

IN MEMORY  
OF G. A. MARTYNOV

## Effect of $\text{Al}(\text{NO}_3)_3$ Addition on Molecular Mobility in Ethyl Ammonium Nitrate According to Molecular Dynamic Simulation Data

M. Ubovich<sup>a,\*</sup>, A. V. Egorov<sup>a</sup>, and V. I. Chizhik<sup>a</sup>

<sup>a</sup>St. Petersburg State University, St. Petersburg, 199034 Russia

\*e-mail: ubovich.milosh@yandex.ru

Received January 14, 2022; revised January 14, 2022; accepted January 18, 2022

**Abstract**—An attempt has been made to reveal the mechanisms responsible for changes in molecular mobility after addition of aluminum nitrate to ethylammonium nitrate using molecular dynamics modeling. The main goal was not only to quantitatively estimate the kinetic characteristics of the components of the mixture at different ratios, but also to correlate the local structure rearrangement at increased salt concentrations with the rotational reorientation of ions. The model systems, radial distribution functions, self-diffusion coefficients, and reorientation times of the intramolecular vectors of the nitrate anion were calculated. At increased concentrations of aluminum nitrate in the system, the reorientation of the nitrate anion and the translational motions of the system components slowed down. It was demonstrated, using the radial distribution functions, that the aluminum ion does not penetrate into the nearest environment of the ethylammonium cation. The appearance of triply charged aluminum ions, however, has a noticeable effect on the ordering of nitrate anions, including those that are part of the environment of the ethylammonium cation. This just leads to a slowdown in the rotational reorientation of the nitrate anion.

**Keywords:** ionic liquids, molecular dynamics, computer simulation, molecular mobility, self-diffusion, radial distribution function

**DOI:** 10.1134/S0036024422070330

Interest in the study of ionic liquids (ILs) has grown significantly over the past decades. Their characteristic feature is that they consist of ions, but, unlike “classical” salts, they are in a liquid state at relatively low temperatures (up to  $\sim 100^\circ\text{C}$ ) [1–5]. Ionic liquids have attracted the attention of researchers due to their remarkable properties such as high thermal stability, high boiling point, low vapor pressure, etc. Due to these properties, ionic liquids can be used in various electrochemical applications (e.g., in lithium ion batteries, supercapacitors, fuel cells, etc.) [6–16]. An important challenge in modern physical chemistry is preparation of ILs with properties required for particular problems. However, this is complicated by the wide variety of possible modifications of ILs (selection of an anion, addition of various functional groups to the cation, addition of admixtures, etc.) and, accordingly, by the need to prepare a large number of samples and perform many experiments. Although many studies have been performed in this area, there are appreciable gaps in the understanding of the nature of ionic liquids. In this case, computer simulation is one of the most promising approaches, which makes it possible to describe ILs at the microlevel. Understanding the mechanisms of formation of the local structure and

correlating them with molecular mobility would help to optimize the search for new variants of ILs.

Systems based on ammonium ions are among the most interesting classes of objects. Ammonium ILs have attracted the attention of researchers due to an unusual combination of properties (in particular, they are relatively inexpensive and have low toxicity). A characteristic representative of this group is ethylammonium nitrate (EAN). As the main object of study we chose mixtures of EAN ( $[\text{C}_2\text{H}_5\text{NH}_3^+][\text{NO}_3^-]$ ) and aluminum nitrate ( $\text{Al}(\text{NO}_3)_3$ ). The addition of inorganic metal salts is one of the promising ways to obtain ILs with desired properties. The addition of an aluminum salt is promising from several viewpoints. Salts with higher valence, e.g., those containing magnesium ( $\text{Mg}^{2+}$ ) or aluminum ( $\text{Al}^{3+}$ ), are currently regarded as potential substitutes for lithium-based ( $\text{Li}^+$ ) salts, as their use could lead to more efficient energy storage systems. Aluminum is characterized by much higher theoretical energy density than lithium (1060 W h/kg and 406 W h/kg, respectively) [17]. In addition, aluminum is more abundant in nature than lithium, which means that the cost of the product will be lower [17]. Previously, mixtures of EAN and aluminum nitrate

**Table 1.** Composition of model systems

$C_{\text{Al}(\text{NO}_3)_3}$ , %	$m$ , mol/kg	Number of ions in the model cell		
		EA <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	Al <sup>3+</sup>
0	0	300	300	0
5	0.489	500	578	26
10	1.028	500	668	56

$C_{\text{Al}(\text{NO}_3)_3}$  is the mole fraction of aluminum nitrate,  $m$  is the molality.

