ЭНЕРГИЯ АКТИВАЦИИ ЭЛЕКТРОПРОВОДНОСТИ 1-БУТИЛ-3-МЕТИЛИМИДАЗОЛИЙ БИС{(ТРИФТОРМЕТИЛ)СУЛЬФОНИЛ}АМИДА И 1-БУТИЛ-3-МЕТИЛПИРИДИНИЙ БИС{(ТРИФТОРМЕТИЛ)СУЛЬФОНИЛ}АМИДА И ИХ РАСТВОРОВ В АЦЕТОНИТРИЛЕ, ДИМЕТИЛСУЛЬФОКСИДЕ И ДИМЕТИЛФОРМАМИДЕ

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На основании анализа литературных данных показано, что энергия активации электропроводности ионных жидкостей и их растворов увеличивается с повышением их концентрации, а температурная зависимость энергии активации не исследована. Согласно представлениям Литовица, эта энергия активации должна увеличиваться прямо пропорционально квадрату обратной абсолютной температуры. По уравнению Аррениуса на основании результатов измерения электропроводности определена ее энергия активации двух ионных жидкостей – 1-бутил-3-метилимидазолий бис{(трифторметил). И далее сульфонил}амида и 1-бутил-3-метилпиридиний бис{(трифторметил) сульфонил}амида и их растворов в ацетонитриле (АН), диметилфлормамиде (ДМФА) и диметилсульфоксиде (ДМСО). Проанализирована погрешность расчета энергии активации. Показано, что энергия активации электропроводности уменьшается при повышении температуры и увеличивается с ростом концентрации ИЖ. На основании литературных данных по диэлектрическим свойствам рассчитана энергия активации предельной высокочастотной электропроводности АН, ДМФА и ДМСО, которая также уменьшается с ростом температуры. Установлено, что зависимости энергии активации растворов ионных жидкостей и предельной высокочастотной электропроводности растворителей подчиняются уравнению Литовица – их энергия активации увеличивается прямо пропорционально квадрату обратной температуры. Показано, что вклад растворителей в энергию активации электропроводности определяется температурной зависимостью их диэлектрических свойств – статической диэлектрической проницаемости и времени дипольной диэлектрической релаксации, отношение которых и определяет предельную высокочастотную электропроводность полярного растворителя. Сопоставлены вклады различных полярных растворителей в энергию активации электропроводности растворов ионных жидкостей. Для растворов ионных жидкостей в воде, диметилсульфоксиде, диметилформамиде и пропиленкарбонате эта величина составляет 10 – 15 кДж/моль. В ацетонитрильных растворах ионных жидкостей этот вклад составляет 5,5 – 6,0 кДж/моль.

Ключевые слова: электропроводность, энергия активации, 1-бутил-3-метилимидазолий бис{(трифторметил) сульфонил}амид, 1-бутил-3-метилпиридиний бис{(трифторметил) сульфонил}амид, растворы, ацетонитрил, диметилсульфоксид, диметилформамид

ACTIVATION ENERGY OF ELECTRICAL CONDUCTIVITY FOR 1-BUTYL-3-METHYLIMIDAZOLIUM BIS{(TRIFLUOROMETHYL)SULFONYL}AMIDE AND 1-BUTYL-3-METHYLPYRIDINIUM BIS{(TRIFLUOROMETHYL)SULFONYL}AMIDE AND THEIR SOLUTIONS IN ACETONITRILE, DIMETHYL SULFOXIDE, AND DIMETHYLFORMAMIDE

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After the analysis of the relevant data in literature, it can be shown that the electrical conductivity activation energy of ionic liquids (ILs) and their solvent solutions increases with the increase in their concentration. The temperature dependence of the activation energy was not studied. According to Litowitz, this activation energy should increase in direct proportion to the square of the reciprocal of absolute temperature. The activation energy of two ionic liquids, 1-butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide and 1-butyl-3-methylpyridinium bis{(trifluoromethyl)sulfonyl}amide, and their solutions was determined using the Arrhenius equation, based on the results of electrical conductivity measurements in acetonitrile (AN), dimethylflormamide (DMF) and dimethyl sulfoxide (DMSO). The error in the calculation of the activation energy was analysed. It was shown that the activation energy of electrical conductivity decreases with increasing temperature and increases with increasing IL concentration. Based on the literature data on the dielectric properties, the limiting high-frequency electrical conductivity activation energy of AN, DMF, and DMSO was calculated, which also decreases with increasing temperature. It has been established that the dependences of the activation energy of solutions of ionic liquids and the limiting high-frequency electrical conductivity of solvents obey the Litowitz equation - their activation energy increases in direct proportion to the square of the reciprocal temperature. It was shown that the contribution of solvents to the activation energy of electrical conductivity is determined by the temperature dependence of their dielectric properties – static permittivity and dipole dielectric relaxation time, the ratio of which determines the limiting high-frequency electrical conductivity of a polar solvent. The contributions of various polar solvents to the activation energy of the electrical conductivity of solutions of ionic liquids were compared. For solutions of ionic liquids in water, dimethyl sulfoxide, dimethylformamide, and propylene carbonate, this value is 10 – 15 kJ/mol. In acetonitrile solutions of ionic liquids, this contribution is 5.5 – 6.0 kJ/mol.

