

# Structure of Lithium Ion-Conducting Polymer Membranes Based on Nafion Plasticized with Dimethylsulfoxide

A. I. Karelin, R. R. Kayumov, E. A. Sanginov, and Yu. A. Dobrovolsky\*

*Institute of Problems of Chemical Physics, Russian Academy of Sciences,  
Chernogolovka, Moscow oblast, 142432 Russia*

\*e-mail: [dobr@icp.ac.ru](mailto:dobr@icp.ac.ru)

Received December 28, 2015

**Abstract**—The products of solvation of lithiated Nafion with dimethylsulfoxide (DMSO) have been studied by ATR IR spectroscopy in the frequency range of 50–4000  $\text{cm}^{-1}$  in a vacuum at room temperature. Degree of solvation  $n = \text{DMSO}/\text{Li}$  has been varied in a range of 1.5–18.4. Based on analysis of the dependence of the spectral parameters on the  $n$  value, it has been concluded that the test samples contain DMSO molecules of two types. The first type includes molecules coordinated to the lithium ion through the formation of the metal–oxygen bond, and the second is DMSO molecules associated by intermolecular bonds similar to those in the liquid DMSO phase. The structure of the salt depends on  $n$ : the changes are attributed to the reorientation of polymer chain units. The coordination number of lithium has been estimated at four. It has been shown that the IR data are consistent with the data on the conductivity of lithiated Nafion membranes as a function of DMSO content, according to which the simplest transport unit is the tetrasolvate  $[\text{Li}(\text{DMSO})_4]^+$ . At temperatures below 0°C, all the samples exhibit an abrupt change in conductivity, which is attributed to the freezing of DMSO in the membrane matrix.

**Keywords:** polyelectrolyte, lithiated Nafion, dimethylsulfoxide, solvation, ATR IR spectroscopy

**DOI:** 10.1134/S0965544116110074

## INTRODUCTION

In view of the vigorous development of electrochemical energy sources, considerable attention is paid to the development of novel materials exhibiting high lithium ion conductivity [1, 2]. The greatest progress has been made in the design of solid polymer electrolytes exhibiting unipolar cation conductivity because these materials are characterized by high mechanical and structural properties, a broad range of operating temperatures, and a wide electrochemical stability window [3, 4].

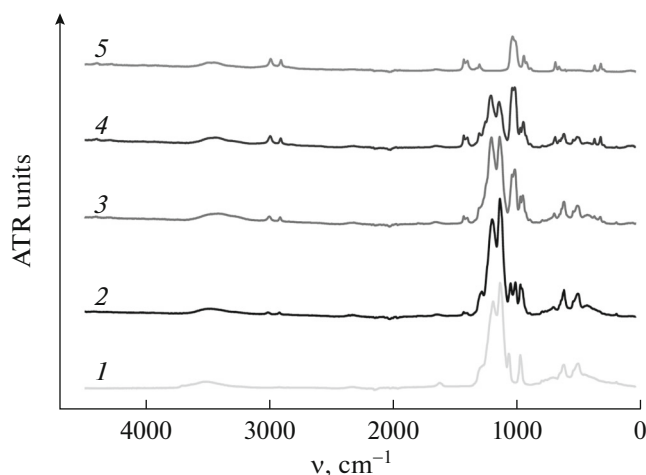
Of all electrolytes exhibiting unipolar cation conductivity, significant prospects are assigned to polymer electrolytes based on ionomers containing perfluorinated ionic groups ( $-\text{CF}_2\text{SO}_3^-$ ,  $-\text{SO}_2\text{N}^-\text{SO}_2\text{CF}_3$ , etc.) [5–14], which are among the weakest coordinating anions providing a high counterion concentration in nonaqueous media, which in turn contributes to ion transport, particularly at high electrolyte concentrations. To date, most of the published studies in this field have been focused on the of lithium ion transport in Nafion, which is a promising polymer electrolyte for rechargeable lithium ion cells. High ionic conductivity values were obtained in the case of plasticizing lithiated Nafion with *N*-methylformamide, *N,N*-dimethylformamide, and dimethylsulfoxide (DMSO)

in which the degree of swelling of the membrane is higher than 100% and the ionic conductivity values at room temperature exceed 1 mS/cm [5–8]. Only DMSO-based electrolytes exhibit sufficient electrochemical stability for use in rechargeable lithium ion cells [8]. Despite a significant number of reports on the transport properties of these electrolytes, data on their structure, in particular, vibrational spectroscopy data, are not available in the literature.

This study describes the attenuated total reflectance IR (ATR IR) spectroscopy and impedance spectroscopy data for Nafion- $\text{Li}^+$ /DMSO membranes.

## EXPERIMENTAL

Nafion-115 membrane samples were pretreated in a 3%  $\text{H}_2\text{O}_2$  solution at 60–80°C for 2 h, washed with water, then held in 0.1 M HCl (special purity grade) at 60–80°C for 1 h, and thoroughly washed with water. To provide the replacement of mobile protons by lithium ions, the samples were held in a 2 M LiOH aqueous alcohol solution (1 : 1 vol/vol) at 60–80°C for 2 h and then thoroughly washed with water. To remove water, the samples were initially dried at 110°C for 1 h and then in a desiccator over  $\text{P}_2\text{O}_5$  for 1 week.