**Table 2.** Parameters of model potentials for the nitrate anion and aluminum cation

Ion	Site	$q$ ,  e	$\sigma$ , Å	$\mathcal{E}$ , kJ/mol
NO <sub>3</sub> <sup>-</sup> , variant I [28]	N	+0.860	3.9000	0.8370
	O	-0.620	3.1540	0.6490
NO <sub>3</sub> <sup>-</sup> , variant II [22]	N	+0.905	3.2500	0.7118
	O	-0.635	2.9600	0.8792
NO <sub>3</sub> <sup>-</sup> , variant III [29]	N	+1.310	3.1000	0.3077
	O	-0.770	3.0000	0.3077
Al <sup>3+</sup> [30]	Al	+3.000	1.4472	0.9063

with concentrations from 0 to 25 mol % salt have already been studied in [17]. The authors considered in detail the effect of the Al(NO<sub>3</sub>)<sub>3</sub> addition on the local microstructure of the mixture, but did not give any estimates for molecular mobility.

In the present study, we made an attempt to reveal the mechanisms responsible for changes in molecular mobility after addition of aluminum nitrate to EAN using the molecular dynamics (MD) method. The main goal was not only to quantitatively evaluate the kinetic characteristics of the mixture components at their different ratios, but also to reveal the relationship between the local structure rearrangement after addition of the salt and the rotational reorientation of ions.

## SIMULATION PROCEDURE

Three systems were modeled here using the MD method: pure IL EAN without additives and two mixtures with 5 and 10 mol % aluminum nitrate. The data on the composition of the model systems are given in Table 1. The modeling was performed in a cubic cell with periodic boundary conditions in an *NPT* ensemble at 298 K and atmospheric pressure using the MDynaMix v5.0 software package [18]. The temperature was kept constant with a Nose–Hoover thermostat [19, 20], and the pressure was maintained with a Hoover barostat [21].

To describe the intermolecular interactions between ethylammonium cations (EA<sup>+</sup>), we chose the

potential proposed in [22, 23]. Previously ([17, 22, 24–26]), it was shown that it reproduces the density and the main structural characteristics of this ionic liquid quite well. The nitrate anion was regarded as a four-site planar structure in which the nitrogen atom lies at the center, the oxygen atoms lie at a distance of 1.22 Å from it, and all the O–N–O angles are equal to 120° [27]. The interactions between the atoms of the model nitrate anion and other species is the sum of the Coulomb and Lennard-Jones (12–6) potentials:

$$U_{ij} = \sum_l \sum_k \frac{q_k q_l}{r_{kl}} + 4\mathcal{E} \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right].$$

Several variants for the corresponding parameters have been proposed in the literature [22, 28, 29], but it is impossible to reasonably choose one of them based on the published data. Therefore, to assess the effect of the parameters of the model potentials for the nitrate anion on the calculated characteristics of ILs and mixtures, we considered three different variants of parameters [22, 28, 29], whose values are given in Table 2. About a dozen potentials have been proposed in the literature to describe the aluminum ion (e.g., [30–37]), but the sum of the Coulomb and Lennard-Jones (12–6) potentials were considered only in two cases [30, 31]. The preliminary test modeling showed that the variant proposed in [30] predicted an overestimated size of the first solvation shell of the aluminum cation, and only the potential of [30], whose parameters are given in Table 1, was used in further calculations.

