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PHYSICAL PROPERTIES OF LIQUID EUTECTIC IONIC SYSTEMS NaF–LaF$_3$ AND NaF–NdF$_3$

Physical properties – viscosity, electric conductivity, and thermoelectric power – of liquid ionic systems NaF–LaF$_3$ and NaF–NdF$_3$ at eutectic concentrations have been studied.

Keywords: liquid ionic systems, eutectics, viscosity, electric conductivity, thermal emf.

1. Introduction

According to the classification given in work [1], substances in the liquid state can be divided into liquids (atomic, molecular, ionic, ion-electron) and liquid systems (solutions, mixtures, colloid systems, liquid crystals). For today, the most investigated are solutions; first of all, these are molecular solutions [2]. The physical properties of ion-electron liquids and their solutions (liquid metals) have been studied to a much less extent [3]. The researches of the physical properties of ionic liquids or their solutions have still not acquired a comprehensive character. This fact can be explained by technical difficulties associated with both high temperatures of the liquid state realization and the aggressive behavior of the specimens. First of all, this concerns ionic liquids or their solutions, which are the melts of certain salts, for which the temperature interval of the liquid state considerably exceeds room temperatures.

There exists a new class of ionic liquids, which were created artificially, and the temperature interval of which includes room temperatures. As a whole, such liquids and their solutions are electrically neutral. They contain cations and anions of complicated structures. Ionic liquids belonging to this class have already obtained a wide application [4–6] – first of all, as ecologically safe substances – which allows the available power-consuming technologies, e.g., the gas separation, to be improved.

This work aimed at studying some physical properties of ionic liquid systems with the eutectic compositions, namely, Na^+F^- (71 mol.%)–$La^{3+}F_3^-$ (29 mol.%) and Na^+F^- (74 mol.%)–$Nd^{3+}F_3^-$ (26 mol.%). To be more specific, these were the temperature dependences of viscosity, electric conductivity, and thermoelectric power.

2. Experimental Materials and Methods

For our researches, we prepared NaF–LaF$_3$ and NaF–NdF$_3$ specimens with the corresponding eutectic compositions. The results of differential thermal researches [7] showed that NaF–LaF$_3$ is a bi-

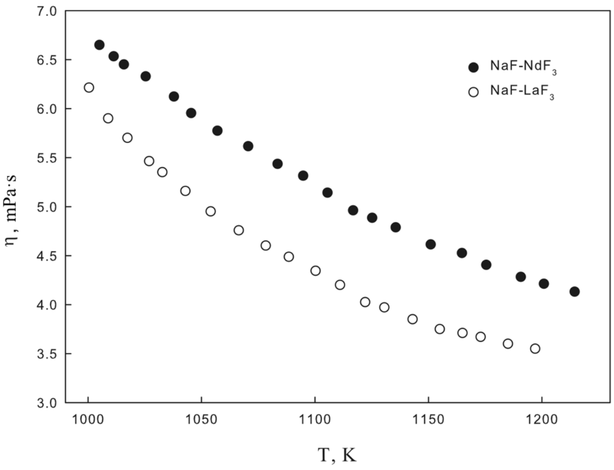

Fig. 1. Temperature dependences of the viscosity in NaF–LaF_3 and NaF–NdF_3 melts

nary system, in which the compound $NaLiF_4$ with the noncongruent melting character is formed. The system with the composition NaF(71 mol.%)–LaF_3(29 mol.%) is characterized by a single eutectics and a single peritectics with melting temperatures of 998 ± 2 K and 1053 ± 2 K, respectively. The system NaF(74 mol.%)–NdF_3(26 mol.%) has one eutectics with a melting temperature of 1003 ± 2 K and two peritectics, $NaNdF_4$ and $Na_5Nd_9F_{32}$.