**Fig. 1.** Survey ATR IR spectra of Nafion- $\text{Li}^+$ /DMSO and pure DMSO samples. Spectral curves 1, 2, 3, and 4 correspond to the molar ratios of components of DMSO/Li = 0, 1.5, 5.5, and 18.4, respectively; curve 5 shows the spectrum of the liquid DMSO phase.

Before using, DMSO was distilled over  $\text{CaH}_2$  at a low pressure at  $T_{\text{boil}} = 74\text{--}75^\circ\text{C}$  and stored over activated molecular sieves.

To provide membrane swelling, the dried Nafion samples in the lithium ion form were held in DMSO in the presence of activated molecular sieves at room temperature for 2 days. To prepare lithiated Nafion samples with a lower plasticizer content, the dry samples were briefly immersed in DMSO, blotted with filter paper, and held for 2 days to provide a uniform distribution of DMSO over the sample. DMSO content (wt %) in the membrane was determined as the ratio of the amount of absorbed DMSO to the weight of the dry membrane.

The prepared Nafion- $\text{Li}^+$ /DMSO samples with a thickness of 165–200  $\mu\text{m}$  were analyzed in a vacuum (<1 hPa) by ATR IR spectroscopy (a Bruker Vertex 70V FTIR spectrometer with a diamond attachment). Spectra were recorded in the range of 50–4000  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$  and a number of scans of 50. The recording conditions eliminated the absorption of water and carbon dioxide vapors and, in addition, provided the access to the far IR region. In the figures of the spectra, the intensities of the bands correspond to a scale in terms of ATR units. This choice of the scale makes it possible to easily identify a number of weak bands in a frequency range of 2500–4000  $\text{cm}^{-1}$  and—a feature of particular importance—in a long-wavelength range of 50–100  $\text{cm}^{-1}$ . In the case of conversion of ATR units to absorbance units, a continuous background appears in the long-wavelength region and rapidly increases with decreasing frequency with an increase in the depth of penetration of light into the sample. The time of the procedure in which the hygroscopic sample stayed in the air while being transferred into the attachment before the beginning of pumping

of the cell compartment of the spectrometer took no more than 0.5 min.

The conductivity of the samples was determined by impedance spectroscopy. Impedance measurements were conducted on a Z-3000 instrument (OOO Elins) in a frequency range of 100 Hz to 1 MHz on Ti/Nafion- $\text{Li}^+$ /Ti symmetrical cells with an active area of 0.2  $\text{cm}^2$ . The amplitude of the external AC signal was 50 mV. The resistance of the membrane samples ( $R_m$ ) was determined via extrapolating the high-frequency portions of impedance hodographs to the axis of active resistances. Membrane conductivity  $\sigma$  (in S/cm) was calculated according to the following relationship:  $\sigma = d/(R_m S)$ , where  $d$  is the thickness of the swollen membrane,  $R_m$  is the membrane resistance, and  $S$  is the electric contact area.

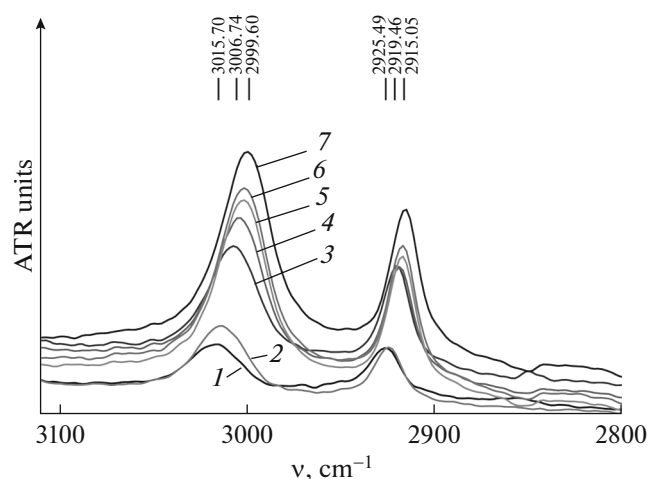
All procedures involving the polymer electrolyte were conducted in a glove box in an argon atmosphere; the  $\text{O}_2$  and  $\text{H}_2\text{O}$  content in the atmosphere in the box was less than 1 ppm.

## RESULTS AND DISCUSSION

The main purpose of the study was to derive spectroscopic data on the structure of the DMSO molecule in lithiated Nafion. Preliminary tests showed that it is necessary to study the Nafion- $\text{Li}^+$ /DMSO system in the utmost wide range of concentrations. The samples for spectroscopic studies contained different amounts of DMSO (degree of solvation DMSO/Li =  $n$ ). The total number of prepared and studied samples was nine: samples with  $n = 0, 1.5$  (10.8 wt %), 2.6 (18.4 wt %), 4.2 (30.1 wt %), 5.5 (39.3 wt %), 8.9 (63 wt %), 12.3 (87 wt %), 13.7 (98 wt %), and 18.4 (131 wt %).

Figure 1 (curves 1–4) shows typical survey spectra for four samples ( $n = 0, 1.5, 5.5,$  and 18.4). Survey spectra give a general idea of the behavior of the sample composition dependence. The spectral curves are artificially shifted relative to one another in order to avoid the overlap of contours. Comparison of these spectra with the IR absorption spectra of Nafion- $\text{H}^+$  [15] and Nafion- $\text{Li}^+$  [16] reveals many similar features. For comparison, Fig. 1 shows the spectrum of the liquid DMSO phase (curve 5).

