

**ELECTRICAL CONDUCTIVITY AND ASSOCIATION
OF 1-BUTYL-3-METHYLPYRIDINIUM
BIS{(TRIFLUOROMETHYL)SULFONYL}AMIDE
IN SOME POLAR SOLVENTS**

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Abstract

The influence of alternating current frequency in the determination of the electrical conductivity of ionic liquids' (ILs) dilute solutions in polar solvents has been considered. The frequency ranges in which the influence of polarization processes on electrodes occur and ionic relaxation occurs in the bulk of the solution have been excluded from the results of the electrical conductivity measurements. The association constants for K_a ILs in polar solvents published in literature were analyzed. A discrepancy between the values of K_a was noted, which is associated with the use of different calculation equations for electrical conductivity and the insufficiently correct consideration of the frequency dependence of the measured resistance. Based on the measured values of the electrical conductivity of dilute solutions of 1-butyl-3-methylpyridinium bis{(trifluoromethyl)sulfonyl}amide ([Bmpy][NTf₂]) in acetonitrile (AN), dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) in the 20–65 °C temperature range, the thermodynamic characteristics of the [Bmpy][NTf₂] association were determined. The effect of temperature on the molar electrical conductivity of [Bmpy][NTf₂] at infinite dilution λ_0 and the association constant K_a have been considered. The Walden product ($\lambda_0\eta$), where η is the viscosity of the solvent, was also analysed. It was shown that in AN, DMSO, and DMF, $\lambda_0\eta$ changes

Keywords

*1-butyl-3-methylpyridinium
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dimethylformamide*

in different ways with increasing temperature; however, the value of $\lambda_0\eta/(\epsilon T)$ corrected for permittivity ϵ and absolute temperature T does not depend on the temperature and nature of the solvent. As the temperature rises, the electrical conductivity of the dilute solutions of [Bmpy][NTf₂] increases in direct proportion to the ratio of the permittivity to dipole dielectric relaxation time of the solvent

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Introduction. Ionic liquids (ILs) occupy a special place in the physical chemistry of liquid states, being both a solute and a solvent. Possessing a low vapor pressure, high thermal stability and that they remain liquid over a large temperature range [1], ILs replace volatile organic solvents not only in scientific research, but also in practical applications in various branches of chemistry and technology [2–7]. Possessing significant electrical conductivity (EC), ILs and their solutions in polar solvents show promise for use in various electrochemical devices — current sources and electric energy storage devices [8–10]. By combining various cations and anions of ILs, it is possible to obtain liquids with the suitable set of physical and chemical properties required for practical use. Therefore, ILs can be classified as “designer solvents” [3].

For the practical application of ILs, their mixtures and solutions in polar solvents, it is necessary to study their physicochemical properties in a wide range of temperatures and compositions. In the case of their application in electrochemical devices, information is needed on the conductivity of ILs, as well as their state in the processes of solvation and dissociation in solutions.

Based on the results of the EC measurements of dilute solutions, it is possible to determine the value of molar EC at infinite dilution λ_0 and the association constant K_a of ILs in polar solvents. Currently, there are publications in literature related to the results of determining λ_0 and K_a mainly for the ILs based on the 1-alkyl-3-methylimidazolium cation ($[Rmim]^+$, $R = C_nH_{2n+1}$) [11–21]. It should be noted that if the values of λ_0 in these publications are in good agreement with each other (the discrepancy between the values of λ_0 does not exceed 5–10 %), then the association constants K_a can differ significantly (the error in determining the association constants, as a rule, is twice as large as the error λ_0). As an example, let us compare the values of the molar EC at infinite dilution (λ_0 , S cm²/mol) and the association constants (K_a , L/mol) of some ionic liquids based on the 1-butyl-3-methylimidazolium cation in methanol and acetonitrile at 25 °C (Table 1).

Molar EC values of λ_0 and association constants K_a of ionic liquids based on 1-butyl-3-methylimidazolium ([Bmim]⁺) cation in methanol and acetonitrile at 25 °C at infinite dilution

Ionic liquid	Solvent	λ_0 , S cm ² /mol	K_a , L/mol	References
[Bmim][BF ₄]	Methanol	121.84	37.7	[11]
		126.9	55.0	[12]
	Acetonitrile	189.29	15.7	[13]
		190.3	18.2	[14]
		181.4	712	[15]
[Bmim][PF ₆]	Acetonitrile	184.70	15.6	[13]
		158.52	27.0	[16]
		179.1	683	[15]
[Bmim]Cl	Acetonitrile	196.52	88.5	[16]
		178.45	725.21	[17]

In a methanolic solution of 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄]), K_a according to the data of [11], turned out to be almost 1.5 times less than in [12]. The values of λ_0 according to [11, 12] differ by only 4 %. The association constants of the same IL in acetonitrile are close, according to the data of [13] and [14] (the difference between the K_a values does not exceed 15 %), but differ significantly from the K_a value (712 L/mol) of [Bmim][BF₄] obtained in the work [15]. The same large difference is observed for the association constants of [Bmim][PF₆] in this solvent according to the data of [15] (683 L/mol), [13] (15.6 L/mol) and [16] (27.0 L/mol). In acetonitrile, the association constants of [Bmim]Cl are 88.5 [16] and 725.21 L/mol [17], so they also differ significantly (more than eight times).

