,
М. Лепихин, А. Галеева, Ф. Мальчик*

Центр физико-химических методов исследования и анализа, Казахский национальный университет имени аль-Фараби, 96А, ул. Толе би, Алматы, Казахстан

АННОТАЦИЯ

В данной работе систематически исследованы физико-химические свойства водных растворов LiTFSI в широком диапазоне концентраций. Были измерены плотность, вязкость, электропроводность и активность воды растворов, что позволило установить количественные соотношения между макроскопическими параметрами и структурными характеристиками электролита. Анализ электропроводности с учетом поправок на вязкость показал практически полную ионную ассоциацию при высоких концентрациях (выше 10 моль/кг), при этом активность воды достигала исключительно низких значений ($\sim 0,15$) при максимальной растворимости. Исследование выявило нелинейные изменения плотности с увеличением концентрации, что указывает на существенную структурную реорганизацию в концентрированных растворах. Числа гидратации, рассчитанные с использованием нового термодинамического подхода, сочетающего данные по активности воды и электропроводности, показали неожиданное сольватационное поведение: LiTFSI демонстрировал более высокие числа гидратации, чем традиционные соли лития в разбавленных растворах, несмотря на более низкую плотность заряда TFSI⁻, что объясняется пространственным захватом молекул воды его объемной структурой. Эта закономерность менялась на противоположную при более высоких концентрациях из-за усиления ионной ассоциации и эффектов экранирования заряда. Рассчитанные параметры хорошо согласуются с результатами молекулярно-динамического моделирования, что подтверждает правильность нашего макроскопического подхода. Исследование показало, что стандартные физико-химические измерения могут точно определять структурные параметры электролита, что дает практические преимущества для оптимизации составов электролитов, особенно в системах, содержащих полимерные добавки и сорастворители, где молекулярно-динамическое моделирование сталкивается со значительными трудностями.

Ключевые слова: литий-ионные аккумуляторы, водные электролиты, LiTFSI, физико-химические свойства, активность воды, числа гидратации, ионная ассоциация

LiTFSI концентрлі сулы ерітінділерінің құрылымын зерттеудің макроскопиялық тәсілі

Я. Жигаленок, С. Абдимомын, М. Рябичева,
М. Лепихин, А. Галеева, Ф. Мальчик*

Физика-химиялық әдістерді талдау және зерттеу орталығы, әл-Фараби атындағы ҚазҰУ, Төле би к-сі, 96А, Алматы, Қазақстан

АНДАТПА

Бұл жұмыста LiTFSI сулы ерітінділерінің физика-химиялық қасиеттері кең концентрация аралығында жүйелі түрде зерттелді. Ерітінділердің тығыздығы, тұтқырлығы, электр өткізгіштігі және судың белсенділігі өлшеніп, электролиттің макроскопиялық параметрлері мен құрылымдық сипаттамалары арасындағы сандық қатынастар анықталды. Тұтқырлық түзетулерін ескере отырып жүргізілген электр өткізгіштігін талдау жоғары концентрацияларда (10 моль/кг жоғары) толық дерлік иондық ассоциацияны көрсетті, бұл ретте судың белсенділігі максималды ерігіштік кезінде өте төмен мәндерге ($\sim 0,15$) жетті. Зерттеу концентрацияның жоғарылауымен тығыздықтың сызықтық емес өзгерістерін анықтады, бұл концентрацияланған ерітінділерде елеулі құрылымдық қайта ұйымдастырудың жүретінін көрсетеді. Судың белсенділігі мен электр өткізгіштігі бойынша деректерді біріктіретін жаңа термодинамикалық тәсілді қолдана отырып есептелген гидратация сандары күтпеген сольватациялық мінез-құлықты көрсетті: LiTFSI сұйылтылған ерітінділерде TFSI⁻ зарядының төмен тығыздығына қарамастан, дәстүрлі литий тұздарына қарағанда жоғары гидратация сандарын көрсетті, бұл оның көлемді құрылымымен су молекулаларының кеңістіктік қармалуымен түсіндіріледі. Бұл заңдылық иондық ассоциация мен заряд экрандау әсерлерінің күшеюіне байланысты жоғары концентрацияларда қарама-қарсы өзгерді. Есептелген параметрлер молекулалық-динамикалық модельдеу нәтижелерімен жақсы үйлеседі, бұл біздің макроскопиялық тәсіліміздің дұрыстығын растайды. Зерттеу стандартты физика-химиялық өлшеулердің электролиттің құрылымдық параметрлерін дәл анықтай алатынын көрсетті, бұл электролит құрамдарын оңтайландыру үшін практикалық артықшылықтар береді, әсіресе молекулалық-динамикалық модельдеу елеулі қиындықтарға тап болатын полимерлік қоспалар мен қосымша еріткіштері бар жүйелерде.

Түйінді сөздер: литий-ионды аккумуляторлар, сулы электролиттер, LiTFSI, физика-химиялық қасиеттер, судың белсенділігі, гидратация сандары, иондық ассоциация.