The equations of motion were solved by the Verlet method at a step of 2 fs. The structure of the model nitrate anion was preserved using the SHAKE algorithm [37]. The electrostatic interaction potentials were calculated by the Ewald method. The equilibration time of each model system was 2 ns; the subsequent simulation time was 1 ns.

## RESULTS AND DISCUSSION

### Density of Model Systems

As the first criterion of correctness of the simulation data, we calculated the densities of both pure IL and mixtures with aluminum nitrate. The results are shown in Table 3 together with the experimental data published in the literature [17, 24]. The potential parameters of the nitrate anion evidently have a significant (up to 11%) effect on the density of the model system. Based on a comparison of the calculated data with experiment, it can be concluded that all the variants in question can be used to analyze the molecular mobility of the systems.

*Molecular Mobility in a Mixture of Ethylammonium Nitrate and Aluminum Nitrate*

**Self-diffusion coefficients.** The rate of the translational motion of substance particles is characterized by the coefficient of self-diffusion ( $D$ ). It was calculated here as the ratio of the mean square displacement of molecules over a certain period of time to the duration of this period:

$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle,$$

where  $\vec{r}(t)$  is the radius vector that characterizes the position of a particle at a moment of time  $t$ , and  $\vec{r}(0)$  is the radius vector at the initial moment of time. The calculated self-diffusion coefficients are listed in Table 4.

The simulation time is not long enough to calculate the characteristics of the model system with high accuracy, but makes it possible to estimate the main effects occurring after the addition of aluminum nitrate to the IL. Note that although the values of the potential parameters of the nitrate anion have a noticeable effect on the  $D$  value, all the three values are approximately of the same order. As mentioned above, the main purpose of the numerical experiment was to reveal the relationship between the local structure rearrangement of the IL after addition of the salt and the rotational reorientation of ions. According to the simulation data, with an increase in the mole fraction of  $\text{Al}(\text{NO}_3)_3$ , the translational motion in the system slows down, but the effect is rather weak.

**Rotational reorientation of the nitrate anion.** The autocorrelation functions of rotational reorientations of various intramolecular vectors are another important characteristic of molecular mobility, analyzing which enables us to obtain information on the rotational motion of ions. Four vectors can be considered to describe the reorientation of the nitrate anion (Fig. 1):  $\overline{\text{NO}}_1$ ,  $\overline{\text{NO}}_2$ , and  $\overline{\text{NO}}_3$  are directed along three N–O chemical bonds, while the  $\overline{\text{N}}_n$  vector is perpendicular to the anion plane. An analysis of the simulation data showed that in the case of the nitrate anion, these functions can be approximated with satisfactory accuracy by one exponential of the form

$$F(x) = \exp\left(-\frac{x}{\tau_c}\right),$$

where  $\tau_c$  is the rotational reorientation time of the given vector. The estimated rotational reorientation times of the given intramolecular vectors of the  $\text{NO}_3^-$  ion are shown in Table 5.

First, the autocorrelation functions of rotational reorientation of the  $\overline{\text{NO}}_1$ ,  $\overline{\text{NO}}_2$ , and  $\overline{\text{NO}}_3$  vectors, as might be expected, are almost identical. Second, the difference between the reorientation times obtained using different model potentials for the nitrate anion is

**Table 3.** Density of the systems ( $\text{g}/\text{cm}^3$ )

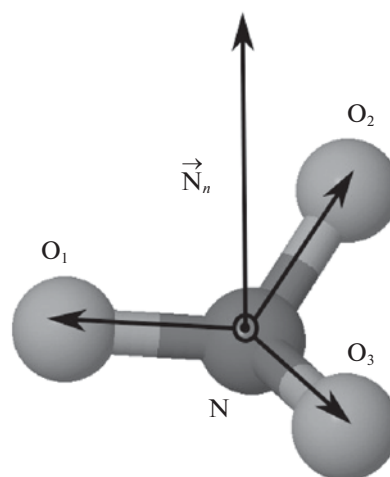
$C_{\text{Al}(\text{NO}_3)_3}, \%$	Modeling			Experiment
	Potential I	Potential II	Potential III	
0	1.198	1.294	1.214	1.206 [24]
5	1.230	1.338	1.206	1.26 [17]
10	1.267	1.383	1.280	1.31 [17]

$C_{\text{Al}(\text{NO}_3)_3}$  is the mole fraction of aluminum nitrate.