The spectral analysis results showed, in particular, that the initial Nafion- $\text{Li}^+$  and DMSO samples and the Nafion- $\text{Li}^+$ /DMSO membrane samples contain residual traces of moisture. Weak bands of  $\nu(\text{OH})$  and  $\delta(\text{HOH})$  of adsorbed water are detected in all the samples—without any exception—at 3420 and 1658–1668  $\text{cm}^{-1}$ , respectively. With an increase in the DMSO content in the Nafion- $\text{Li}^+$ /DMSO samples, the intensity of these bands slightly increases, as evidenced, in particular, by the spectra shown in Fig. 1. Taking into account the low water uptake (about 0.3–0.6 water molecules per sulfo group according to the calibration data) and the absence of any effect on the



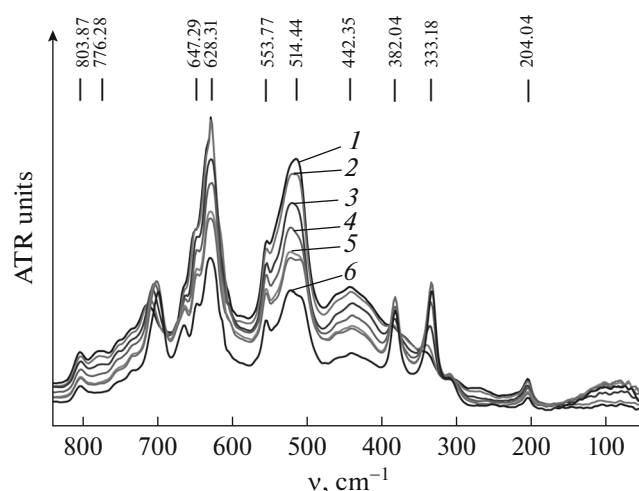
**Fig. 2.** Envelopes of the  $\nu(\text{CH})$  bands in the ATR IR spectra of Nafion- $\text{Li}^+$ /DMSO samples. Spectral curves 1, 2, 3, 4, 5, 6, and 7 correspond to the molar ratio of components of DMSO/Li = 1.5, 2.6, 5.5, 8.9, 12.3, 13.7, and 18.4, respectively.

analyzed bands, the impurity content can be neglected.

The presence of DMSO in Nafion- $\text{Li}^+$ /DMSO is detected according to the set of vibrational frequencies characteristic of the molecules of this solvent. However, this set is not rigidly fixed; instead, it qualitatively depends on the amount of the solvent in the sample. The DMSO vibrational frequencies of different types averaged over all the samples are as follows: 333, 704, 1024–1045, 1312, 1407, 1438, 2918, and 3003  $\text{cm}^{-1}$ . Close values were obtained by the authors of [17] in the study of  $\text{LiClO}_4$  solutions in DMSO by IR absorption spectroscopy.

Exact frequency values depend on the amounts of DMSO in Nafion- $\text{Li}^+$ . An increase in the DMSO content is accompanied by a systematic decrease in these values. It is known that the methyl group does not exhibit a tendency to hydrogen bonding. However, it is the example of the spectrum of the methyl group that clearly shows the effect of the short-range order. Figure 2 depicts the concentration dependence of the frequencies of the symmetric and antisymmetric stretching vibrations of  $\text{CH}_3$ . In fact, the shifts are small; in particular, with an increase in  $n$  from 1.5 to 18.4, the  $\nu_s(\text{CH}_3)$  and  $\nu_{as}(\text{CH}_3)$  vibrational frequencies decrease from 2925 and 3015 to 2915 and 2999  $\text{cm}^{-1}$ , respectively. In addition, a change in the DMSO concentration leads to a change in the ratio of intensities of the bands corresponding to the bending vibrations of the methyl group  $\nu_s(\text{CH}_3)$  and  $\nu_{as}(\text{CH}_3)$ .

This relationship cannot be attributed to anything other than the effect on the short-range order, which changes from one sample to another, on the DMSO molecule. The possible causes of changes in the fre-



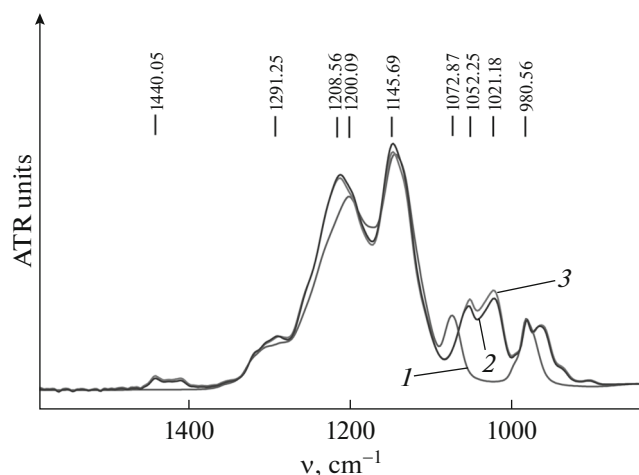
**Fig. 3.** Envelopes of the  $\nu(\text{CS})$ ,  $\delta(\text{SO}_3) \leftrightarrow \delta(\text{CCF})$ ,  $\delta(\text{CCF})$ ,  $\nu(\text{LiO})$ ,  $\delta(\text{CSO})$ , and  $\chi(\text{CCF})$  bands and bands of the molecular dipole–dipole interactions in the ATR IR spectra of Nafion- $\text{Li}^+$ /DMSO samples. Spectral curves 1, 2, 3, 4, 5, and 6 correspond to  $n = 1.5, 2.6, 5.5, 8.9, 13.7,$  and 18.4, respectively.

quencies and probabilities of vibrational transitions of CH are as follows: electrostatic interactions with  $\text{Li}^+$  and associative interactions between the DMSO molecules.