To fabricate specimens, sodium fluorides of the chemically pure grade, and lanthanum and neodymium trifluoride of the pure grade were used. The components were carefully ground in an agate mortar, weighted, mixed, ground again, and transferred into a platinum crucible, where they had been melted for an hour at a temperature of 1100 K. The cooled alloy was crushed, ground, and loaded into a container in an installation for viscosity measurements [8], as well as in an installation for electric conductivity and termoelectric power measurements [3]. Multizone cells fabricated from boron nitride and supplied with graphite electrodes were used for complex measurements of the electric conductivity σ (to a relative error of ±2%) and the thermopower S (to a relative error of ±5%)in the studied melts under the argon pressure and in the temperature interval from 950 K to the maximum experimental temperature of 1250 K. The application of such cells enabled the component of the σ-measurement error that arose owing to the penetration of the examined melt into the ceramic body of a measurement cell to be excluded from the experimental results [3].

The thermoelectric power was measured following a standard technique [3] by creating a temperature difference of 10÷20 K along the specimen. The temperature was measured with the use of tungsten-rhenium WRe5/20 thermocouples. In order to protect the thermal junction against the aggressive environment (the ionic melt), it was arranged in the graphite volume. Separate thermocouple electrodes were used as potential probes, when measuring the electric conductivity.

The temperature dependence of the viscosity in the ionic liquid system formed after the eutectics NaF–LaF_3 and NaF–NdF_3 had melted was studied with the help of a viscometer by the method of damping torsional vibrations of a cylinder filled with the examined specimen [8]. A graphite crucible was filled with the obtained melt and arranged in the indicated cylinder. In order to prevent the probable evaporation, the crucible was hermetically sealed with a cover, and an excess argon pressure was created in the chamber. The experiment was carried out in the cooling mode. The viscosity was calculated from the results of measurements using the formulas obtained by Shvidkovskii [9] for torsional viscosimeters of this type. The described method provided a relative error of 5% for viscosity measurements.

3. Experimental Results and Their Discussion

In Fig. 1, the data obtained for the temperature dependences of the viscosity in the ionic liquid systems NaF–LaF_3 and NaF–NdF_3 with the corresponding eutectic compositions are depicted. The results testify to a monotonous dependence of the viscosity in the examined systems on the temperature. A comparison between those dependences for ionic liquid systems differing by the lanthanides (La in the first case and Nd in the second one) demonstrates that the substitution of La by Nd in the analyzed system brings about the viscosity growth at a constant temperature. Taking into account that the melting temperatures in the studied eutectics almost coincide, there is no necessity to apply the law of corresponding states to compare their physical properties. The substitution of lanthanum fluoride by neodymium fluoride does not change the interaction force between the ions in the system substantially. However, the neodymium cation is more massive, and this can be one of the reasons for that the mobility of ions in the NaF–NdF_3 system is lower, and, accordingly, the viscosity increases.

The processing of the obtained data on the basis of the Arrhenius law

$$\eta(T) = \eta_0 \exp\left(\frac{Q}{RT}\right), \qquad (1)$$

where Q is the activation energy for the viscous flow, showed that, in the case of the ionic liquid system NaF–LaF_3, they are satisfactorily approximated by a straight line with a cusp at the temperatures $T = 1130 \pm 10$ K. This fact testifies that, in the temperature interval 1000÷1130 K, the melt changes its structure, which is connected with the noncongruent melting of the $NaLaF_4$ compound, so that the ionic liquid system becomes homogeneous if the temperature grows. The ionic liquid system NaF–LaF_3 is characterized by the activation energy of a viscous flow equal to 32.5 kJ/mol below a temperature of 1130 ± 10 K and to 15.5 kJ/mol at higher temperatures. This change in the temperature regime of the viscous flow can be associated with the fact that, at temperatures higher that $T = 1130 \pm 10$ K, the examined ionic liquid system transforms into a homogeneous ionic solution, for which the activation energy of a viscous flow is naturally lower than that for the heterogeneous liquid system with the noncongruently melting $NaLaF_4$ compound. The activation energy of the viscous flow determined for the ionic liquid system with neodymium fluoride amounts to 23.1 kJ/mol and shows a tendency to a reduction to 21.2 kJ/mol.