**Table 4.** Calculated self-diffusion coefficients for the systems

Potential of $\text{NO}_3^-$	$C_{\text{Al}(\text{NO}_3)_3}, \%$	$10^{11} D, \text{m}^2/\text{s}$		
		$\text{Al}^{3+}$	$\text{NO}_3^-$	$\text{EA}^+$
I	0	—	0.54	0.41
	5	0.16	0.46	0.38
	10	0.15	0.40	0.37
II	0	—	0.62	0.46
	5	0.13	0.52	0.42
	10	0.15	0.50	0.32
III	0	—	0.31	0.28
	5	0.09	0.34	0.33
	10	0.09	0.29	0.26

much more pronounced than in the case of self-diffusion coefficients. However, the characteristic changes in the mobility of the  $\text{NO}_3^-$  ion are similar: at increased mole fraction of aluminum nitrate, the rotational reorientation significantly slows down in the system in all cases. Third, the rotational reorientation time of



**Fig. 1.** Intramolecular vectors in the nitrate anion, for which the autocorrelation functions of rotational reorientations were calculated.

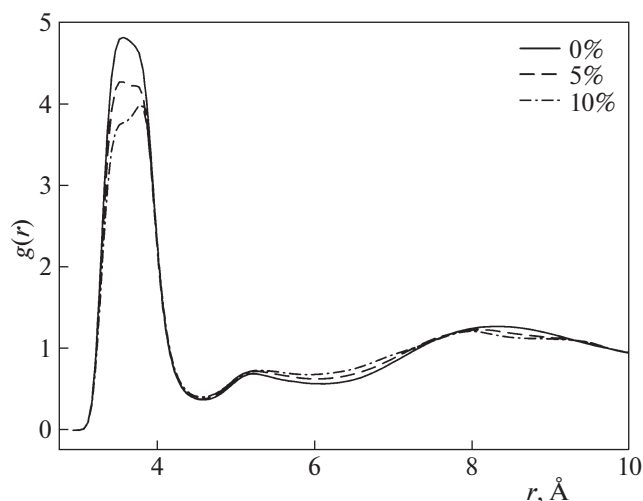
**Table 5.** Rotational reorientation times of the intramolecular vectors of the  $\text{NO}_3^-$  ion (Fig. 1). Potential I

$C_{\text{Al}(\text{NO}_3)_3}$ , %	Reorientation times of corresponding vectors, ps			
	$\overline{\text{NO}}_1$	$\overline{\text{NO}}_2$	$\overline{\text{NO}}_3$	$\overline{\text{N}}_n$
0	160 ± 20	150 ± 20	160 ± 20	510 ± 50
5	360 ± 30	360 ± 30	380 ± 30	650 ± 60
10	640 ± 60	640 ± 60	570 ± 60	680 ± 70
0	240 ± 20	240 ± 20	260 ± 20	610 ± 60
5	440 ± 40	460 ± 40	460 ± 40	830 ± 80
10	820 ± 80	810 ± 80	820 ± 80	1100 ± 100
0	920 ± 90	890 ± 90	910 ± 90	2400 ± 300
5	1400 ± 100	1300 ± 100	1300 ± 100	2900 ± 300
10	1900 ± 200	1900 ± 200	1900 ± 200	3300 ± 300

the  $\overline{\text{N}}_n$  vector considerably exceeds that for the vectors directed along the N–O chemical bond in all cases. This indicates that the frequency of rotational movements in the plane of the nitrate anion is higher than the frequency of rotational movements of the plane itself. Note that this natural effect was quantified.