Key words: electrical conductivity, activation energy, 1-butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide, 1-butyl-3-methylpyridinium bis{(trifluoromethyl)sulfonyl}amide, solutions, acetonitrile, dimethylsulfoxide, dimethylformamide

INTRODUCTION

Ionic liquids (ILs) have high thermal stability, low vapor pressure, and a large range of liquidus states [1]. These properties allow them to replace volatile organic solvents in the fields of both scientific research and technology [2, 3]. Due to their relatively high electrical conductivity (EC), ILs and their solutions in polar solvents are promising for use in various electrochemical devices such as current sources and electric energy storage devices [4, 5]. The practical application of ILs and their solutions requires knowledge of their transport properties, in particular, their conductivities and its temperature dependences.

An increase in the specific electric conductivity (EC) of Type 2 conductors (melts and electrolyte solutions) with increasing temperature is qualitatively explained by an increase in the mobility of the ions and a decrease in the viscosity [6]. According to the theory of absolute reaction rates [7] and the "hole" theory of EC [8], the temperature dependence of the specific EC of solutions can be described by the Arrhenius equation:

$$\kappa = \kappa_{max} exp(-\frac{E_\kappa}{RT}), \qquad (1)$$

where E_κ is the activation energy of a specific EC and κ_{max} is a pre-exponential factor, which can be considered as an EC at the absolute temperature T tending to infinity.

Activation energy is traditionally used to describe the temperature dependence of the conductivity of aqueous [9-11] and non-aqueous [12-14] electrolyte solutions. When analyzing the temperature dependences of the EC of ILs solutions in polar solvents, in addition to the Arrhenius equation (1), other equations are also required [15-31].

An analysis of the specific EC logarithm dependences on the reciprocal temperature showed that these dependences are not linear [15-22, 27, 31], and the temperature dependence of the specific EC of ILs solutions in polar solvents is better described by the Vogel–Tammann–Fulcher (VTF) equation [32], when, as applied to the specific EC, can be represented as [31]:

$$\kappa = A_\kappa exp(-\frac{B}{T-T_g}) = \kappa_{max} exp(-\frac{E_\kappa}{R(T-T_g)}). \quad (2)$$

In the the Vogel–Tammann–Fulcher (VTF) equation (2), A_κ, B and T_g are empirical adjustable parameters. It should be noted that the VTF equation goes into the Arrhenius equation (1) under the $A_\kappa = \kappa_{max}$, $B = E_\kappa /R$ and $T = (T - T_g)$ condition.

The VTF equation (2) quite accurately describes the temperature dependence of the EC of IL solutions in polar solvents [20, 22-26, 28-30], but this equation is unable to describe the dependence of the specific EC on the IL concentration.

For a simultaneous description of the specific EC dependence on the concentration and temperature, the equation (3) containing four adjustable parameters $B_1 - B_4$ was proposed in [26]:

$$\kappa = x^{0,5} exp(-\frac{B_1 x}{T - B_2} + B_3 T + B_4), \qquad (3)$$

where x is the mole fraction of an IL in the solution and T is the absolute temperature.