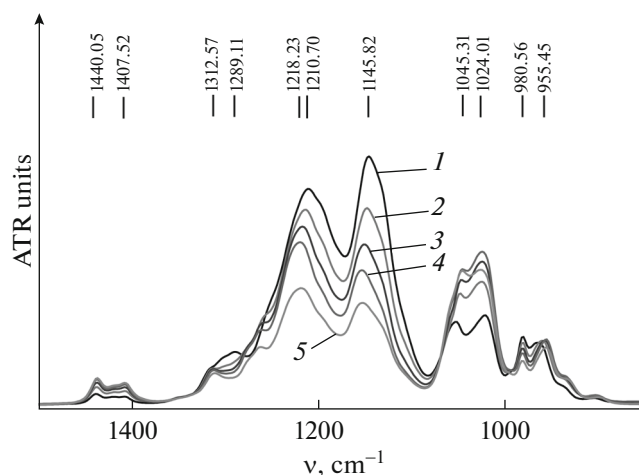
Figure 3 shows the concentration dependence of the frequency of the stretching vibrations of the CS bond of the DMSO molecule. The peak of the  $\nu(\text{CS})$  band for the membrane with  $n = 1.5$  is observed at 714  $\text{cm}^{-1}$ . With an increase in the  $n$  value, it is shifted to lower frequencies. The peak position in the spectrum of the membrane with  $n = 18.4$  corresponds to the frequency of 699  $\text{cm}^{-1}$ . The figure shows that a dependence of frequency on the  $n$  value is also observed in some other cases.

At the same time, examination of the dependence of the frequency of stretching vibrations of the SO bond of the DMSO molecule on the  $n$  value revealed that it exhibits a more complex behavior than that of the dependence of the vibrational frequency of CH or CS (Figs. 4, 5). In particular, the value of  $n = 1.5$  corresponds to a narrow  $\nu(\text{SO})$  singlet at 1021  $\text{cm}^{-1}$ , while  $n = 18.4$  corresponds to a  $\nu(\text{SO})$  doublet at 1024 and 1045  $\text{cm}^{-1}$ . It is reasonable to compare these data with the IR absorption spectroscopy data for the liquid DMSO phase.

Associative interactions (in the simplest case, dimerization) of DMSO molecules in the liquid phase complicate the  $\nu(\text{SO})$  contour: the peak of the band corresponds to a frequency of  $1027 \pm 2 \text{ cm}^{-1}$  [17]. To avoid discrepancies with our data because of different methods used for frequency determination, the spectrum of the liquid phase was recorded again; this time, the ATR IR technique was used. The repeated recording revealed the presence of a  $\nu(\text{SO})$  triplet, the indi-



**Fig. 4.** Envelopes of the  $\nu(\text{CF})$ ,  $\nu(\text{SO})$ , and  $\nu(\text{CO})$  bands in the ATR IR spectra of the nonsolvated Nafion- $\text{Li}^+$  membrane and the membrane minimally solvated with DMSO. Spectral curves 1, 2, and 3 correspond to the molar ratio of components of DMSO/Li = 0, 1.5, and 2.6, respectively.



**Fig. 5.** Envelopes of the  $\nu(\text{CF})$ ,  $\nu(\text{SO})$ , and  $\nu(\text{CO})$  bands in the ATR IR spectra of the Nafion- $\text{Li}^+$ /DMSO samples. Spectral curves 1, 2, 3, 4, and 5 correspond to the molar ratio of components of DMSO/Li = 2.6, 5.5, 8.9, 12.3, and 18.4, respectively.

vidual components of which are not resolved ( $\text{cm}^{-1}$ ): 1020 (shoulder), 1040 (peak), 1060 (shoulder).

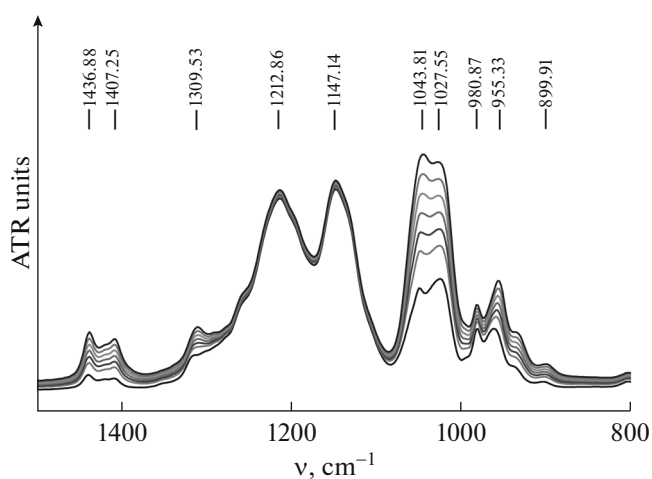
Comparison of the ATR spectroscopy data for the membranes and the liquid DMSO phase shows that, at  $n = 18.4$ , the doublet significantly approaches the  $\nu(\text{SO})$  triplet of the liquid phase with respect to a number of parameters (peak frequency, intensity, large width, degree of asymmetry). The approach indicates the probability of formation of DMSO molecule associates in the membrane. All parameters of the singlet at  $n = 1.5$  are extremely different from the parameters of the  $\nu(\text{SO})$  triplet. The probable cause is the absence of molecular association because of the inclusion of DMSO molecules into the composition of the inner coordination sphere of the lithium ion and the formation of the  $[\text{Li}(\text{DMSO})_n]^+$  complex ion. It should be noted that the singlet is resolved not only at low  $n$ , but also at high  $n$  values. At  $n = 18.4$ , it is represented by one of the two peaks in the broad contour of the enveloping curve of  $\nu(\text{SO})$ . The second peak in this contour occurs owing to the overlap of the narrow band of  $\nu_s(\text{SO}_3)$  of the Nafion and the broader band of  $\nu(\text{SO})$  of the molecular associates. The position of the former and the latter corresponds to a frequency of 1024 and 1045  $\text{cm}^{-1}$ , respectively (Fig. 5). A decrease in frequency to 1021  $\text{cm}^{-1}$  is caused by the polarization of the S=O group by the lithium ion during the coordination of DMSO. In this aspect, the behavior of the DMSO molecule in the membranes is similar to the behavior in lithium perchlorate solutions. The authors of [17] found that the  $\nu(\text{SO})$  frequency decreases from the initial value of 1030 to 1007  $\text{cm}^{-1}$  upon switching from low to high  $\text{LiClO}_4$  concentrations in DMSO. Therefore, the coordination of DMSO by the  $\text{Li}^+$  ion in solution causes a frequency shift of  $\Delta\nu \sim 23 \text{ cm}^{-1}$ . A