In dilute aqueous solutions, ionic liquids based on the imidazolium cation are weakly associated. According to [18], for imidazolium chlorides $2.5 \leq K_a \leq 6$ L/mol. The association constant for 1-butyl-3-methylimidazolium halides is less than 10 L/mol [19]. For [Bmim][BF₄] $K_a = 0.19$ L/mol [20]. In [15], the association constant is clearly overestimated: it is 70–100 L/mol for 1-alkyl-3-methylimidazolium bromides (alkyl C₄, C₆, C₈, C₁₀, and C₁₂) and 105 L/mol for [Bmim][BF₄].

The discrepancy between the values of K_a published in various works is noted [14, 20, 21]. It is indicated that a possible reason for the variation in the association constants can be caused by a different procedure for processing conductometric data [14]. In particular, in [12, 14, 15], the Lee — Wheaton

electrical conductivity equation [22–24] is used to calculate the association parameters, and in [11, 13, 16, 18–20], the Fuoss — Justice equation is applied for the analysis of conductometric data in the framework of “Low Concentration Chemical Model” proposed by Barthel *et al* [25]. In [17], the λ_0 and K_a were calculated using the Fuoss equation [26]. The use of different electrical conductivity equations is the first reason for the discrepancy between the association constants noted above. In our opinion, these values should be compared only within the framework of one calculation equation, which, for example, was correctly carried out in [27].

The second reason for the discrepancy between the values of the association constants may be the use of different procedures for measuring the electrical resistance of the solution R , in particular, the analysis of its frequency dependence in order to exclude the influence of the polarisation processes. In [12, 14, 15, 17, 19], such an analysis was not carried out and R measurements were carried out at one frequency (1 kHz [12, 14, 17]; 1.1 kHz [15] and 1 MHz [19]).

The experimentally measured electrical resistance of the solution in the conductometric cell R decreases with increasing frequency F . To improve the accuracy of conductometric measurements, it is recommended to extrapolate the measured resistance to an infinite frequency, i.e., analyze the dependence of the measured resistance R on the frequency F in the coordinates $R-1/F$ [28, 29]. This procedure was used in [11, 13, 18, 20]. At the same time, to eliminate the influence of polarization processes on the electrodes, the dependences $R-1/F^{0.5}$ [30] and $R-1/F^2$ [31] are also used. Analysis of the frequency influence on the accuracy of conductometric measurements was carried out in the experimental part of this work.

The brief analysis carried out above shows that the ionic association of mainly dialkylimidazolium ILs in polar solvents has been studied. The association of ILs based on other organic cations, in particular 1-alkyl-3-methylpyridinium, has practically not been studied. It is of practical interest to elucidate the nature of the association of the 1-butyl-3-methylpyridinium [bis{(trifluoromethyl)sulfonyl}amide, [Bmpy][NTf₂] ionic liquid. Solutions of ILs with this anion have a fairly high specific conductivity and a relatively wide electrochemical window [32].

In this work, we analyze the conductometric studies' results of the thermodynamic characteristics of [Bmpy][NTf₂] association in acetonitrile (AN), dimethyl sulfoxide (DMSO), and dimethylformamide (DMF) and consider the relationship between the electrical conductivity of dilute solutions of this IL and the dielectric properties of the solvent.

Experimental part. [Bmpy][NTf₂] (1-butyl-3-methylpyridinium bis{(trifluoromethyl)sulfonyl}amide) (Fig. 1) was obtained by a metathesis reaction between the aqueous solutions of 1-butyl-3-methylpyridinium chloride and an excess of lithium bis{(trifluoromethyl)sulfonyl}amide at Queen's University of Belfast Ionic Liquid Laboratories (QUILL) in Northern Ireland.

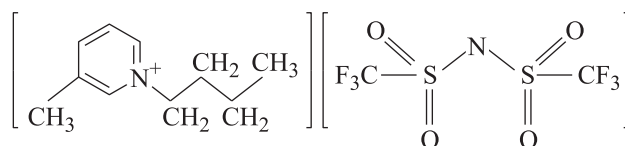


Fig. 1. Structure of 1-butyl-3-methylpyridinium bis{(trifluoromethyl)sulfonyl}amide

The purity of the ionic liquids (99.5 %) was also monitored using NMR spectroscopy at QUILL. Characteristics of IL: molar mass 430.41 g/mol, melting point 8.15 °C and density 1.4187 g/cm³ (20 °C).