Based on the analysis of the results of the temperature effect on the specific EC of solutions of 1-ethyl-3-methylimidazolium dicyanamide ([Emim][DCA]) solutions in propylene carbonate (PC) and γ-Butyrolactone (GBL), it was found in [26] that the activation energy of the EC of these solutions increases in direct proportion to the mole fraction x of [Emim][DCA] in accordance with the equation:

$$E_\kappa = E_\kappa^0 + x E_{\kappa,IL}. \qquad (4)$$

Equation (4) contains two contributions to the EC activation energy: the independent of the [Emim][DCA] concentration contribution of the solvent E_κ^0 and the molar fraction-dependent contribution of an IL $E_{\kappa,IL}$. The value of $E_{\kappa,IL}$ in [26] is considered as a molar increase in the EC activation energy as a result of interionic interactions in solution. For [Emim][DCA] in propylene carbonate (PC), the values на in PC, the values E_κ^0 and $E_{\kappa,IL}$ turned out to be 12.6465 and 8.0085 kJ/mol, while for this IL in GBL they turned out to be almost the same, 10.0640 and 10.5796 kJ/mol [26]. It should be noted here that the accuracy of the values of activation energies given in [26] (5-6 digits), in our opinion, is clearly overestimated, since, as will be shown below, it sharply decreases due to the large contribution of the EC difference values to the E_κ error.

Equation (3) was also used in [28] to analyze the concentration and temperature dependences of the specific EC of six imidazolium IL solutions in GBL. As in [26], the concentration dependence of the activation energy is described by Eq. (3). The value of E_κ^0 obtained in [28] for a pure solvent (GBL) turned out to be 9.07-11.91 kJ/mol, which is in good agreement with the value of $E_\kappa^0 = 10.640$ kJ/mol for GBL given in [26].

Consisting of two components (solvent E_κ^0 and electrolyte $E_{\kappa,EL}$) and described by equation (4), the EC activation energy is also used when considering the temperature dependence of the specific EC of electrolyte solutions in non-aqueous solutions [12-14]. For a solution of LiAsF$_6$ in acetonitrile, as an example, $E_\kappa^0 = 5.5$, and $E_{\kappa,EL} = 28.16$ kJ/mol [14].

It should be noted that the above-mentioned absence of a linear dependence of the EC logarithm on

the reciprocal absolute temperature indicates the possible existence of a dependence of the EC activation energy on temperature. The existence of such a dependence for the transport properties of solutions was first considered by Litowitz in [33] and used in the analysis of the temperature dependence of the EC of imidazolium and tetraalkylammonium bis{(trifluoromethyl)sulfonyl}amide solutions in acetonitrile in [30].

In his work [33], Litowitz suggested that the activation energy of the transport properties E is proportional to the inverse square of the temperature:

$$E = \frac{B_L}{T^2}, \qquad (5)$$

and the dependence of the specific EC on temperature can be described by the equation [30]:

$$\kappa = \kappa_{max} exp(-\frac{B_L}{RT^3}). \qquad (6)$$

The Litowitz constant B_L in equation (5) relates the EC activation energy E_κ to temperature.

In order to determine the activation energy, the dependences $\ln\kappa - 1/T$, $\ln\kappa - 1/(T - T_0)$, and $\ln\kappa - 1/T^3$ described by equations (1), (2), and (6) were considered in [30]. As a result, it was found that the highest activation energy (6.9-8.1 kJ/mol) is obtained using the Arrhenius equation (1). This value is 1.5-2 times greater than the activation energy (4.1-5.0 kJ/mol) obtained from the VTF equation (2). Finally, when using the Litowitz equation (6), the smallest value of E_κ is obtained: 2.0-3.2 kJ/mol (the B_L constant in the Litowitz equation (6) is $(2.4-2.8)\cdot10^5$ kJ K^2/mol [30]). A significant difference (by 2-4 times) in the E_κ values obtained in [30] does not allow one to give preference to any of the equations (1), (2) or (6), and also does not make it possible to relate the EC activation energy of IL solutions with the nature of the solvent.

At the same time, an important result obtained in [30] is the presence of the dependence of the activation energy on temperature, described by Eq. (5). According to [30, 33], as the temperature rises, the activation energy decreases as a result of an increase in the thermal motion of molecules. It is also important to note that, using the Arrhenius equation (1) and the fact that the EC activation energy decreases with increasing temperature, one can try to describe the temperature dependence of the specific EC of ILs solutions. A similar way of describing the EC temperature dependence is used for aqueous electrolyte solutions [34]. In this work, this approach is used to analyze the EC temperature dependences of ILs solutions.

The above brief analysis of the EC activation energy E_κ of ILs solutions shows that if the dependence of E_κ on the concentration is established (E_κ increases in proportion to the mole fraction of the IL, equation

(4)), then the temperature dependence of EC activation energy is practically not studied.

