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Local Structure and Molecular Mobility in Ternary System $LiNO_3$–$NaNO_3$–H_2O at Room Temperature, According to Data from Molecular Dynamics Simulation

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Abstract—An integrated approach is used to study the local structure and molecular mobility in the ternary system $LiNO_3$–$NaNO_3$–H_2O. Coefficients of self-diffusion are measured via NMR on ^1H and ^7Li nuclei for a binary aqueous solution of $LiNO_3$ and two series of a ternary solution. It is found that when 0.5 mol/kg $NaNO_3$ is added, the mobility of lithium cations and water molecules is virtually the same as in the binary solution of $LiNO_3$. This effect is studied by means of molecular dynamics. The structure of the solution at the molecular level is considered in detail with quantitative analysis of variants of the composition of the solvate shells of ions. It is established that adding $NaNO_3$ salt to the lithium solution in the considered range of concentrations has a fairly weak effect on the solvation of lithium cations. When 0.5 mol/kg $NaNO_3$ is added, the local environment of the lithium cation is virtually the same as the one in the binary solution of $LiNO_3$, and the resulting excess of nitrate anions is predominantly redistributed to structures formed in the local environment of sodium cations.

Keywords: molecular dynamics, aqueous electrolyte solutions, ternary solutions, ion solvation, coefficients of self-diffusion, local microstructure

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INTRODUCTION

In modern scientific literature, special attention is given to studying melts and concentrated aqueous solutions containing lithium salts. This interest is due primarily to the widespread use of lithium-ion batteries and the constant search for ways to improve them (e.g., increasing their power, lowering the freezing temperature of the electrolyte, reducing the cost of production, simplifying disposal). Studying aqueous solutions of lithium with impurities or complex compositions is a promising area of research in the search for new electrolytes. Mixed electrolytes are used to develop new types of water-based ion batteries [1–7]. The choice of the composition and ratio of electrolyte components obviously has a considerable impact on such battery characteristics as capacity, operating voltage, and stability. Impurities can also alter the characteristics of batteries, especially by raising or lowering molecular mobility. Work in this area began relatively recently, and positive results have been obtained for only a limited number of systems [8–11]. The wide variety of possible electrolyte compositions and the need to prepare and experimentally verify many samples makes this task extremely laborious. Understanding the patterns of microstructure growth in systems containing lithium salts and their relation to the mobility of solution components would substantially optimize the search for new potential electrolytes. Computer modeling has been increasingly used for this purpose in recent years, allowing us to describe liquid systems at the molecular level. However, the quality of the results from such studies depends on the model representations that are used. Despite all efforts, computer modeling can therefore not be used directly to predict the properties of real systems without experimental verification. In other words, we must use an integrated approach based on coordinated application of several research techniques.

NMR diffusometry and molecular dynamics (MD) modeling were used in this work to consider the effect adding sodium nitrate has on the molecular mobility of hydrated lithium ions in the ternary $LiNO_3$–$NaNO_3$–H_2O system. Pairs of Li^+/Na^+ cations are widely used in a new type of hybrid storage batteries [1, 5]. It was shown in [9] that a notable increase in ion mobility and electronic conductivity is observed for a mixed electrolyte based on Li^+/Na^+ pairs, compared to a binary solution containing only lithium cations. The nitrate anion, the salts of which are highly soluble, was chosen as the counterion. It was shown in [12] that an aqueous solution of $LiNO_3$ has better electrochemical characteristics than a solution of Li_2SO_4.

NMR Diffusometry

Diffusion on ^1H nuclei was measured using a Bruker 500 MHz Avance III spectrometer, and diffusion on ^7Li nuclei was measured using a Bruker AVANCE III 400WB MHz spectrometer equipped with a 5 mm Bruker Diff/50 diffusion sensor. A stimulated echo with a pulsed sinusoidal gradient was used on the former, and smoothed rectangular pulses were used on the latter. All measurements were made at a temperature of 25°C. Standard registration parameters were a gradient pulse duration of 1 to 5 ms, a period of delay between pulses of 20 to 1000 ms, and a gradient value that varied in the range of 2 to 95% of the maximum possible amplitude. Data were approximated by means of least squares. The error in the measured coefficients of self-diffusion did not exceed 7% for ^1H nuclei or 5% for ^7Li nuclei.