Before preparing the solutions, [Bmpy][NTf₂] was dried in a vacuum fume hood at 60 °C for five hours. Solutions of [Bmpy][NTf₂] were prepared by the gravimetric method; in this case, taken with an accuracy of ± 0.00001 g, a weighed portion of the ionic liquid was quantitatively transferred into a preliminarily prepared volumetric flask. After that, a solvent was added to this ionic liquid. The water content in the solvents used in this work (AN, DMSO, and DMF) was controlled by the Karl Fischer method and did not exceed 0.1 %.

The conductometric cell used in the work is made of Pyrex glass and is a glass tube with an inner diameter of ≈ 10 mm, at the ends of which there are two spherical containers into which platinum electrodes are soldered. The length of the cell glass tube is ≈ 45 mm. The cell is soldered into a glass jacket, through which liquid (water) is pumped from a thermostat. The accuracy of solution temperature control was ± 0.05 °C. The electrodes of the contact cell were platinised to reduce the polarisation resistance. The cell constant was determined by measuring the resistance of KCl aqueous solutions according to the standard procedure [28]. Its value is 0.1723 ± 0.0003 cm. The error in the specific EC of the solutions did not exceed 0.5 %. The solution resistance R was measured using an E7-20 digital AC bridge (immittance meter) in the 0.1–10 kHz frequency range with an error that did not exceed 0.1 %.

An important issue in determining the thermodynamic characteristics of the association (in addition to the choice of the equation $\lambda = f(c)$ considered above and the method of analysing conductometric data (using the procedure for calculating K_a and λ_0 from the dependance of the molar EC λ

on the concentration c) is also the restriction on the maximum concentration of solutions c_{\max} and the requirements for high accuracy measurements of dilute ILs solutions' electrical conductivity in various polar solvents.

The highest concentration of the solution c_{\max} , the molar EC of which is used in calculating the thermodynamic characteristics of the association, depends on the dielectric permittivity (DP) of the solvent ε , the absolute temperature T , and the equation, describing the dependance of λ on the concentration c . In [24], the following equation was proposed for estimating c_{\max} (mol/L):

$$c_{\max} = 9.1 \cdot 10^{-15} (\varepsilon T)^3. \quad (1)$$

In his work [33], Fuoss proposed to take into account only the dielectric permittivity of the solvent ε when calculating c_{\max} :

$$c_{\max} = 3.2 \cdot 10^{-7} \varepsilon^3. \quad (2)$$

The c_{\max} values for the solvents used in this work are compared below.

The molar EC of IL solutions λ is determined on the basis of specific EC κ , which, in turn, is calculated using the value of the cell constant k and the measured solution resistance R . In this case: $\kappa = 1 / (kR)$, $\lambda = \kappa / c$.

The measured electrical resistance of the solution R_{meas} decreases with an increase in the frequency of the alternating current F , as a result of polarization processes on the electrodes [34, 35] and ionic relaxation in the volume of the solution [36]. Electrode polarization leads to the fact that the measured resistance R_{meas} exceeds the resistance of the solution R [34, 35], while ionic relaxation in the volume of solutions reduces the measured resistance R_{meas} compared to the value of R [36]. Therefore, the problem of correctly measuring the resistance R of ILs solutions, in particular, the analysis of the frequency dependance of this value, needs special consideration.

To exclude polarisation processes on the electrodes, the resistance of the solution is measured, as a rule, in the frequency range of 0.1–10 kHz and R is found by extrapolation to an infinite frequency in the $R_{meas} - 1 / F$ coordinates [11, 13, 18, 20, 28, 29]. When analyzing the frequency dependance of the measured resistance R_{meas} of dilute IL solutions, it is also necessary to consider the ionic relaxation in the bulk of solution [36]. The procedure for accounting for this phenomenon will now be considered.

In the general case, the electrical equivalent circuit of a solution is represented in the form of solution resistance R and electric capacitance C connected in parallel that model its specific conductivity κ and dielectric permittivity ε . At the same time [36]:

$$R = \frac{1}{k\kappa}, \quad C = k\varepsilon\varepsilon_0, \quad (3)$$

where k is the proportionality factor having the dimension of length (conductometric cell constant); ε_0 is the vacuum DP ($\varepsilon_0 = 8.854 \cdot 10^{-12}$ F/m).

The measured solution resistance R_{meas} is related to the resistance R and electrical capacitance C of the solution by the relation [36]:

$$R_{meas} = \frac{R}{1 + (\omega CR)^2}, \quad (4)$$

where $\omega = 2\pi F$ is the angular frequency.

The exclusion of polarization processes' influence on the measured solution resistance in the $R_{meas}-1/F$ coordinates is valid under the condition $\omega CR \ll 1$. Only in this case, the measured solution resistance R_{meas} will be equal to the desired resistance R [36].