In [21], the dependence of E_κ on the reciprocal absolute temperature ($1/T$) for six ILs based on the [Bmim]$^+$ cation is given, according to which E_κ decreases monotonically with decreasing $1/T$ (with increasing temperature) and with decreasing anion size. In this work, however, it is not indicated how the temperature dependence of E_κ was obtained and why the EC activation energy decreases with increasing temperature and with decreasing anion size. It would also be expedient to analyze the dependence of the activation energy on the square of the reciprocal absolute temperature $E_\kappa = f(1/T^2)$ and find out whether the dependence of the EC activation energy on temperature for pure ILs and for their solutions in polar solvents obeys equation (5).

The aim of this work is to establish the effect of temperature on the EC activation energy E_κ of 1-butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide ([Bmim][NTf$_2$]) and 1-butyl-3-methylpyridinium bis{(trifluoromethyl)sulfonyl}amide ([Bmpy][NTf$_2$]) and their solutions in acetonitrile (AN), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). The choice of these ionic liquids is explained by the fact that ILs with bis{(trifluoromethyl)sulfonyl}imide anions are characterized by the maximum electrical conductivity both as pure ILs and their solutions [1, 30]. It is also of interest to compare the EC values and their activation energies for different [Bmim]$^+$ and [Bmpy]$^+$ cations while retaining the same [NTf$_2$]$^-$ anion. ILs with this anion are promising for their use, since they are characterized by relatively low viscosities and high electrochemical stability [35].

AN, DMF, and DMSO were used as solvents for ILs. AN and DMF are taken for comparison, since they have close dielectric permittivities (DP) [36]. DMF and DMSO are characterised by close values of density and molar mass. Some of the properties of ILs and solvents used in this work are presented in Table 1 below.

EXPERIMENTAL TECHNIQUE AND PROCESSING OF RESULTS

Imidazolium ([Bmim][NTf$_2$]) and pyridinium ([Bmpy][NTf$_2$]) bis{(trifluoromethyl)sulfonyl}amides were synthesized at QUILL (Queen's University Belfast Ionic Liquid Laboratories) in Northern Ireland. The purity of the ionic liquids (99.5%) was also monitored using NMR spectroscopy at QUILL.

Before measuring the EC of pure ILs and preparing their solutions, [Bmim][NTf$_2$] and [Bmpy][NTf$_2$] were dried for five hours in a vacuum fume hood at 60 °C. Solutions of ILs were prepared by the gravimetric method; in this case, taken with an accuracy of

± 10⁻⁵ g, a weighed portion of IL was quantitatively transferred into a dry volumetric flask. After that, a weighed portion of the solvent was added to this ionic liquid. The water content in organic solvents (AN, DMSO, and DMF) was controlled by the Karl Fischer method and did not exceed 0.1%.

Measurements of the specific EC of ILs and their solutions were carried out using an E7-20 digital AC bridge (immittance meter) in the frequency range F 0.1-10 kHz. To eliminate the influence of polarization effects on the results of measuring the resistance of solutions R, the desired resistance was determined by extrapolating its measured value to an infinite frequency in the coordinates $R - 1/F$ [37]. The temperature-controlled conductometric cell with platinum electrodes was made of Pyrex glass. In the 20-80 °C temperature range, distilled water was used as a thermostating liquid. At 90-210 °C temperatures, thermostating was carried out using glycerol. The cell constant was determined by measuring the resistance of aqueous KCl solutions according to the standard procedure [37]. Its value was 0.1723 ± 0.0003 cm. The error in determining the specific EC of ILs solutions did not exceed 0.5%.

The activation energy E_κ was calculated based on the analysis of the temperature dependence of the specific EC, measured with a step of 5 degrees. In particular, if the values of κ_1, κ_2, and κ_3 are experimentally measured at temperatures T_1, T_2, and T_3, then the specific EC activation energy of E_κ is [34]:

$$E_\kappa = RT_2^2 \cdot \frac{\kappa_3 - \kappa_1}{\kappa_2(T_3 - T_1)}; \qquad (7)$$

In equation (7), R is the universal gas constant, T is the absolute temperature, K. The most important issue in the procedure for determining E_κ is the choice of the temperature step (value ΔT). The calculation error of the EC activation energy δE_κ according to equation (7) depends on the error in determining the difference $\Delta\kappa = \kappa_3 - \kappa_1$. With a decrease in ΔT, the difference $\Delta\kappa$ decreases and the calculation error E_κ increases significantly, which is determined by the expression [34]:

$$\delta E_\kappa = \delta_\kappa \left(\frac{\kappa_3 + \kappa_1}{\kappa_3 - \kappa_1} + 1 \right). \qquad (8)$$

In expression (8), δ_κ is the relative error in determining the specific EC (0.5%).