Modeling Technique

We used the MDynaMix 5.0 software package [13] in our MD modeling. Calculations were made using an NPT ensemble in a cubic periodic cell at atmospheric pressure and a temperature of 25°C. The temperature and pressure were kept constant using a Hoover thermostat-barostat [14]. We used the SPC/E model of a water molecule [15]. The model nitrate anion was a planar structure with a nitrogen atom in the center and three oxygen atoms at distances of 1.22 Å from it; all O–N–O angles were 120° [16]. The interactions of model particles were described by the sum of the Coulomb and Lennard-Jones (12–6) potentials. The parameters of the Lennard-Jones (12–6) potential for Li^+, Na^+, and NO_3^- were chosen from [17–19], respectively. The geometry of the model molecules was saved using the SHAKE algorithm [20]. The equations of motion were solved according to Verlet with a step of 2.0 fs. The potentials of Coulomb interactions were calculated according to Ewald. Each of the considered systems was preliminarily balanced for 2 ns, and the subsequent period of was also 2 ns.

RESULTS AND DISCUSSION

Two approaches can be used when studying ternary systems of the $LiNO_3$–$NaNO_3$–H_2O type. In the first, some of the lithium cations are replaced by sodium cations, while the ratio of the total number of ion pairs and water molecules does not change. In the second, the concentration of one of the salts is fixed, and the concentration of the second varies within a given range. We used the second approach in this work. Two series of the $LiNO_3$–$NaNO_3$–H_2O ternary solution were considered. In one, the concentration of $NaNO_3$ was constant at 0.5 or 3.46 mol/kg, respectively. (Here and below, all concentrations are expressed in mol per kilogram of H_2O.) In the other, the concentration of $LiNO_3$ varied in the range of 1.01 to 4.63 mol/kg. For comparative analysis, a binary solution of lithium nitrate was modeled in the same range of concentrations. The compositions of the solutions considered in this work are given in Table 1. Due to the lack of literature data, additional diffusion measurements were made on ^1H and ^7Li nuclei for seven aqueous solutions of lithium nitrate in the 0.95 to 6.68 mol/kg range of concentrations. In all cases, the error in preparing concentrations did not exceed 1%. Table 1 also presents the calculated and experimental values of the densities of the considered systems. Density was measured gravimetrically on a chemical balance at a temperature of 20°C with an error of no more than 0.01%. A comparison shows that the densities obtained via molecular dynamics deviated from the experimental ones by no more than 2%.

The values measured for the coefficients of the self-diffusion of lithium cations and water molecules are given in Fig. 1. As expected, the mobility of water molecules fell by approximately 25% upon adding 3.47 mol/kg of $NaNO_3$ with a corresponding drop in the number of water molecules per ion pair, while that of lithium cations fell by approximately 20%, compared to the binary solution. The mobility of water molecules also fell by approximately 10% when 0.5 mol/kg $NaNO_3$ was added, relative to the binary solution. However, the mobility of lithium cations remained virtually the same. An increase in the mobility of lithium cations was thus observed in the ternary $LiNO_3$–$NaNO_3$–H_2O system upon raising the concentration of the solution by adding a small amount of the second salt. A similar effect was noted for the ternary $LiNO_3$–$Ca(NO_3)_2$–H_2O system in [22]. However, the authors did not give a clear explanation of the molecular mechanism behind the increased mobility of lithium cations.

Coefficients of the self-diffusion of lithium cations and water molecules, based on data from molecular dynamics modeling, are given in Fig. 2. It should be noted that the calculated and experimental data are close in order of magnitude, and the modeling generally reproduces the main trends of the change in the mobility of the components of the considered systems. The values of the coefficients of self-diffusion of water molecules fell by approximately 35% when 3.46 mol/kg $NaNO_3$ was added. Those of the lithium cation fell by approximately 30%, compared to the binary solution. The modeling predicted a somewhat greater slowing of molecular mobility. Adding 0.5 mol/kg $NaNO_3$ raised the coefficients of the self-diffusion of lithium cations by about 8%, compared to

Table 1. Composition of model solutions, number *n* of water molecules per ion pair, densities calculated from modeling data, and densities measured experimentally