Ionic relaxation in the volume of the solution leads to a decrease in the measured resistance R_{meas} with increasing frequency and it affects the measurement results already under the $\omega CR > 0.1$ condition. Under the $\omega CR = 1$ condition, according to Eq. (4), the measured resistance R_{meas} will be two times lower than the desired resistance R , which can be perceived as a twofold increase in the specific EC, and, consequently, the molar EC of dilute IL solutions. Such a sharp increase in the molar EC with decreasing concentration can occur in very dilute solutions of ILs in weakly polar solvents characterized by low DP values.

Equation (4) can be rewritten as:

$$\frac{1}{R_{meas}} = \frac{1}{R} + (\omega C)^2 R = \frac{1}{R} + AF^2. \quad (5)$$

Here $A = (2\pi C)^2 R$. Accounting for ionic relaxation in precision conductometric measurements is carried out by extrapolating the inverse measured resistance $1/R_{meas}$ to zero frequency in the $1/R_{meas}-F^2$ coordinates [36]. Such accounting must be carried out in the frequency range in which the following inequality is satisfied:

$$0.1 \leq \omega CR \leq 10. \quad (6)$$

Equation (6) limits the frequency range in which it is necessary to consider the effect of ionic relaxation on the measured solution resistance in the $1/R_{meas}-F^2$ coordinates.

It should be noted that under the condition $\omega CR \gg 1$, Eq. (4) is transformed into the equality

$$R_{meas} = \frac{1}{(\omega C)^2 R}. \quad (7)$$

Thus, under the condition $\omega CR \gg 1$, the measured resistance R_{meas} decreases in proportion to the square of the reciprocal frequency and is not equal to the desired solution resistance R . In this case, the solution resistance R must be calculated based on its measured value R_{meas} , considering the angular frequency ω and the electric capacitance of the solution C . From Eq. (7), we obtain:

$$R = \frac{1}{(\omega C)^2 R_{meas}}. \quad (8)$$

Equation (8) must be used, first of all, when determining the electrical conductivity of polar solvents, the electrical resistance of which is very high, and the inequality $\omega CR \gg 1$ for them is already satisfied at low frequencies.

The value of ωCR is the ratio of displacement currents to conduction currents [36]. Using Eq. (3), we can write

$$\omega CR = \frac{\omega \varepsilon \varepsilon_0}{\kappa}. \quad (9)$$

Taking into account Eq. (9), inequality (6) can be written as

$$0.1 \leq \frac{\omega \varepsilon \varepsilon_0}{\kappa} \leq 10.$$

Ionic relaxation leads to a decrease in the measured resistance with increasing frequency already under the $\omega \varepsilon \varepsilon_0 \geq 0.1\kappa$ condition. From here, one can find the boundary cut-off frequency F_{bound} , at which the measured resistance of the solution begins to decrease due to ionic relaxation:

$$F_{bound} \geq \frac{0.1\kappa}{\varepsilon \varepsilon_0} = \frac{1.8 \cdot 10^9 \kappa_{bound}}{\varepsilon}. \quad (10)$$

In Eq. (10), the specific conductivity is expressed in S/m, and the permittivity is expressed in relative units. From Eq. (10) for any frequency F , one can also find the boundary value of the specific electric field κ_{bound} , below which ionic relaxation will affect the results of measuring the solution resistance in a conductometric cell:

$$\kappa_{bound} \leq \frac{\varepsilon \varepsilon_0 F}{0.1} \leq 5.56 \cdot 10^{-10} \varepsilon F. \quad (11)$$

In Table 2, for the solvents used in this work (AN, DMSO, and DMF) the values of DP ε , calculated using Eq. (11), the boundary values of the specific

EC κ_{bound} below which ionic relaxation begins to affect the results of resistance measurements at a frequency of 1 kHz, and also the maximum concentrations of solutions c_{max} (1) and c_{max} (2) calculated using equations (1) and (2) utilised in calculations of K_a and λ_0 are shown. For comparison, in Table 2 these values for aqueous solutions are also shown.

Table 2

Dielectric permittivity of solvents ε , boundary specific electrical conductivity κ_{bound} and maximum concentrations c_{max} for some polar solvents; $t = 25$ °C

Solvent	ε [37]	κ_{bound} , 10^5 , S/m	c_{max} , mol/L	
			(1)	(2)
AN	37.5	2.08	0.017	0.013
DMF	37.0	2.06	0.016	0.012
DMSO	47.0	2.61	0.033	0.025
Water	78.3	4.35	0.150	0.120

From the calculated values in Table 2, the following conclusions can be drawn. The limiting specific electrical conductivity κ_{bound} is much higher than the conductivity of pure organic solvents [38]. Therefore, when measuring their specific electrical conductivity, it is necessary to consider ionic relaxation, which leads to an overestimation of the electrical conductivity. Such an overestimation will also take place in the case of the specific EC measurements of sufficiently dilute ($c \leq 10^{-4}$ M) IL solutions under consideration. The maximum concentrations c_{max} calculated using Eqs. (1) and (2) are close and for the solvents used in the work do not exceed 0.02–0.04 mol/L.