shift of the  $\nu(\text{SO})$  frequency of the same order of magnitude, namely  $\Delta\nu = 19 \text{ cm}^{-1}$ , is observed in the ATR IR spectra upon switching from the liquid DMSO to the membrane with DMSO/Li = 1.5, where it is reasonable to assume that almost all molecules are coordinated by the  $\text{Li}^+$  ion through the formation of a  $\text{Li}^+ \dots \text{O}$  bond.

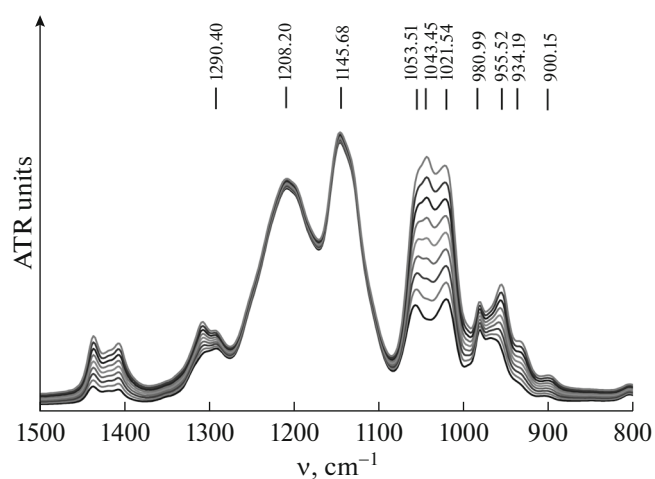
A clear idea of the effect of the different states of the DMSO molecule on the formation of the relief of the intrinsic  $\nu(\text{SO})$  band is provided by our model calculations. The spectrum of the membrane ( $n = 0, 1.5, 2.6, 4.2$ ) was summed with the spectrum of the liquid DMSO phase multiplied by an arbitrary coefficient (0.1, 0.2, 0.3, etc.) to derive a family of curves simulating the shape of a real contour of the  $\nu(\text{SO})$  band for moderate and high solvent concentrations. It was found that the spectral contours of the  $\nu(\text{SO})$  band are best reproduced at the selected experimental value of  $n = 4.2$  (Fig. 6). The smallest discrepancies between the calculated and experimental data are also found in the case of the value of  $n = 2.6$ . However, at the selected value of  $n = 1.5$  (Fig. 7) and, particularly,  $n = 0$ , the discrepancies become unacceptably large. The final result can be treated as an indication that, under favorable conditions, the DMSO molecules do form associates between each other, as in the liquid phase. The most favorable conditions occur if the lithium cation (coordination number of 4) loses free vacancies. It is assumed that the DMSO molecule association products are located in the membrane channels.

Analysis of the long-wavelength region of the ATR IR spectra revealed analytical bands for each of the two types of DMSO molecules.

The existence of DMSO molecules coordinated by the  $\text{Li}^+$  ion is confirmed directly by the identification



**Fig. 6.** Envelopes of  $\nu(\text{SO})$  calculated by the summation of the spectra of the membrane ( $n = 4.2$ ) and the liquid DMSO phase.



**Fig. 7.** Envelopes of  $\nu(\text{SO})$  calculated by the summation of the spectra of the membrane ( $n = 1.5$ ) and the liquid DMSO phase.

of the band of the lithium–oxygen stretching vibrations. The respective band has a broad asymmetrical contour; the band peak corresponds to a frequency of  $442 \text{ cm}^{-1}$  at  $n = 1.5$  (Fig. 3). With an increase in  $n$ , the  $\nu(\text{LiO})$  vibration frequency decreases to  $439 \text{ cm}^{-1}$ . The shape of the  $\nu(\text{LiO})$  contour hardly depends on the  $n$  value. This feature can be attributed to two factors: either the distribution of DMSO molecules between lithium ions is statistically nonuniform at low  $n$  values or the  $\text{LiO}_4$  coordination polyhedron has a low symmetry at medium and high  $n$  values, which provides the elimination of the degeneracy of the vibrational levels. Note that previous IR absorption spectroscopy studies of  $\text{LiClO}_4$  solutions in DMSO revealed the occurrence of a band of the same origin in the long-wavelength region; the band had the same broad asymmetric contour and the band peak was shifted to higher frequencies owing to the isotopic substitution  $^7\text{Li}-^6\text{Li}$ :  $440 \rightarrow 468 \text{ cm}^{-1}$  [18].