#### *Changes in the Microstructure of Ethylammonium Nitrate @ after Addition of Aluminum Nitrate*

As mentioned above, the main goal of this study was to reveal a possible relationship between the local structure rearrangement occurring after addition of the salt and the molecular mobility. To describe the microstructure of the systems under study, 16 radial distribution functions (RDFs) were calculated. Note

**Fig. 2.** RDF of the nitrogen atom in  $\text{NO}_3^-$ –nitrogen atom of the  $\text{NH}_3$  group. Potential I.

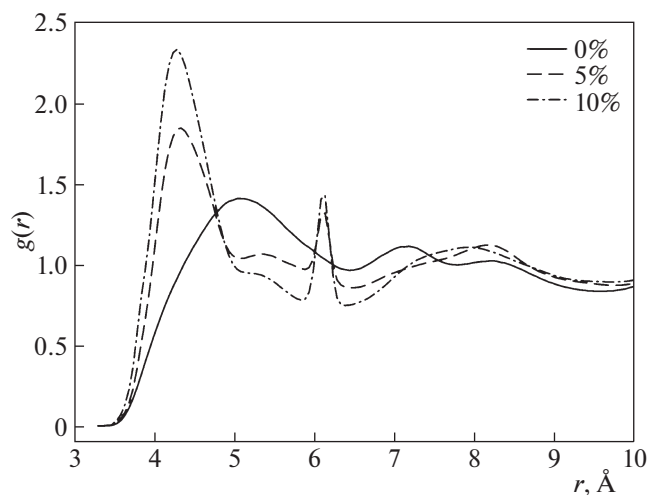
that there were no significant differences in the form of all these RDFs obtained using different model potentials for the nitrate anion.

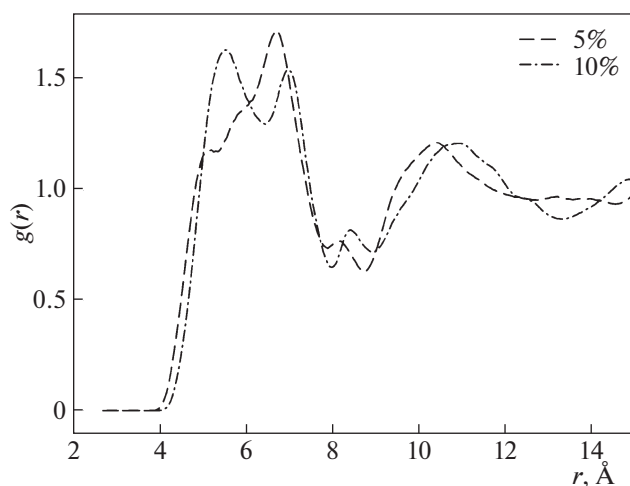
An analysis of the simulation data led to the following conclusions:

(1) The form of the RDF between the atoms of the  $\text{EA}^+$  ion ( $\text{CH}_2$  and  $\text{CH}_3$  carbon– $\text{CH}_2$  and  $\text{CH}_3$  carbon,  $\text{CH}_3$  carbon– $\text{NH}_3$  nitrogen,  $\text{NH}_3$  nitrogen– $\text{NH}_3$  nitrogen,  $\text{NH}_3$  nitrogen– $\text{CH}_2$  and  $\text{CH}_3$  carbon) does not change after addition of aluminum nitrate. This suggests that addition of the salt in a concentration of up to 10 mol % does not lead to any significant changes in the local ordering of the  $\text{EA}^+$  cation.

(2) In the case of the RDF between the atoms of  $\text{EA}^+$  ions ( $\text{NO}_3^-$  nitrogen– $\text{CH}_3$  carbon, oxygen– $\text{CH}_3$  carbon,  $\text{NO}_3^-$  nitrogen– $\text{NH}_3$  nitrogen, and oxygen– $\text{NH}_3$  nitrogen) shown in Fig. 2, the intensity of the first RDF peak decreased at increased mole fraction of aluminum nitrate. This suggests that the local changes are associated with the redistribution of the nitrate anions. These data are consistent with the results of [17].