An important conclusion from the data in Table 2 is also the fact that when determining the thermodynamic characteristics of ionic association based on the results of measuring the EC of dilute solutions, there are restrictions on both the maximum and minimum concentrations. The minimum concentration determines the value of the boundary EC of the solution κ_{bound} , above which ionic relaxation does not affect the frequency dependence of the measured resistance. Since the measurements of the resistance R are carried out in the frequency range of 0.1–10 kHz, the minimum concentration of the studied solutions should be such that the value of their specific electrical conductivity should not fall below the value of κ_{bound} described by Eq. (11), which depends on the DP of the solvent ε and the frequency F .

The desired resistance R of all solutions in this work was determined by extrapolation of its measured value to an infinite frequency in the $R-1/F$

coordinates [29]. The frequency interval was chosen so that for all the studied solutions the condition $\omega CR \ll 1$ is satisfied, under which ionic relaxation does not affect the results of measuring the resistance R . As the concentration increases, the measured resistance decreases, therefore, to fulfill the condition $\omega CR \ll 1$, a transition to the region of higher frequencies is needed. Such a transition is also necessary when the measurement temperature rises, since with increasing temperature, the measured resistance R_{meas} decreases.

To determine the molar electrical conductivity at infinite dilution λ_0 , the ion association constant K_a and the parameter of the closest approach of ions R from the experimental conductometric data, we used the experimental data processing method [39], which consists of minimizing the function:

$$F = \sum_{i=1}^n \left(\lambda_i^{theor} - \lambda_i^{exp} \right)^2,$$

where λ_i^{exp} is the experimental value of the electrical conductivity; λ_i^{theor} is the theoretical value of the molar EC calculated using the Lee — Wheaton equation [22–24], which is a function of concentration c , permittivity ϵ , viscosity η , temperature T , and the desired parameters λ_0 , K_a and R . The values of λ_0 , K_a and R were calculated using a programme compiled in *Microsoft Office Excel* [39], in which the values of ϵ , η , T and all measured molar EC λ_i^{exp} at the corresponding concentrations c_i were entered. As a result of the calculation, the numerical values of λ_0 , K_a and R and the absolute error values of these quantities ($\pm \Delta\lambda_0$, $\pm \Delta K_a$ and $\pm \Delta R$) were obtained.

Results and discussion. The molar EC of [Bmpy][NTf₂] solutions in AN, DMF, and DMSO decreases with increasing concentration. Figure 2 as an example shows the $\lambda-c^{1/2}$ dependences for the solutions of [Bmpy][NTf₂] in DMF (Fig. 2, *a*) and DMSO (Fig. 2, *b*). In the entire studied range of concentrations and temperatures, the following pattern of change in molar conductivity is observed:

$$\lambda_{AN} > \lambda_{DMF} > \lambda_{DMSO}.$$

This pattern is consistent with the results in the molar EC of dilute solutions changes of other ILs in AN, DMF, and DMSO [13, 21].

The molar EC calculated by the Lee — Wheaton method at an infinite dilution λ_0 [Bmpy][NTf₂] in the studied solvents changes in the same way as the values of λ , i.e., decrease upon going from AN to DMF and to DMSO. To explain the temperature dependance of λ_0 , the Walden empirical rule [40] is usually used, according to which, the product of the molar EC at an infinite