The  $\nu(\text{LiO})$  band wings in the membranes are shielded owing to the overlapping of bands of different origin. In the low-frequency range at  $n > 0$ , a triplet at  $306$ ,  $333$ , and  $382 \text{ cm}^{-1}$  is resolved. In accordance with the assignment of [17], it should correspond to three types of bending vibrations of the DMSO molecule: the very weak band at  $306 \text{ cm}^{-1}$  is attributed to  $\delta(\text{CSC})$ , while the other two correspond to the in-plane and out-of-plane  $\delta(\text{CSO})$  vibrations. In the high-frequency range, a medium-intensity  $\delta(\text{CCF})$  triplet at  $514$ ,  $522$ , and  $554 \text{ cm}^{-1}$  is observed. Two peaks of the triplet ( $522$ ,  $554 \text{ cm}^{-1}$ ) are insufficiently resolved.

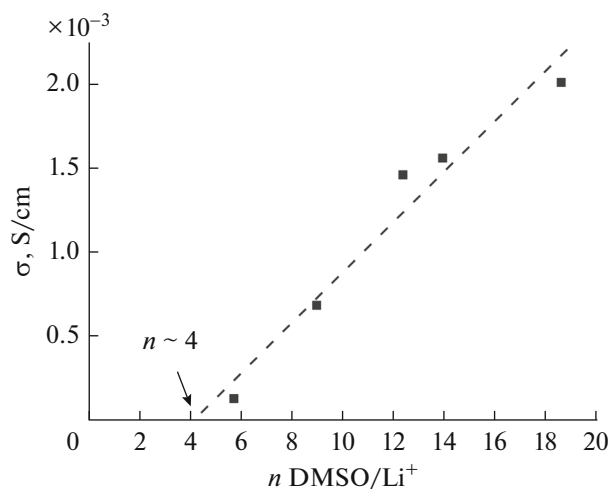
The existence of associated DMSO molecules is confirmed directly by the identification of a broad band with a peak at  $90 \pm 10 \text{ cm}^{-1}$  in the study of the ATR IR spectra of the liquid DMSO phase and the membranes with  $n > 4$ . The intensity of the band

increases with increasing  $n$  value. In the case of the membranes with  $n < 4$ , the band almost disappears (Fig. 3). Conditions under which this band appears and disappears in the boundary region of the long-wave range give grounds to attribute the origin of this band to the dipole–dipole interactions of the molecules. The disappearance of the band at  $n < 4$  means that, in this case,  $\text{Li}^+$  has an effect on all molecules. The cation binding of the DMSO molecules leads to a breakdown of the intermolecular bonds.

Thus, there are only two types of DMSO molecules, coordinated in the inner and in the outer sphere, in the membranes. The inner-sphere and outer-sphere locations facilitate isolation and self-association, respectively. The filling of all inner-sphere vacancies is completed by the formation of  $[\text{Li}(\text{DMSO})_4]^+$ . Equilibrium is established between the two types of molecules. The extent of shift of equilibrium in either direction depends on the  $n$  value. The results of examination of the long-wavelength range show that the complex ion can undergo partial dissociation in the case of  $n = 4$  according to the following scheme:



The study of the ionic conductivity of the polymer electrolyte samples on the DMSO content revealed a correlation with the spectroscopic data. Figure 8 shows the dependence of the ionic conductivity of the lithiated electrolyte on the DMSO content at  $30^\circ\text{C}$ . The ionic conductivity linearly increases with increasing DMSO content. A linear extrapolation of the dependence gives a value of  $n \sim 4$ , which suggests that the smallest transport unit is tetrasolvate  $\text{Li}^+(\text{DMSO})_4$ . The temperature dependences of conductivity exhibit a more complex behavior. At positive temperatures, the conductivity obeys the Arrhenius equation; as the  $n$  value increases from  $5.5$  to  $18.4$ , the activation energy of conductivity decreases  $30.5$  to

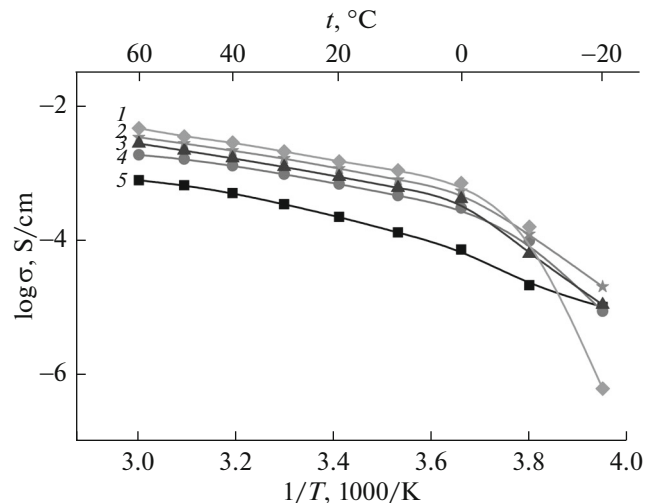


**Fig. 8.** Ionic conductivity of the lithiated electrolyte as a function of the DMSO content at 30°C.

22.6 kJ/mol (Fig. 9); this finding is apparently attributed to the formation of a developed system of transport channels with increasing plasticizer content. At temperatures below 0°C, all samples exhibit an abrupt change in conductivity associated with the freezing of DMSO in the membrane matrix. In addition, for the sample with  $n = 5.5$ , the change is least pronounced apparently owing to the coordination of DMSO by lithium ions.