(3) The RDFs ( $\text{NO}_3^-$  nitrogen– $\text{NO}_3^-$  nitrogen) presented in Fig. 3 clearly demonstrate significant changes in the relative position of nitrate anions after addition of the salt. The presence of triply charged aluminum ions in the system leads to a significant increase in the ordering of nitrate anions in the system, which manifests itself as increased intensity of the peaks of the corresponding RDFs. The observed changes are consistent with the significant decrease in the mobility of the rotational reorientation of the nitrate anion.

**Fig. 3.** RDF of the nitrogen atom in  $\text{NO}_3^-$ –nitrogen atom in  $\text{NO}_3^-$ . Potential I.

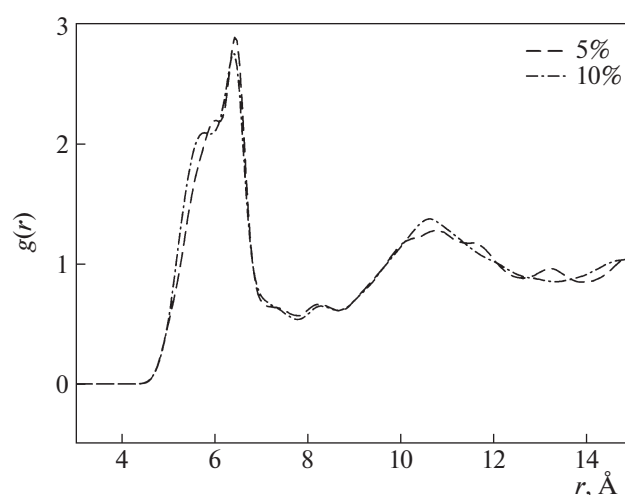


**Fig. 4.** RDF of the aluminum atom in  $\text{NO}_3^-$ —carbon atom of the  $\text{CH}_3$  group. Potential II.

(4) The positions of aluminum ions relative to the  $\text{EA}^+$  ion, described by the RDF (aluminum— $\text{CH}_3$  carbon, aluminum— $\text{NH}_3$  nitrogen) are shown in Figs. 4 and 5. The  $\text{Al}^{3+}$  and  $\text{EA}^+$  cations experience electrostatic repulsion and have little effect on each other. The RDF of the  $\text{EA}^+ - \text{Al}^{3+}$  type does not change significantly (which was also demonstrated in [17]) as the aluminum ion cannot penetrate into the nearest environment of the  $\text{EA}^+$  cation. The multiply charged aluminum ion forms a shell of nitrate anions around itself, including those that are part of the  $\text{EA}^+$  environment, which leads to a slowdown of the rotational reorientation of  $\text{NO}_3^-$ .

Thus, three systems were modeled by the MD method: pure EAN and two mixtures of this IL with aluminum nitrate (5 and 10 mol %). The modeling was performed for three different sets of potential parameters of the nitrate anion. The following characteristics were calculated: the density of model systems, various radial distribution functions, self-diffusion coefficients, and reorientation times of the intramolecular vectors of the  $\text{NO}_3^-$  ion.

Evaluation of the self-diffusion coefficients showed that the translational motion in the system slows down at increased molar fraction of aluminum nitrate, but the effect is relatively weak. It was shown that the values of the sets of potential parameters for the nitrate anion affect the self-diffusion coefficient, but the order of magnitude is the same for all variants. In addition, the reorientation time of the nitrate anion was estimated. It was shown that at increased salt concentrations, the reorientation of the nitrate anion slows down, leading to a decrease in the total diffusion in the systems under study.