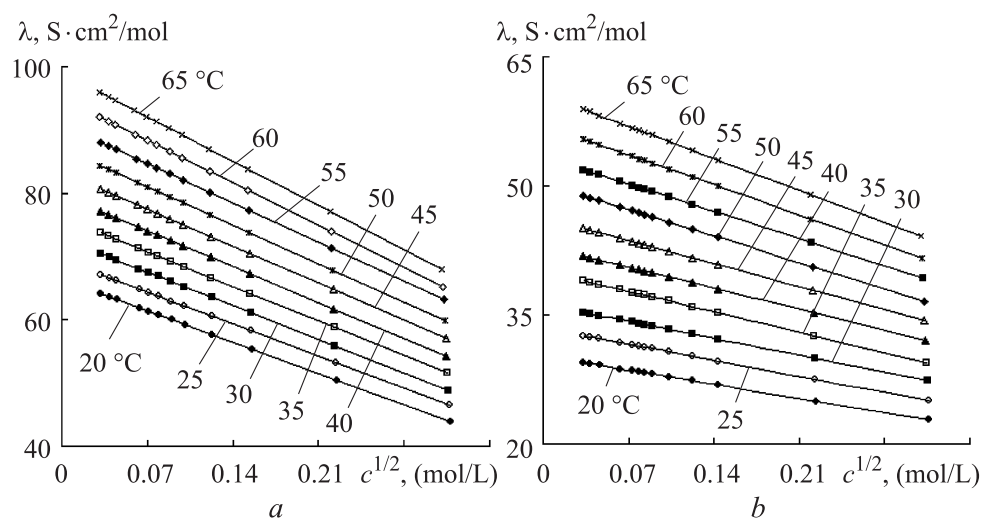


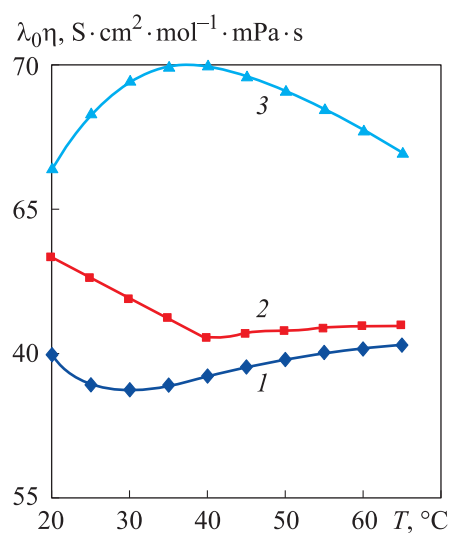
Fig. 2. Dependence of the molar EC of [Bmpy][NTf₂] solutions in DMF (*a*) and DMSO (*b*) on the square root of the concentration in the 20–65 °C temperature range

dilution of λ_0 and the solvent viscosity η is a constant value. Since the opposite pattern is observed for the viscosity of solvents $\eta_{AN} < \eta_{DMF} < \eta_{DMSO}$, one would expect that the values of the products $\lambda_0\eta$ for the studied ILs in the temperature range (20–65 °C) would be the same for all three solvents. An analysis of the dependences of the product $\lambda_0\eta$ on temperature (Fig. 3) shows

Fig. 3. Dependence of the Walden product $\lambda_0\eta$ for solutions of [Bmpy][NTf₂] in AN (1), DMF (2) and DMSO (3) on temperature (20–65 °C)

that these values do not coincide and vary in different ways depending on temperature: the value of $\lambda_0\eta$ passes through a minimum with increasing temperature in AN and DMF (curves 1 and 2, see Fig. 3) and passes through a maximum in DMSO (curve 3, see Fig. 3).

It should be noted that the Walden rule is also not valid for solutions of other ionic liquids in polar solvents [14, 20, 21].



In [41], it was proposed to analyze the temperature dependance of λ_0 of non-aqueous electrolyte solutions depending on the dielectric properties of solvents, in particular, on the $\varepsilon T/\eta$ ratio. As a result, it turned out that with increasing temperature, λ_0 increases in direct proportion to the value of $\varepsilon T/\eta$. This pattern was also confirmed for IL solutions in polar solvents [42]. The dependance of λ_0 on the ratio $\varepsilon T/\eta$ for [Bmpy][NTf₂] solutions in three solvents (AN, DMF, and DMSO) in the 20–65 °C temperature range is shown in Fig. 4, *a*. The values of the molar EC at infinite dilution for AN, DMF, and DMSO fit into one straight line, i.e., the value of λ_0 increases in direct proportion to the ratio $\varepsilon T/\eta$. Similarly, in proportion to the value of $\varepsilon T/\eta$, the molar EC at infinite dilution λ_0 of [Bmim][BF₄] increases in various polar solvents (see Fig. 4, *b*). The dependance in Fig. 4, *b* was plotted using the data for λ_0 , ε , and η provided in [21].