$NaNO_3$, mol/kg	$LiNO_3$, mol/kg	$Na^+/Li^+/NO_3^-/H_2O$	nH_2O	ρ_{MD}, g/cm^3	ρ_{exp}, g/cm^3
0	1.01	0/20/20/1100	55	1.0379	1.0369
	2.22	0/20/20/500	25	1.0656	1.0798
	3.47	0/20/20/320	16	1.0990	1.1206
	4.63	0/20/20/240	12	1.1291	1.1552
0.5	1.01	20/40/60/2200	36.7	1.0556	1.0622
	2.22	20/88/108/2200	20.4	1.0893	1.0998
	3.47	20/138/158/2200	13.9	1.2200	1.1256
	4.63	20/185/205/2200	10.7	1.1491	1.1706
3.47	1.01	20/6/26/320	12.3	1.1800	1.1878
	2.22	20/13/33/320	9.7	1.2035	1.2138
	3.47	20/20/40/320	8	1.2259	1.2487
	4.63	20/27/47/320	6.8	1.2453	1.2648

The densities for aqueous solutions of $LiNO_3$ were taken from [21].

the binary solution. At the same time, however, the mobility of water molecules remains virtually the same (i.e., a more pronounced increase in the mobility of one of the ternary system's components was noted).

To identify a possible molecular mechanism explaining the observed effect, differences in the microstructure of ternary systems were analyzed at different concentrations of sodium nitrate. The functions of the "cation–oxygen atom of the water molecule" and "cation–nitrogen atom of the nitrate anion" radial distributions were calculated, along with the corresponding coordination numbers (CN). The results obtained for lithium cations are given in Fig. 3; those for the sodium cation, in Fig. 4. It should be remembered that the calculated CN is an integral characteristic, and the solution contains a set of possible configurations of cation solvation shells, which must generally be described in the form of a distribution. In addition to the CN for all cations, we estimated the fraction of solvate shells that include only water molecules in their composition. This fraction is 88% in a binary $LiNO_3$ solution with a 1.01 mol/kg

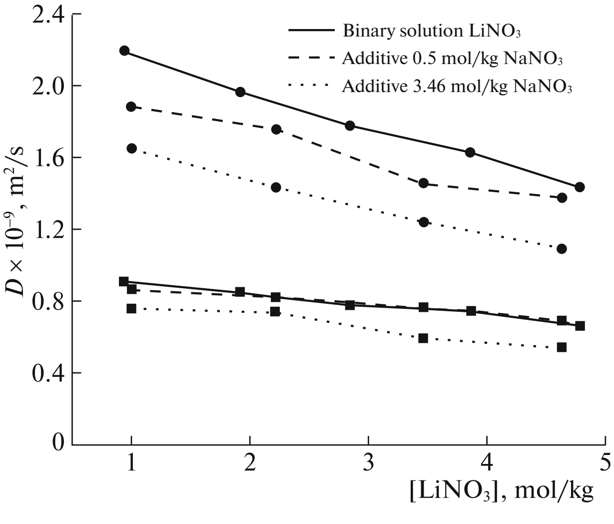

Fig. 1. Concentration dependence of the coefficients of self-diffusion of lithium cations (■) and water molecules (•) in binary $LiNO_3$ and ternary $LiNO_3$–$NaNO_3$–H_2O aqueous solutions, according to data from NMR diffusometry.

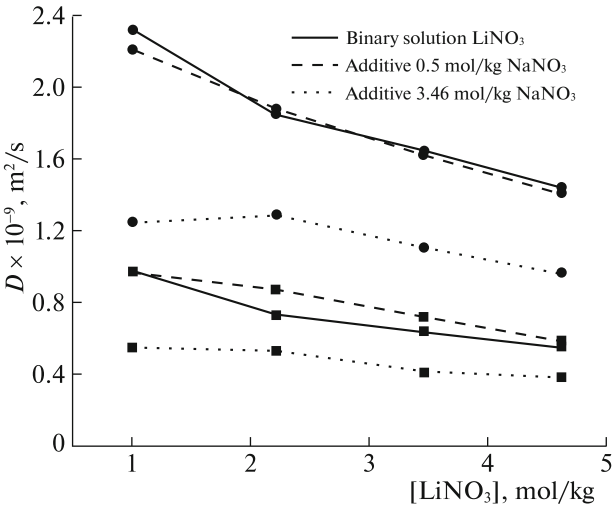

Fig. 2. Concentration dependence of the coefficients of self-diffusion of the lithium cation (■) and water molecules (•) for a binary aqueous solution of $LiNO_3$ and ternary $LiNO_3$–$NaNO_3$–H_2O systems, according to data from molecular dynamics.