**Fig. 5.** RDF of the aluminum atom in  $\text{NO}_3^-$ —nitrogen atom of the  $\text{NH}_3$  group. Potential I.

It was also shown that the addition of aluminum nitrate to the IL changes insignificantly the form of the radial distribution functions of the type:  $\text{EA}^+$  cation— $\text{EA}^+$  cation,  $\text{Al}^{3+}$ — $\text{EA}^+$  cation. This indicates that the aluminum ion does not penetrate into the nearest environment of the IL cation; i.e., the presence of  $\text{Al}^{3+}$  does not significantly affect the nearest neighbors of the  $\text{EA}^+$  cation. For the radial distribution functions of the nitrate anion—nitrate anion type, a pronounced second peak appears after the addition of aluminum nitrate, indicating that the addition of  $\text{Al}(\text{NO}_3)_3$  results in structure ordering.

#### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

#### REFERENCES

1. *Ionic Liquids - Classes and Properties*, Ed. by S. Handy (InTech, 2011).
2. *Ionic Liquids in Synthesis*, Ed. by P. Wasserscheid and T. Welton (Wiley-VCH, Weinheim, 2008).
3. *Ionic Liquids*, Ed. by B. Kirchner, and B. Clare, *Topics in Current Chemistry* (Springer, Heidelberg, 2009).
4. *Electrochemical Aspects of Ionic Liquids*, 2nd ed., Ed. by H. Ohno (Wiley, Hoboken, NJ, 2011).
5. K. Ghandi, *Green Sustain. Chem.* **4**, 44 (2014). <https://doi.org/10.4236/gsc.2014.41008>
6. D. R. MacFarlane, M. Forsyth, P. C. Howlett, et al., *Acc. Chem. Res.* **40**, 1165 (2007). <https://doi.org/10.1021/ar7000952>
7. M. Arm, F. Endres, and D. R. MacFarlane, et al., *Nat. Mater.* **8**, 621 (2009). <https://doi.org/10.1038/nmat2448>