The analysis of the results obtained (Fig. 2) demonstrates that, for the liquid system NaF–NdF_3, the experimental data are also well approximated by a straight line with a cusp at the temperatures $T = 1150 \pm 10$ K. This fact testifies that the process of noncongruent melting of the $NaLaF_4$ compound comes to the end above the indicated temperature, and the studied ionic liquid system becomes a homogeneous liquid.

Comparing the results obtained for the viscosity in the binary liquid systems NaF–LaF_3 and NaF–NdF_3 with the corresponding results obtained by us for the ternary systems NaF–LiF–LaF_3 and NaF–LiF–NdF_3 [10], one can see that the presence of LiF almost does not change the viscosity of corresponding eutectic melts. In the case with lanthanum, the noncongruent decomposion of the $NaLaF_4$ compound is observed within the temperature interval from T_{melt} to $T_{\text{melt}} + 120$ K in both the binary and ternary systems.

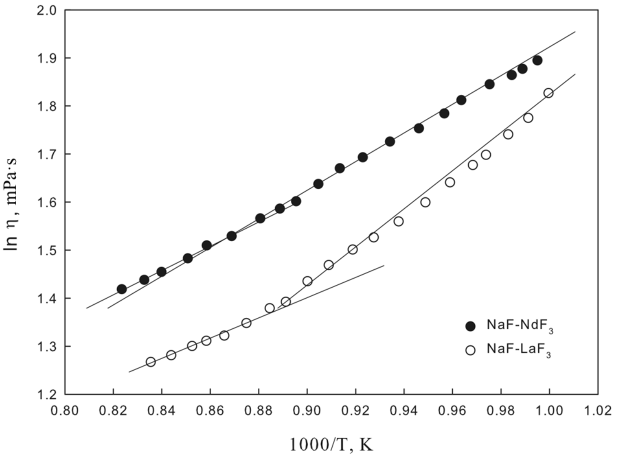

Fig. 2. The same as in Fig. 1, but in the $\log \eta$ versus $1000/T$ coordinates

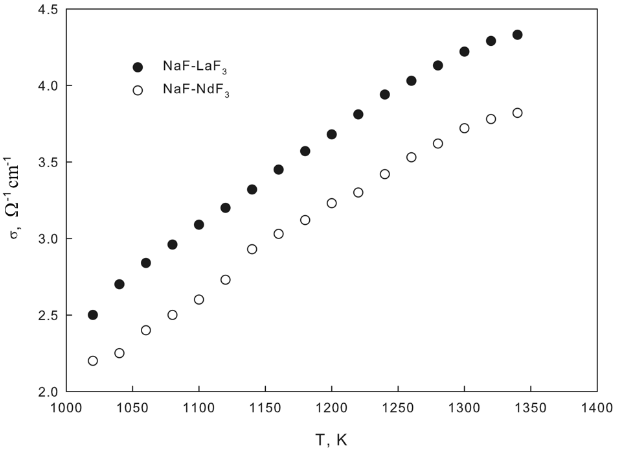

Fig. 3. Temperature dependences of the electric conductivity in NaF–LaF_3 and NaF–NdF_3 melts

In Fig. 3, the experimental data for the temperature dependence of the electric conductivity in the examined liquid systems are depicted. As one can see, the replacement of a lanthanum cation by a neodymium one results in a reduction of the electroconductivity in the binary system at a constant temperature. The ionization energies of free neodymium and lanthanum atoms are known to be almost identical [11]. Since the neighbors of lanthanum or neodymium in the melts concerned are identical

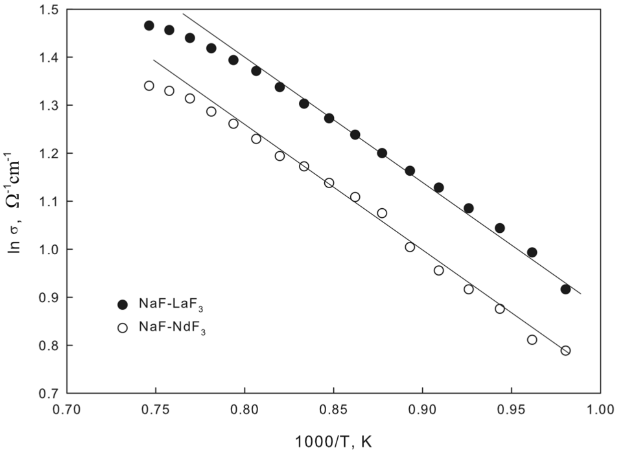

Fig. 4. The same as in Fig. 3, but in the $\log\sigma$ versus $1000/T$ coordinates