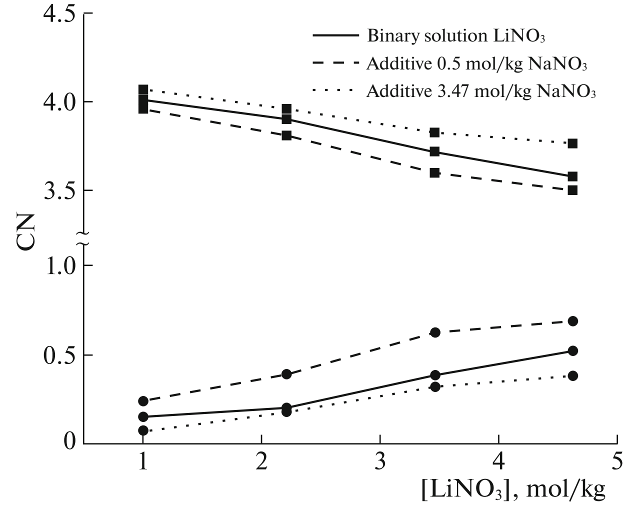

Fig. 3. Concentration dependences of Li^+ coordination numbers based on the radial "lithium cation–oxygen atom of the water molecule" (■) and "lithium cation–nitrogen atom of the nitrate anion" (•) distribution functions for a binary aqueous solution of $LiNO_3$ and ternary $LiNO_3$–$NaNO_3$– H_2O systems.

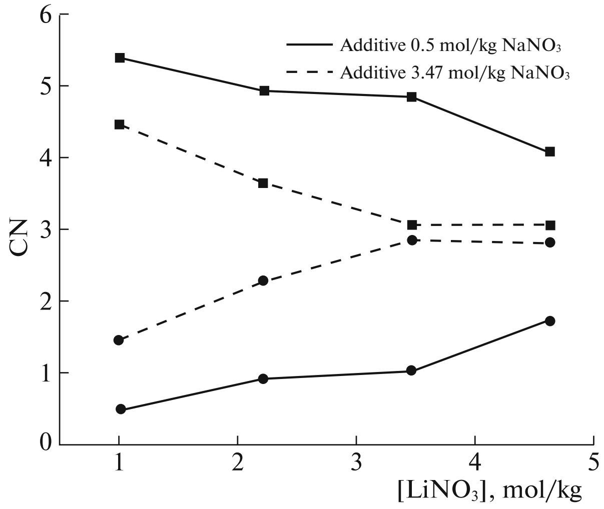

Fig. 4. Concentration dependences of Na^+ coordination numbers calculated based on the radial distribution functions "sodium cation–oxygen atom of the water molecule" (■) and "sodium cation–nitrogen atom of the nitrate anion" (•) for ternary $LiNO_3$–$NaNO_3$–H_2O systems.

concentration of salt. The corresponding average coordination number is close to four, and the fraction of shells containing a nitrate anion is small. Adding sodium nitrate lowers the number of water molecules per ion pair by a factor of 1.5 for 0.5 mol/kg $NaNO_3$ and a factor of 4.5 for 3.47 mol/kg $NaNO_3$. However, the effect exerted on the solvation of the lithium cation is in this case relatively weak. The proportion of completely hydrated cation shells is 85 and 78%, respectively, and the changes in the CN do not exceed 0.1. At the same time, a considerable redistribution of the composition of solvate shells is observed for the sodium cation (see Fig. 4). The fraction of solvate shells that include only water molecules in their composition drops from 60 to 22%, and the corresponding CNs change by approximately 1.0.

Upon raising the concentration of $LiNO_3$ in the ternary system to 4.63 mol/kg and the accompanying drop in the number of water molecules per ion pair, we observe a reduction in the proportion of fully hydrated lithium cations. This reduction can be as much as 70% in a binary solution, 59% when 0.5 mol/kg $NaNO_3$ is added, 49% when 3.47 mol/kg $NaNO_3$ is added. The corresponding change in coordination numbers is around 0.5. At the same time, a much higher degree of redistribution of the composition of solvate shells is observed for sodium cations. The proportion of configurations that include only water molecules in their composition falls to 18% when 0.5 mol/kg $NaNO_3$ is added and 5% when 3.47 mol/kg $NaNO_3$ is added. The coordination numbers change accordingly, by approximately 1.5.