The dissolution of DMSO in a membrane and the adsorption of water in a zeolite [19] may seem to be disparate phenomena only at first sight. The data of spectroscopic studies suggest that these processes are similar. In fact, the state of the molecules depends on the degree of filling of the available channels and cavities in the membrane and the zeolite. If the fill factor is low, then the molecules—whether DMSO or H<sub>2</sub>O—prefer an isolated state; at a high fill factor, the molecules undergo association interactions similar to those in the liquid phase. It stands to reason that a difference between these phenomena really exists (during adsorption, the membrane structure varies within certain limits, while the zeolite structure remains unchanged); however, this fact is not of fundamental importance for further discussion.

The structural dependence of the polymer matrix chains on the  $n$  value is confirmed by shifts of vibrational frequencies. The shifts to higher frequencies are the most significant in the intense bands of the stretching vibrations of the CF bonds with peaks at 1145 and 1218 cm<sup>-1</sup> (Fig. 5). These shifts are less pronounced in the medium-intensity bands of the bending vibrations of the CF bonds with peaks at 628 and 647 cm<sup>-1</sup> and even less so in weak bands of the bending vibrations of CF with peaks at 514, 522, and 554 cm<sup>-1</sup> (Fig. 3). The dependence of the peak frequency of 204 cm<sup>-1</sup> of a very weak band apparently correspond-



**Fig. 9.** Thermal conductivity of the lithiated electrolyte with varying DMSO content. Conductivity curves 1, 2, 3, 4, and 5 correspond to the molar ratio of components of DMSO/Li = 18.4, 13.7, 12.3, 8.9, and 5.5, respectively.

ing to the torsional vibrations of the CF bond on the  $n$  value is negligible (Fig. 3).

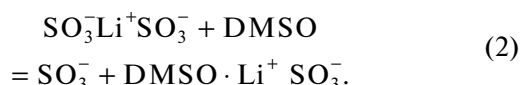
An increase in  $n$  leads to a decrease in the intensity of all bands of the polymer matrix, although to varying degree. As a consequence, one of the two  $\nu(\text{CF})$  bands is significantly superior to the other in intensity at low  $n$  values and inferior to it at high  $n$  values (Fig. 5).

The following data were derived by ATR IR spectroscopy for a frequency range of 50–4000 cm<sup>-1</sup>. In particular, the data show that the vibrational spectrum of the carbon–fluorine bonds of the membrane is very similar to the spectrum of the carbon–fluorine bonds of Teflon: Teflon (Nafion), cm<sup>-1</sup>: 1199 (1218), 1143 (1145), 638 (647), 625 (628), 553 (554), 507 (514, 522), and 202 (204). Using the method of elimination, two medium-intensity bands that are not available in Teflon were assigned to the stretching vibrations of the C–O bonds. The peak of one of the bands corresponds to a frequency of 960 cm<sup>-1</sup>, while the peak of the other is attributed to a frequency of 980 cm<sup>-1</sup> at  $n = 1.5$  (Fig. 4). The first peak is significantly shifted to lower frequencies with increasing  $n$ , while the position of the second peak hardly depends on the  $n$  value (Fig. 5).

An additional source of information on the structure rearrangement was data on the shifts of the vibrational frequency of the ionized SO<sub>3</sub><sup>-</sup> sulfo group in lithiated Nafion. Unfortunately, it is impossible to determine five of six vibrational frequencies of –SO<sub>3</sub><sup>-</sup> because the respective bands are shielded, in particular, by intense bands of vibrational transitions of the carbon–fluorine bonds. Only a single band corresponding to the symmetric stretching vibrations of the sulfur–oxygen bonds is not shielded. A  $\nu_s(\text{SO}_3)$  band was previously detected in dehydrated Nafion–Li<sup>+</sup> at

1060  $\text{cm}^{-1}$  by IR absorption spectroscopy [16]. Analysis of the ATR IR spectrum of the dehydrated sample revealed the frequency of 1073  $\text{cm}^{-1}$  ( $n = 0$ ). With an increase in the DMSO content, the  $\nu_s(\text{SO}_3)$  vibrational frequency decreases: 1073  $\text{cm}^{-1}$  ( $n = 0$ ), 1060  $\text{cm}^{-1}$  ( $n = 1.5$ ), 1052  $\text{cm}^{-1}$  ( $n = 2.6$ ), and 1045  $\text{cm}^{-1}$  ( $n = 8.9$ ).

The discussed data on the dependence of the  $\nu(\text{CF})$ ,  $\nu(\text{CO})$ ,  $\delta(\text{CCF})$ , and  $\nu_s(\text{SO}_3)$  vibrational levels suggest that the polymer structure depends on the  $n$  value. The original polymer chains are apparently crosslinked by lithium ions through the formation of  $-\text{SO}_3^-\text{Li}^+\text{SO}_3^-$  bonds; however, at low  $n$  values, they dissociate according to the following scheme:



At high  $n$  values, the structural changes consist in the reorientation of the polymer chain units under the action of DMSO.