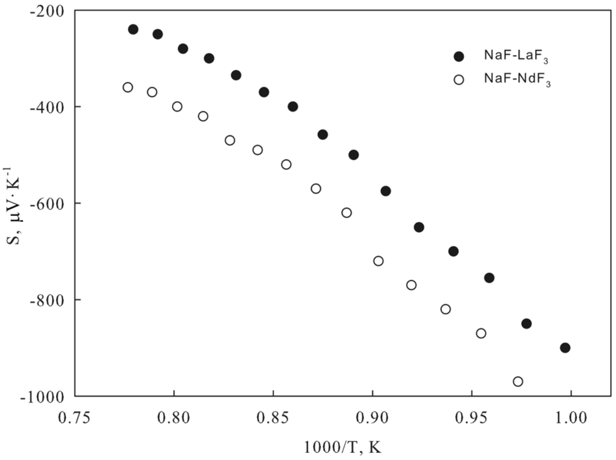

Fig. 5. Temperature dependences of the thermoelectric power in NaF–LaF$_3$ and NaF–NdF$_3$ melts

(Na and F), the ionization energies of neodymium and lanthanum in the melt also have to be identical. The outer electron configurations in lanthanum and neodymium are different – $5d^16s^2$ and $4f^46s^2$, respectively – which is responsible for different characters of the interactions in those systems. In particular, only one compound with the noncongruent character of melting, NaLaF$_4$, is formed in the NaF–LaF$_3$ binary system; and two such compounds, NaLaF$_4$ and Na$_5$Nd$_9$F$_{32}$, in the NaF–LaF$_3$ one. The mass and mobility differences between the La^{3+} and Nd^{3+} cations, and the presence of two noncongruently melting compounds in the system with neodymium fluoride give rise to a reduction of the electric conductivity, when lanthanum fluoride is substituted by neodymium fluoride.

The electric conductivity of the researched systems is described by the exponential law

$$\sigma(T) = \sigma_0 \exp\left(-\frac{\Delta E}{kT}\right), \tag{2}$$

where σ_0 = const, and ΔE is the electroconductivity activation energy. Comparing the obtained results with the corresponding results of work [12] for ionic liquid systems with eutectic compositions, a conclusion can be drawn that the addition of LiF to the binary systems NaF–LaF$_3$ and NaF–NdF$_3$ results in the increase of the electric conductivity by a factor of almost 1.5. This fact can be easily explained, because the lithium cation in the examined fluoride systems has the largest polarizing ability (e/r^2) hindering the fluorine anions from their coordination around the cations of rare-earth elements.

In Fig. 4, the temperature dependences of the electric conductivity are plotted on the logarithmic scale. The found values of activation energy for the NaF–LaF$_3$ and NaF–NdF$_3$ systems practically coincide: 0.43 and 0.46 eV, respectively. The analysis of experimental data shows that the exponential dependence is obeyed in a temperature interval of 1000÷1235 K for the system with lanthanum and in a temperature interval of 1000÷1250 K for the system with neodymium. At temperatures higher that 1235 K for the system with lanthanum and 1250 K for the system with neodymium, the electroconductuivity dependences demonstrate a deviation toward lower values. This fact can testify to the completion of the noncongruent decomposion of compounds with the noncongruent melting character that exist in the given systems.