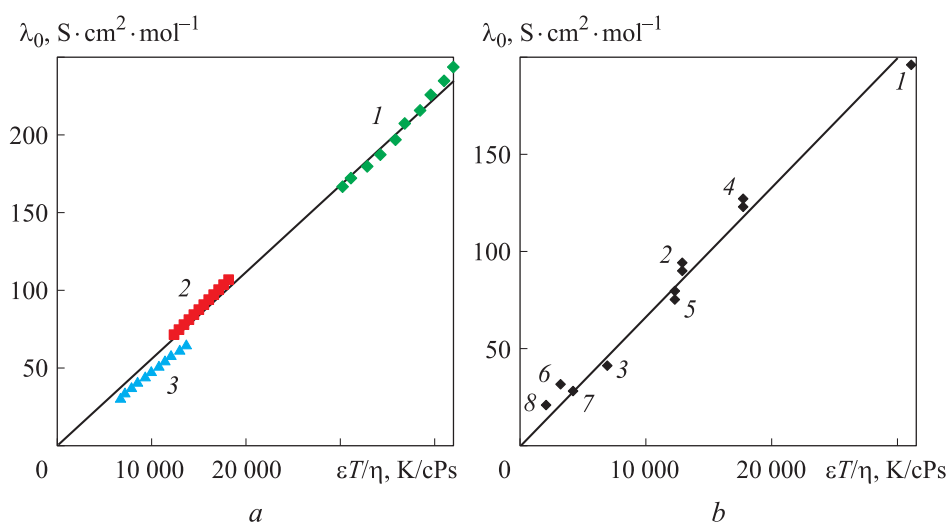


Fig. 4. Dependance of the molar EC of [Bmpy][NTf₂] at infinite dilution in the 20–65 °C temperature range (*a*) and [Bmim][BF₄] at 25 °C (*b*) on the ratio $\varepsilon T/\eta$ in AN (1), DMF (2), DMSO (3), methanol (4), dimethylacetamide (5), 1-propanol (6), 2-propanol (7) and 1-butanol (8)

Thus, the dependances, presented in Fig. 4, confirm the applicability of the previously established pattern, first for aqueous [43] and then for non-aqueous [41] electrolyte solutions, as well as for IL solutions in polar solvents [42]. This pattern establishes a relationship between the electrical conductivity of solutions and the dielectric properties of the solvent: as the temperature rises, the EC of the solutions increases in direct proportion to the ratio of the

permittivity ε to the dipole dielectric relaxation time τ of the solvent [41–43]. With regard to the specific EC, one can write [41–43]:

$$\kappa = k \frac{\varepsilon\varepsilon_0}{\tau} = k\kappa_\infty, \quad (12)$$

were κ_∞ is the limiting high-frequency (HF) EC of a polar solvent, which is equal to the ratio of its absolute DP $\varepsilon\varepsilon_0$ to the dipole relaxation time τ .

The existence of the proportionality described by Eq. (12) means that with increasing temperature, the specific EC of [Bmpy][NTf₂] solutions in the studied polar solvents should increase in proportion to the ratio ε/τ , i.e., proportional to the limiting HF EC κ_∞ of the solvent. The dependences $\kappa-\kappa_\infty$ for 0.1 M solutions of [Bmpy][NTf₂] in AN, DMF, and DMSO are shown in Fig. 5. The considered dependences $\kappa-\kappa_\infty$ differ in the value of the slope

Fig. 5. Dependence of the specific EC of 0.1 M [Bmpy][NTf₂] in AN (1), DMF (2), and DMSO (3) solutions on the limiting HF EC of the solvent

coefficient, which depends on the degree of ionic liquid dissociation and the concentration of solvent molecules in the solution [42].

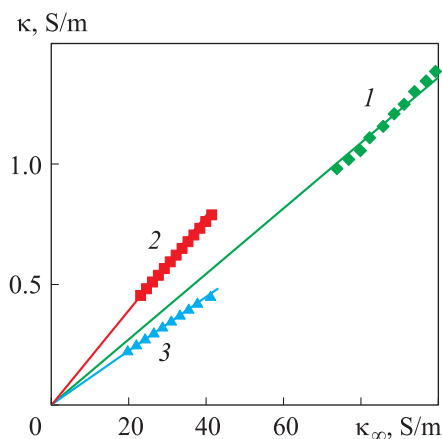
Since, according to the Stokes — Einstein — Debye equation [44], the dipole dielectric relaxation time is proportional to the ratio η/T , taking into account Eq. (12) and the established dependence (see Fig. 5), the Walden rule can be supplemented by the values ε and T :

$$\frac{\lambda_0\eta}{\varepsilon T} = \text{const.} \quad (13)$$

Equation (13) has been proposed to be used to compare the λ_0 values of IL solutions in different solvents at different temperatures.

Based on the temperature dependence of the molar EC at infinite dilution, the activation enthalpy of activation for the Eyring electrical conductivity can be obtained $\Delta H_{\lambda_0}^\ddagger$ [45]:

$$\ln \lambda_0 + \frac{2}{3} \ln \rho = -\frac{\Delta H_{\lambda_0}^\ddagger}{RT} + B,$$



were ρ is the density of the solvent, which takes into account the increase in the volume of the solution with increasing temperature [45].

The dependences of $\ln \lambda_0 + 2/3 \ln \rho$ on the reciprocal temperature are shown in Fig. 6, *a* and the Eyring conduction activation enthalpies calculated on the basis of these dependences are presented in Table 3.