To reduce the error δE_κ, it is desirable to increase the value of $\Delta T = T_3 - T_1$. However, in this case, the calculated value of E_κ decreases, i.e. the accuracy of the analysis of the activation energy temperature dependence decreases. Our analysis shows that if we use a temperature step of less than five degrees ($\Delta T < 10$ K), then the calculation error δE_κ increases sharply due to

a decrease in the difference $\kappa_3 - \kappa_1$ and can reach several tens of percent. An analysis of the error δE_κ described by equation (8) shows that the optimal value of ΔT is 10 K (temperature step five degrees). In this case, if $\delta_\kappa = 0.5\%$, then the calculation error δE_κ does not exceed 5%.

When discussing the results in this work, some additional physicochemical properties of ILs and polar solvents are used, which are presented in Table 1. The physical meaning of the values of the limiting high-frequency (HF) EC κ_∞ and its activation energy κ_∞ is considered below in the discussion of results.

Table 1

Molar mass M (g/mol), density ρ (g/cm³), molar concentration c (mol/l), dielectric constant ε, activation energy EC E_κ of ionic liquids and activation energy of limiting high-frequency electrical conductivity E_κ (kJ/mol) of the solvents; t=25 °C

Таблица 1. Молярная масса M (г/моль), плотность ρ (г/см³), молярная концентрация c (моль/л), диэлектрическая проницаемость ε, энергия активации ЭП E_κ ИЖ и предельной высокочастотной ЭП E_κ (кДж/моль) растворителей; t=25 °C

Compound	M	ρ	c	ε	$E\kappa_\infty$
[Bmim][NTf₂]	419.4	1.436	3.42	15.0[38]	35.4*
[Bmpy][NTf₂]	430.4	1.414	3.28	-	37.7*
AN	41.05	0.7875	19.18	35.9[36]	5.8
DMF	73.09	0.9445	12.92	36.8[36]	8.8
DMSO	78.13	1.1004	14.08	46.4[36]	13.7

Note: *The values of the specific EC activation energy E_κ of ionic liquids are given

Примечание: *Приведены величины энергии активации удельной ЭП E_κ ИЖ

Comparing the properties presented in Table 1 of the studied ILs and polar solvents, the following can be noted. The molar concentration of pure ILs is 4-6 times lower than the molar concentration of pure polar solvents (AN, DMF, and DMSO). In [Bmim][NTf₂] solutions in AN, DMF, and DMSO, the molar concentration of IL will increase from zero to its maximum value of 3.42 mol/L, and in [Bmpy][NTf₂] solutions, from zero to 3.28 mol/L. The activation energy of the limiting HF EC $E\kappa_\infty$ of polar solvents is 3-6 times lower than the value of E_κ of ILs. Therefore, it can be expected that in solutions of IL in AN, DMF, and DMSO, E_κ will increase from the value of $E\kappa_\infty$ of a polar solvent to E_κ of a pure IL, In solutions of [Bmim][NTf₂] in AN, for example, E_κ will increase from 5.8 to 35.4 kJ/mol, and in solutions of [Bmim][NTf₂] in DMSO, from 13.7 to 37.7, Table 1.

DISCUSSION OF RESULTS

According to the concepts of Litovitz [33], the activation energy of the transport properties of solutions should decrease with increasing temperature; the

linear dependence of the EC activation energy on the square of the reciprocal absolute temperature should take place as well, described by Eq. (5). Before considering the dependences of $E_к$ on t and on $1/T^2$ of pure ILs and their solutions in AN, DMF, and DMSO, it is necessary to note the different nature of the dependencies of specific EC ($к$) on temperature (t) for pure ILs and their solutions in polar solvents. In pure ILs, the specific EC sharply increases with increasing temperature due to a significant decrease in their viscosity and the dependencies $к - t$ are concave curves [39-43], while in solutions of polar solvents these dependencies are almost linear or are slightly convex curves [9, 11, 16]. At the same time, the dependencies of the EC activation energy of pure ILs and their solutions on temperature practically do not differ in character.