Our analysis of modeling data shows that adding sodium nitrate to a solution lowers the number of water molecules per ion pair and has a rather weak effect on the solvation of lithium cations. When 0.5 mol/kg $NaNO_3$ is added, the immediate environment of a lithium cation is virtually the same as in a $LiNO_3$ binary solution. A consequence of this is no appreciable changes in the coefficients of the self-diffusion of lithium cations. The resulting excess of nitrate anions is predominantly redistributed into structures formed in the immediate environment of sodium cations. When 3.47 mol/kg $NaNO_3$ is added, a drop in the number of water molecules per ion pair raises the proportion of solvate shells containing one or more nitrate anions in both lithium and sodium, but this effect is much more pronounced for the latter. For additional verification, we considered the composition of the solvate shells of the nitrate anion and estimated the fraction of solvate shells that include water molecules and one or more cations (the corresponding dependences for sodium are shown in Fig. 5). The proportion of solvate shells containing one or more sodium cations remains virtually the same for the ternary system when 0.5 mol/kg $NaNO_3$ is added. The fraction of shells of nitrate anions containing one or more lithium cations is in this case virtually the same as that of the binary solution. The proportion of the corresponding structures falls from 68 to 43% for the ternary system when 3.47 mol/kg $NaNO_3$ is added, but this type of environment continues to dominate. The fraction of nitrate anion shells containing one or more lithium cations does not exceed 16% in any case.

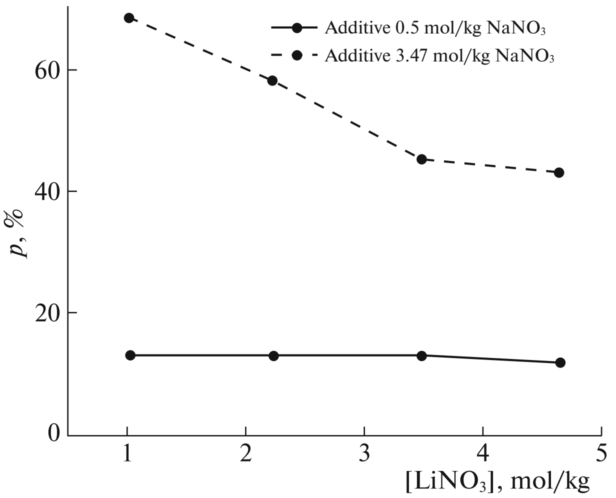

Fig. 5. Concentration dependences of the proportion of solvate shells of nitrate anions that include both water molecules and sodium cations in the considered ternary systems.

CONCLUSIONS

Coefficients of self-diffusion on ^1H and ^7Li nuclei were measured via NMR for a binary aqueous solution of $LiNO_3$ and two series of a ternary solution of $LiNO_3$–$NaNO_3$–H_2O with a constant concentration of $NaNO_3$. It was found that when 0.5 mol/kg $NaNO_3$ was added, the mobility of lithium cations and water molecules was virtually identical to that in a binary solution of $LiNO_3$, despite a drop in the number of water molecules per ion pair. The binary solution of lithium nitrate and the indicated ternary systems were all modeled by means of molecular dynamics to study this effect in detail. A comparison of the calculated and experimental values of the coefficients of self-diffusion showed that the modeling reproduced the main trends of the change in the mobility of the components of the considered systems. The structure of the solution at the molecular level was studied in detail to explain the anomalous mobility of lithium ions and water molecules in the considered ternary systems. We calculated the functions of the "ion–oxygen atom of the water molecule" and "cation–nitrogen atom of the nitrate anion" radial distributions and the corresponding coordination numbers. The modeled variants of the composition of the solvate shells of ions were also analyzed quantitatively.

Our modeling results revealed the relationship between the rearrangement of the structure of the local environment of ions in the ternary $LiNO_3$–$NaNO_3$–H_2O system and features of the translational mobility of its components. Adding $NaNO_3$ salt to the lithium solution had a rather weak effect on the solvation of lithium cations. When 0.5 mol/kg $NaNO_3$ was added, the local environment of the lithium cation was virtually identical to that of the $LiNO_3$ binary solution. A consequence of this was no appreciable changes in the values of the experimentally measured coefficients of self-diffusion. The excess of nitrate anions was in this case predominantly redistributed to structures that form in the local environment of sodium cations.

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