In Fig. 5, the temperature dependences of the thermoelectric power $S(T)$ for the studied systems are exhibited. As one can see, those dependences, unlike the earlier studied NaF–LiF–LaF$_3$ and NaF–LiF–NdF$_3$ systems, have a monotonous character. As the temperature grows, $S(T)$ decreases by the absolute value, but remains negative. Since the neodymium cation has a little smaller ionic radius, it has a larger capability to coordinate fluorine anions around itself and, hence, to reduce their mobility. This is one of the reasons for that the experimental values of thermoelectric coefficient for the system with neodymium fluoride are smaller by the absolute value than that in the system with lanthanum fluoride at the same temperature.

For the ternary ionic liquid systems studied by us earlier [12], the maximum value of thermoelectric power $S \approx -1000\ \mu$V/K was observed for the NaF–LiF–LaF$_3$ system at a temperature of 920 K, and $S \approx -990\ \mu$V/K for the NaF–LiF–NdF$_3$ one at a temperature of 970 K. According to the results of work [4], the closest experimental values amounted to $S = -940\ \mu$V/K for the LiCl melt, $-695\ \mu$V/K for AgCl, and $-714\ \mu$V/K for the CdCl melt. Those substances were intended to be used for the creation of thermoelectric generators with an enhanced efficiency. In the NaF–LaF$_3$ and NaF–NdF$_3$ melts studied by us, $S(T \approx 1000\text{ K}) \approx -1000\ \mu$V/K; therefore, they are also promising objects for the creation of high-temperature thermoelectric generators.

The key parameter for the estimation of whether the indicated substances should be used in thermoelectric generators is the so-called Q-factor,

$$Z = S^2\sigma/\lambda, \tag{3}$$

where S is the thermoelectric power, σ the electric conductivity, and λ the thermal conductivity. In the ionic solutions studied by us, the averaged values of Q-factor at 1000 K fall within the interval $Z = (0.2\div0.4) \times 10^{-4}\ \text{K}^{-1}$, which exceeds the corresponding values for liquid semiconductors used in thermoelectric generators [13].

In order to give a more detailed explanation for the mechanism of thermoelectric power formation in ionic liquid systems, we must understand the temperature dependence of the motion of ions and electrons in the liquid medium. For this purpose, comprehensive researches of the Hall effect in the indicated substances should be carried out, which would allow us to determine the concentration of moving charges. In addition, it is necessary to study the temperature dependences of the diffusion coefficient of ions in the ion-electron liquid systems, which would allow the contribution of the Soret effect to the ion motion to be estimated [14]. Such researches can be carried out with the help of both the method of labeled atoms and the quasielastic scattering of slow neutrons.

4. Conclusions

The temperature dependences of the viscosity, electric conductivity, and thermoelectric power in binary ionic liquid systems NaF–LaF$_3$ and NaF–NdF$_3$ have been studied in a wide temperature interval including the melting temperatures of indicated specimens with the eutectic compositions. The heterogeneous ionic liquid system NaF–LaF$_3$ is demonstrated to become a homogeneous ionic solution at temperatures that exceed the corresponding melting temperature by about 130 K. The same effect is observed for the heterogeneous ionic liquid system NaF–NdF$_3$ at a temperature that exceeds the melting temperature by about 150 K. The both results agree with the results of x-ray diffraction researches for the indicated melts [15]. A comparison is made between the physical properties of the examined binary ionic liquid systems NaF–LaF$_3$ and NaF–NdF$_3$ and the corresponding properties of their ternary analogues formed by addiing LiF to the initial binary systems. It is shown that the addition of LiF almost does not change the temperature dependence of the viscosity in the examined ionic liquid systems, but increases their electroconductivity by a factor of almost 1.5.

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ФІЗИЧНІ ВЛАСТИВОСТІ ІОННИХ РІДИННИХ СИСТЕМ NaF–LaF$_3$ ТА NaF–NdF$_3$ ЕВТЕКТИЧНОГО СКЛАДУ

Резюме

Досліджено температурні залежності в'язкості, електропровідності та термо-ерс бінарних іонних рідинних систем NaF–LaF$_3$ та NaF-NdF$_3$ у широкому температурному інтервалі, що включає температури плавлення цих сплавів евтектичного складу.