The temperature dependencies of the activation energies of ILs and their solutions will now be considered. Fig. 1 shows the $E_к$ dependencies of [Bmim][NTf$_2$] (curve 1) and [Bmpy][NTf$_2$] (curve 2) on temperature (Fig. 1a) and on the square of the reciprocal absolute temperature (Fig. 1b).
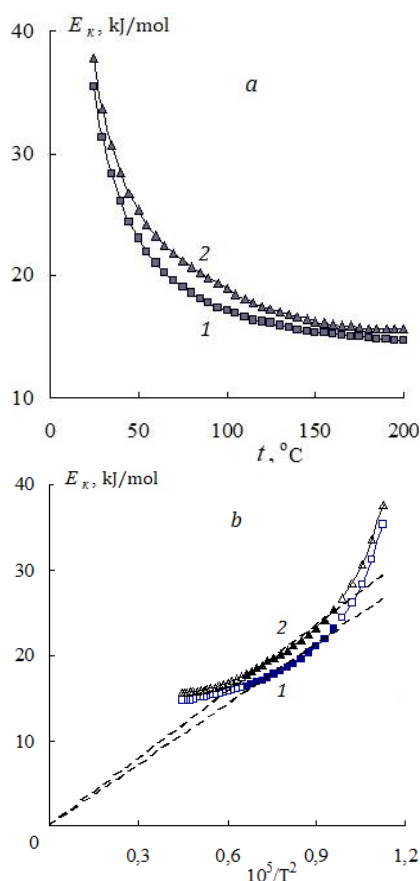
The activation energy of pure ILs decreases monotonically with increasing temperature, and in the temperature range under study (20-200 °C), the $E_к$ of [Bmpy][NTf$_2$] is greater than the $E_к$ of [Bmim][NTf$_2$], Fig. 1a. With regard to the EC activation energy of pure ILs, it should be noted that the Litowitz equation (5) is valid for [Bmim][NTf$_2$] and [Bmpy][NTf$_2$] only in the 50-120 °C temperature range. At t < 50 °C and at t > 120 °C, there is a systematic deviation of the $E_к = f(1/T^2)$ dependence from the direct proportionality described by equation (5).

The EC activation energy of [Bmim][NTf$_2$] and [Bmpy][NTf$_2$] solutions in AN, DMF, and DMSO also decreases with increasing temperature. However, in contrast to the $E_к$ of pure ILs, the linear dependence of $E_к$ (described by equation (5)) on the square of the reciprocal of absolute temperature is observed for the ionic liquid solutions in AN, DMF and DMSO. As an example, the dependence of the specific EC activation energy of [Bmpy][NTf$_2$] solutions is shown in Fig. 2.
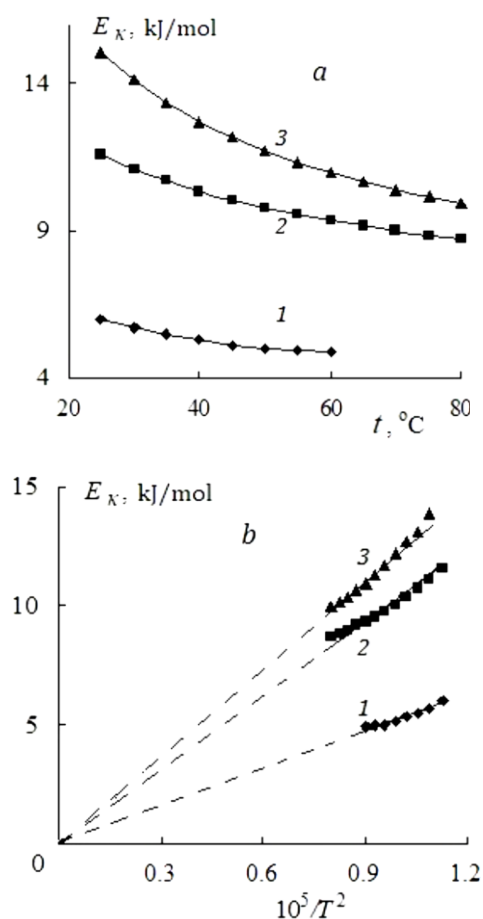

Fig. 1. Dependencies of the EC activation energy $E_к$ of [Bmim][NTf$_2$] (1) and [Bmpy][NTf$_2$] (2) on temperature (a) and on the square of the reciprocal absolute temperature (б)

Рис. 1. Зависимости энергии активации ЭП $E_к$ [Bmim][NTf$_2$] (1) и [Bmpу][NTf$_2$] (2) от температуры (a) и от квадрата обратной абсолютной температуры (б)