In general, the symmetry of the  $-\text{SO}_3^-$  group depends on the number of lithium ions that surround the group and form bonds with oxygen atoms. The number of 2 or 1 seems to be sufficient to cause a decrease in symmetry and thereby eliminate the degeneracy of the  $\nu_{\text{as}}(\text{SO}_3)$  vibrations. Unfortunately, it is impossible to determine whether the degeneracy is really eliminated because, according to our reckoning, the band corresponding to  $\nu_{\text{as}}(\text{SO}_3)$  is masked by an intense  $\nu(\text{CF})$  band at 1218  $\text{cm}^{-1}$ . Another view is that, for the Nafion membrane, the  $\nu_{\text{as}}(\text{SO}_3)$  frequency takes a significantly higher value of 1300  $\text{cm}^{-1}$  [15, 16]. However, this view cannot be accepted in any way because it is completely disproved by the results of IR spectroscopic studies of the ionized states of a long series of sulfonic acids. The studies of trifluoromethanesulfonic ( $\text{CF}_3\text{SO}_3\text{H}$ ) [20] and polystyrenesulfonic acids [21] are the most important. If necessary, these data could be supplemented by the results of similar studies for at least four organic sulfonic acids. In none of the cases known to us, the  $\nu_{\text{as}}(\text{SO}_3)$  vibrational frequency of the  $-\text{SO}_3^-$  ionized group is higher than 1200–1220  $\text{cm}^{-1}$ .

## CONCLUSIONS

The solvation products of lithiated Nafion with DMSO have been studied by ATR IR spectroscopy in the frequency range of 50–4000  $\text{cm}^{-1}$  in a vacuum at room temperature with varying degree of solvation  $n = \text{DMSO}/\text{Li}$  in the range of 1.5–18.4. Based on analysis of the dependence of the spectral parameters on the  $n$  value, it has been concluded that the test samples comprise two types of DMSO molecules. The first type includes molecules coordinated to the lithium ion through the formation of the metal–oxygen bond; the second type covers molecules associated by intermolecu-

lar bonds similar to those in the liquid DMSO phase. The structure of the salt depends on the  $n$  value: the changes are attributed to the reorientation of polymer chain units. The coordination number of lithium has been estimated at four. It has been shown that the IR spectroscopy data are consistent with the data on the conductivity of lithiated Nafion membranes as a function of DMSO content, according to which the simplest transport unit is the tetrasolvate  $\text{Li}^+(\text{DMSO})_4$ . At temperatures below 0°C, all the samples exhibit an abrupt change in conductivity, which is attributed to the freezing of DMSO in the membrane matrix.

## ACKNOWLEDGMENTS

This work was supported by the Ministry of Education and Science of the Russian Federation, agreement no. 14.604.21.0125 dated August 26, 2014 (unique project identifier RFMEFI60414X0125).

## REFERENCES

1. V. Etacheri, R. Marom, R. Elazari, et al., *Energy Environ. Sci.* **4**, 3243 (2011).
2. K. Xu, *Chem. Rev.* **104**, 43030 (2004).
3. E. Quartarone and P. Mustarelli, *Chem. Soc. Rev.* **40**, 2525 (2011).
4. P. V. Wright, *MRS Bull.* **27**, 597 (2002).
5. P. Aldebert, M. Guglielmi, and M. Pineri, *Polym. J.* **23**, 399 (1991).
6. C. M. Doyle, M. E. Lewittes, M. G. Roelofs, et al., *J. Membr. Sci.* **184**, 257 (2001).
7. S. Sachan, C. A. Ray, and S. A. Perusich, *Polym. Eng. Sci.* **42**, 1469 (2002).
8. E. A. Sanginov, E. Yu. Evshchik, R. R. Kayumov, and Yu. A. Dobrovolskii, *Russ. J. Electrochem.* **51**, 986 (2015).
9. W. Navarrini, B. Scrosati, S. Panero, et al., *J. Power Sources* **178**, 783 (2008).
10. Zh. Jin, K. Xie, and X. Hong, *J. Mater. Chem. A* **1**, 342 (2013).
11. Zh. Jin, K. Xie, and X. Hong, *RSC Adv.* **3**, 8889 (2013).
12. Zh. Cai, Y. Liu, S. Liu, et al., *Energy Environ. Sci.* **5**, 5690 (2012).
13. Y. Liu, Zh. Cai, L. Tan, and L. Li, *Energy Environ. Sci.* **5**, 9007 (2012).
14. Zh. Jin, K. Xie, X. Hong, et al., *J. Power Sources* **218**, 163 (2012).
15. R. S. Buzzoni, S. Bordiga, G. Ricchiardi, et al., *J. Phys. Chem. B* **99**, 11937 (1995).
16. M. Wang, F. Zhao, and S. Dong, *J. Phys. Chem. B* **108**, 1365 (2004).
17. Z. Wang, B. Huang, S. Wang, et al., *Electrochim. Acta* **42**, 2611 (1997).
18. P. P. Schmidt and M. W. Severson, *J. Phys. Chem.* **90**, 1046 (1986).
19. L. H. Little, *Infrared Spectra of Adsorbed Molecules* (Academic, London, 1966).
20. P. S. Gejji and J. Lindgren, *J. Phys. Chem.* **97**, 6986 (1993).
21. G. Zundel, *Hydration and Intermolecular Interaction: Infrared Investigations with Polyelectrolyte Membranes* (Academic, New York, 1969).

Translated by M. Timoshinina