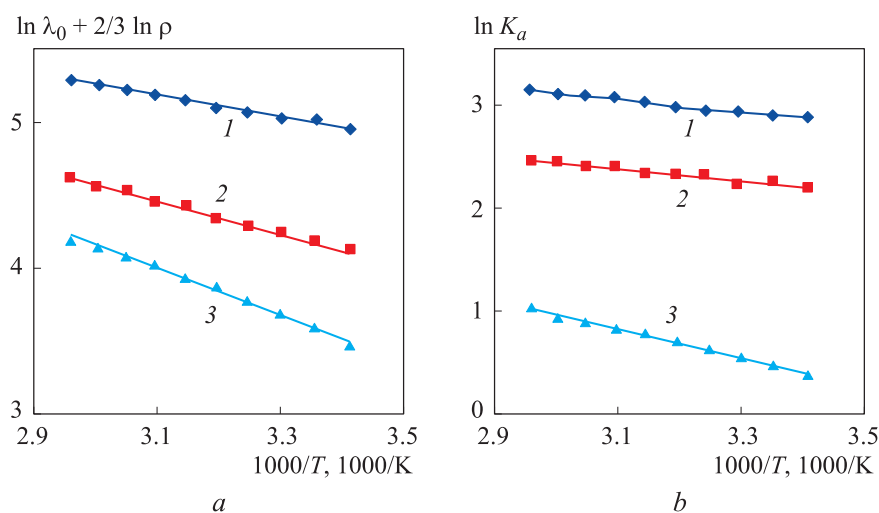


Fig. 6. Dependence of $\ln \lambda_0 + 2/3 \ln \rho$ (*a*) and $\ln K_a$ (*b*) of [Bmpy][NTf₂] on the reciprocal temperature T in AN (1), DMF (2) and DMSO (3)

Table 3

**Enthalpy of activation for electrical conductivity ($\Delta H_{\lambda_0}^\ddagger$)
and thermodynamic characteristics of [Bmpy][NTf₂] association (ΔH° , ΔS°)
in polar solvents in the 20–65 °C temperature range**

Solvent	$\Delta H_{\lambda_0}^\ddagger$, kJ/mol	ΔH° , kJ/mol	ΔS° , J/(mol·K)
AN	6.47	5.10	41.3
DMF	9.20	4.90	35.0
DMSO	13.3	11.1	41.1

The $\Delta H_{\lambda_0}^\ddagger$ values of [Bmpy][NTf₂] in AN and DMF are close to each other, and the Eyring activation energy for an IL solution in DMSO is about two times higher than in AN. It should be noted that the obtained values of $\Delta H_{\lambda_0}^\ddagger$ are close for other ionic liquids in AN and DMSO. For [Bmim][BF₄] in AN, for example, $\Delta H_{\lambda_0}^\ddagger = 6.24$ kJ/mol [13], and for this IL in DMSO, $\Delta H_{\lambda_0}^\ddagger = 13.37$ kJ/mol [11].

The association constant K_a of the studied IL increases with increasing temperature in AN, DMF and DMSO (Fig. 6, *b*). In the studied temperature range, the following pattern of change in the association constants was observed:

$$K_{a,AN} > K_{a,DMF} > K_{a,DMSO}. \quad (14)$$

The pattern of changes in the association constants described by inequality (14) in AN, DMF, and DMSO is also valid for other ionic liquids [21]. In general, [Bmim][BF₄] is weakly associated in AN, DMF, and DMSO. Therefore, dilute solutions of [Bmim][BF₄] are close in their behavior to solutions of simple inorganic electrolytes [47].

Based on the dependences $\ln K_a - 1/T$, the enthalpies and entropies of [Bmpy][NTf₂] association in solvents were also determined (see Table 3). The enthalpy of association of [Bmpy][NTf₂] in DMSO is about two times higher than in AN and DMF, and the entropies of association are approximately the same. The values obtained for the enthalpies and entropies of association in AN and DMSO are of the same order of magnitude as for other ILs in these solvents [13, 25].

Conclusion. It was shown that the difference in the results of determining the association constants of ILs in polar solvents is caused by the use of different electrical conductivity equations and insufficiently correct consideration of the frequency dependence of the measured solution resistance. The frequency ranges in which the influence of polarization processes on the electrodes occurs and ionic relaxation in the bulk of the solution occur are excluded from the results of the electrical conductivity measurements. The thermodynamic characteristics of [Bmpy][NTf₂] association in acetonitrile, dimethylsulfoxide, and dimethylformamide were determined by the conductometric method in the 20–65 °C temperature range. The effect of temperature on the molar electrical conductivity of [Bmpy][NTf₂] at an infinite dilution λ_0 and the association constant K_a have been considered. The Walden product ($\lambda_0\eta$) has been analyzed. It was shown that in AN, DMSO, and DMF, $\lambda_0\eta$ changes in different ways with increasing temperature; however, the value of $\lambda_0\eta/(\varepsilon T)$ ($\lambda_0\eta$ corrected for permittivity ε and absolute temperature T) does not depend on the temperature and nature of the solvent. As the temperature rises, the electrical conductivity of dilute solutions of [Bmpy][NTf₂] in AN, DMSO, and DMF increases in direct proportion to the ratio of the permittivity to the dipole dielectric relaxation time of the solvent.

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