Fig. 2. Dependence of EC activation energy $E_к$ 0.1 M of [Bmpy][NTf$_2$] solutions on temperature (a) and on the square of the reciprocal temperature (б) in AN (1), DMF (2), and DMSO (3)

Рис. 2. Зависимость энергии активации ЭП $E_к$ 0,1 М растворов [Bmim][NTf$_2$] от температуры (a) и от квадрата обратной температуры (б) в АН (1), ДМФА (2) и ДМСО (3)

The specific EC activation energy $E_\text{к}$ monotonically increases with an increase in the molar concentration c of an IL. Fig. 3a shows the dependence of $E_\text{к}$ of [Bmpy][NTf$_2$] on molarity in AN, DMF, and DMSO as an example.
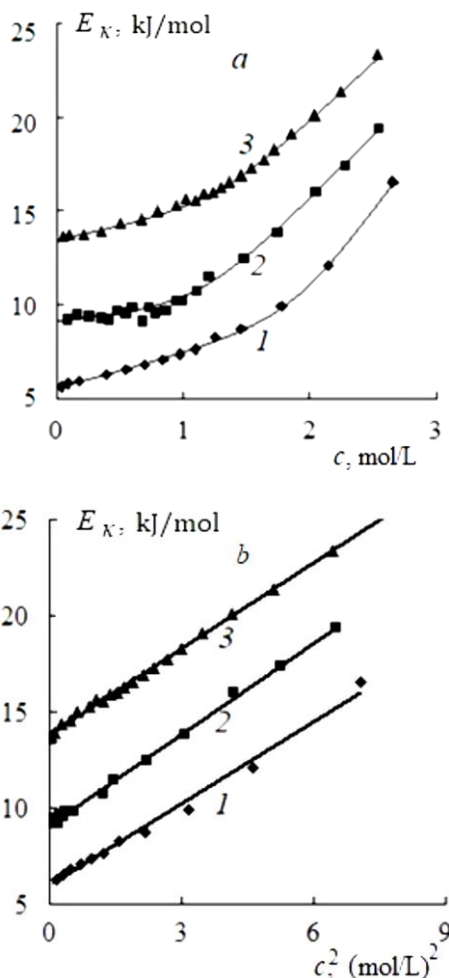

Fig. 3. Dependence of electrical conductivity activation energy $E_\text{к}$ of [Bmpy][NTf$_2$] solutions on the concentration (a) and the squared concentration (б) in (1) AN, (2) DMF, and (3) DMSO; t=25 °C

Рис. 3. Зависимость энергии активации удельной ЭП растворов [Bmpy][NTf$_2$] в АН (1), ДМФА (2) и ДМСО (3) от концентрации (а) и квадрата концентрации (б); t=25 °C

The curves shown in this Figure are easily straightened if the square of the molar concentration is used as an argument, Fig. 3b. All three dependencies presented in this figure are described by a single equation:

$$E_\text{к} = E_\text{к}^0 + K\,c^2, \qquad (9)$$

where $E_\text{к}^0$ is its contribution to the activation energy determined by the dielectric properties of the solvent (5.9, 9.1, and 13.8 kJ/mol, respectively, for AN, DMF, and DMSO) and K is the contribution of the IL to the activation energy, which is the same for all solvents and is (1.50±0.07) kJ·mol/L^2.

The contribution of the solvent to the activation energy $E_\text{к}^0$ is determined by the temperature dependence of the dielectric properties of the solvent, in particular, the static permittivity (DP) ε_s and the dipole dielectric relaxation time τ. The ratio of these quantities determines the limiting high-frequency (HF) EC of a polar solvent [44]:

$$\kappa_\infty = \frac{\varepsilon_s \varepsilon_0}{\tau}. \qquad (10)$$

In equation (10), ε_0 is the absolute DP of vacuum ($\varepsilon_0 = 8.854 \cdot 10^{-12}$ F/m).

The activation energy of the limiting HF EC $E\kappa_\infty$ of acetonitrile was determined in [45] and at 25 °C is 5.8 ± 0.8 kJ/mol. The limiting HF EC of DMF and DMSO, as well as its activation energies, were derived from the dielectric properties of these solvents, as published in [46-50]. The limiting HF EC and its activation energy AN, DMF, and DMSO are shown in Table 2.