8. X. Lu, G. Burrell, F. Separovic, et al., *J. Phys. Chem. B* **116**, 9160 (2012).  
<https://doi.org/10.1021/jp304735p>
9. M. V. Fedorov and A. A. Kornyshev, *Chem. Rev.* **114**, 2978 (2014).  
<https://doi.org/10.1021/cr400374x>
10. S. Menne, J. Pires, M. Anouti, et al., *Electrochem. Commun.* **31**, 39 (2013).  
<https://doi.org/10.1016/j.elecom.2013.02.026>
11. L. Mayr-Provencher, S. Lin, D. Lazzarini, et al., *J. Power Sources* **195**, 5114 (2010).  
<https://doi.org/10.1016/j.jpowsour.2010.02.073>
12. L. Timperman, P. Skowron, A. Boisset, et al., *Phys. Chem. Chem. Phys.* **14**, 8199 (2012).  
<https://doi.org/10.1039/C2CP40315C>
13. L. Timperman, H. Galiano, D. Lemordant, et al., *Electrochem. Commun.* **13**, 1112 (2011).  
<https://doi.org/10.1016/j.elecom.2011.07.010>
14. L. Timperman, F. Béguin, E. Frackowiak, et al., *J. Electrochem. Soc.* **161**, A228 (2014).  
<https://doi.org/10.1149/2.016403jes>
15. M. Salanne, *Top. Curr. Chem.* **375**, 63 (2017).  
<https://doi.org/10.1007/s41061-017-0150-7>
16. H. Matsuoka, H. Nakamoto, M. A. B. H. Susan, et al., *Electrochim. Acta* **50**, 4015 (2005).  
<https://doi.org/10.1016/j.electacta.2005.02.038>
17. V. Gómez-González, B. Docampo-Álvarez, H. Montes-Campos, et al., *Phys. Chem. Chem. Phys.* **20**, 19071 (2018).  
<https://doi.org/10.1039/C8CP02933D>
18. A. P. Lyubartsev and A. Laaksonen, *Comput. Phys. Commun.* **128**, 565 (2000).  
[https://doi.org/10.1016/S0010-4655\(99\)00529-9](https://doi.org/10.1016/S0010-4655(99)00529-9)
19. S. Nose, *Mol. Phys.* **52**, 255 (1984).  
<https://doi.org/10.1080/00268978400101201>
20. G. J. Martyna, D. J. Tobias, and M. L. Klein, *J. Chem. Phys.* **101**, 4177 (1994).  
<https://doi.org/10.1063/1.467468>
21. G. J. Martyna, M. E. Tuckerman, D. J. Tobias, et al., *Mol. Phys.* **87**, 1117 (1995).  
<https://doi.org/10.1080/00268979600100761>
22. Y. Umehayashi, W.-L. Chung, T. Mitsugi, et al., *J. Comput. Chem. Jpn.* **7**, 125 (2008).  
<https://doi.org/10.2477/jccj.H2013>
23. J. Choe, K. Kim, and S. Chang, *Bull. Korean Chem. Soc.* **21**, 200 (2000).
24. T. Mendez-Morales, J. Carrete, O. Cabeza, et al., *J. Phys. Chem. B* **118**, 761 (2014).  
<https://doi.org/10.1021/jp410090f>
25. V. Gómez-González, B. Docampo-Álvarez, O. Cabeza, et al., *J. Chem. Phys.* **143**, 124507 (2015).  
<https://doi.org/10.1063/1.4931656>
26. V. Gómez-González, B. Docampo-Álvarez, J. Otero-Mato, et al., *Phys. Chem. Chem. Phys.* **20**, 12767 (2018).  
<https://doi.org/10.1039/C8CP01180J>
27. C. Ebner, R. Sansone, S. Hengrasmee, et al., *Int. J. Quant. Chem.* **75**, 805 (1999).  
[https://doi.org/10.1002/\(SICI\)1097-461X\(1999\)75:4/5<805::AID-QUA45>3.0.CO;2-Y](https://doi.org/10.1002/(SICI)1097-461X(1999)75:4/5<805::AID-QUA45>3.0.CO;2-Y)
28. T. Megyes, S. Balint, E. Peter, et al., *J. Phys. Chem. B* **113**, 4054 (2009).  
<https://doi.org/10.1021/jp806411c>
29. A. Laaksonen and H. Kovacs, *Can. J. Chem.* **72**, 2278 (1994).  
<https://doi.org/10.1139/v94-290>
30. T. M. C. Faro, G. P. Thim, and M. S. Skaf, *J. Chem. Phys.* **132**, 11450 (2010).  
<https://doi.org/10.1063/1.3364110>
31. A. Rappé, C. Casewit, K. Colwell, et al., *J. Am. Chem. Soc.* **114**, 10024 (1992).  
<https://doi.org/10.1021/ja00051a040>
32. J. M. Martínez, R. R. Pappalardo, and E. S. Marcos, *J. Am. Chem. Soc.* **121**, 3175 (1999).  
<https://doi.org/10.1021/ja9830748>
33. D. Spangberg and K. Hermansson, *J. Chem. Phys.* **120**, 4829 (2004).  
<https://doi.org/10.1063/1.1641191>
34. E. Wasserman, J. R. Rustad, and S. S. Xantheas, *J. Chem. Phys.* **106**, 9769 (1997).  
<https://doi.org/10.1063/1.473866>
35. T. S. Hofer, B. R. Randolph, and B. M. Rode, *Phys. Chem. Chem. Phys.* **7**, 1382 (2005).  
<https://doi.org/10.1039/B417491G>
36. A. Lauenstein, K. Hermansson, J. Lindgren, et al., *Int. J. Quantum Chem.* **80**, 892 (2000).  
[https://doi.org/10.1002/1097-461X\(2000\)80:4/5<892::AID-QUA39>3.0.CO;2-Q](https://doi.org/10.1002/1097-461X(2000)80:4/5<892::AID-QUA39>3.0.CO;2-Q)
37. J.-P. Ryckaert, G. Ciccotti, and H. J. C. Berendsen, *J. Comput. Phys.* **23**, 327 (1977).  
[https://doi.org/10.1016/0021-9991\(77\)90098-5](https://doi.org/10.1016/0021-9991(77)90098-5)

*Translated by L. Smolina*

SPELL: OK