Table 2

Limiting high-frequency electrical conductivity к (S/m) and its activation energy $E_\text{к}$ (kJ/mol) of acetonitrile, dimethylformamide and dimethyl sulfoxide

Таблица 2. Предельная высокочастотная электропроводность к (См/м) и энергия ее активации $E_\text{к}$ (кДж/моль) ацетонитрила, диметилформамида и диметилсульфоксида

t, °C	AN		DMF		DMSO	
	κ_∞	$E\kappa_\infty$	κ_∞	$E\kappa_\infty$	κ_∞	$E\kappa_\infty$
20	81.2	-	23.4	-	19.8	-
25	82.1	5.8	24.8	8.8	21.9	13.5
30	82.9	5.7	26.3	8.6	24.1	12.9
35	83.7	5.5	27.8	8.4	25.8	12.3
40	84.6	5.4	29.3	8.2	28.2	11.8
45	85.4	5.2	30.7	8.1	29.9	11.4
50	86.3	5.1	32.2	7.9	31.9	11.0
55	87.1	5	33.7	7.8	34.3	10.6
60	87.9	4.9	35.2	7.7	36.2	10.4
65	88.8	4.9	36.7	7.6	38.1	10.1
70	-	-	38.1	7.5	40.2	9.9

It should be noted that the $E_\text{к}$ values that cut off on the y-axis at the concentrations of [Bmpy][NTf$_2$] and [Bmim][NTf$_2$] tending to zero coincide quantitatively with those given in Table 2 $E\kappa_\infty$ values of AN, DMF, and DMSO. Consequently, the contribution of solvents to the EC activation energy $E_\text{к}^0$ is determined by the temperature dependence of their dielectric characteristics, in particular, by the temperature dependence of the limiting high-frequency EC of the solvent, determined by equation (10).

The values of the EC activation energy $E_\text{к}^0$ of various polar solvents published in literature and obtained in this work are summarized in Table 3.

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EC activation energy E_κ^0 (kJ/mol) of various polar solvents; t=25 °C
Таблица 3. Энергия активации ЭП E_κ^0 (кДж/моль) различных полярных растворителей; t=25 °C

Solvent	$E\kappa^0$	Solvent	$E\kappa^0$
Water	14.0 [18]	GBL	10.06 [26]
Water	14.8 [45]	GBL	9.07-11.91[28]
PC	12.13 [14]	AN	5.5 [14]
PC	12.2 [18]	AN	5.9
PC	12.65 [26]	DMF	10.3 [18]
DMSO	13.8	DMF	9.1

The $E\kappa^0$ values for various polar solvents published in different works are in good agreement with each other, Table 3. For solutions of ionic liquids in water, dimethyl sulfoxide, dimethylformamide and propylene carbonate, this value is 10-15 kJ/mol. In acetonitrile solutions of ionic liquids, this contribution is 5.5-6.0 kJ/mol. Since the $E\kappa^0$ values obtained in this work coincide with the HF EC activation energies $E\kappa_\infty$ of AN, DMF, and DMSO, it can be assumed that for other polar solvents, the $E\kappa^0$ values will also be determined by the temperature dependence of the dielectric properties of the solvent, as shown in Table 3.

CONCLUSIONS

It is shown from analysis of the results of determining the electrical conductivity (EC) activation energy E_κ of ionic liquids (ILs) and their solutions in polar solvents that these values increase with an increase in the concentrations of ILs. The temperature dependance of the EC activation energy of ILs solutions has not been studied, although, according to the ideas of Litowitz [33], the E_κ of solutions should increase in direct proportion to the square of the reciprocal absolute temperature.

The specific EC activation energy E_κ of the two ionic liquids and their solutions in acetonitrile (AN), dimethylflormamide (DMF), and dimethylsulfoxide (DMSO) was determined using the Arrhenius equation. It was shown that E_κ decreases with increasing temperature and increases with increasing IL concentration. Based on the literature data on the dielectric properties, the limiting high-frequency (HF) EC activation energy $E\kappa_\infty$ of AN, DMF, and DMSO was calculated, which also decreases with increasing temperature. It has been found that the EC activation energy E_κ of ILs solutions and the limiting HF EC activation energy $E\kappa_\infty$ of the solvent obey the Litowitz equation (5), i.e. E_κ and $E\kappa_\infty$ increase in direct proportion to the square of the reciprocal temperature.

It is shown that the contribution of solvents to the EC activation energy E_κ^0 is determined by the temperature dependance of their dielectric properties – static dielectric permittivity ε_s and the dipole dielectric relaxation time τ. The ratio of these values determines the limiting high-frequency electrical conductivity of a polar solvent κ_∞, equation (10).

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