Dr Agnieszka Boruń
University of Łódź
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Appendix No 3

SUMMARY OF PROFESSIONAL ACCOMPLISHMENTS

Łódź 2017

1. *First name and surname* **Agnieszka Boruń** (maiden name **Chmielewska)**

2. *Scientific diploma and degrees*

03.07.1998 - MSc degree

University of Łódź, Faculty of Physics and Chemistry, Department of Chemical Didactics
Speciality: physical chemistry of solutions
MSc dissertation: Potentiometric and conductometric studies of NaI solutions in water + n-butanol mixtures and their physicochemical properties at 298.15 K
Supervisor: Prof. dr hab. Adam Bald
Studies completed with very good results, awarded a letter of congratulation by the Rector of the University of Łódź for outstanding results in Science.

29.01.2003 - PhD degree

University of Łódź, Faculty of Physics and Chemistry, Department of Chemical Didactics
Speciality: physical chemistry of solutions
PhD dissertation: Viscosimetric and conductometric properties of aqueous solutions of selected carboxylic acids and their salts
Supervisor: Prof. dr hab. Adam Bald

3. *Employment*

1998 – 2002 PhD student
University of Łódź, Faculty of Physics and Chemistry

2002 – 2003 Assistant
University of Łódź, Department of Chemical Didactics

2003 – 2008 Associate Professor
University of Łódź, Department of Chemical Didactics

2007– 2010 Head
University of Łódź, Faculty of Chemistry, Postgraduate Studies in Chemistry

2008 – 2014 Associate Professor
University of Łódź, Department of Physical Chemistry of Solutions,

science 2014 Associate Professor
University of Łódź, Department of Physical Chemistry, Department of Physical Chemistry of Solutions

4. *Scientific achievements submitted for the habilitation procedure*

As an achievement resulting from Article 16, section 2 of the Act on Academic Degrees and Titles and about Degrees and Titles in the Field of Fine Arts of March 14, 2003 (Dz. U. No 65/2003, item 595, with subsequent amendments), ten scientific publications are described [H1-H10].

a) title of scientific achievements

Conductance and ionic association of selected imidazolium ionic liquids in various solvents

b) list of publications comprising the scientific achievement

[H1] Agnieszka Boruń, Adam Bald*, *J. Chem. Eng. Data*, 57 (2012) 475-481
Conductometric studies of 1-ethyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium tetrafluoroborate in N, N-dimethylformamide at temperatures from (283.15 to 318.15) K
IF = 2.004 MNiSW = 35p

[H2] Agnieszka Boruń, Adam Bald*, *J. Chem. Eng. Data*, 57, (2012) 2037-2043
Conductometric studies of sodium tetraphenylborate, tetrabutylammonium bromide, and sodium tetrafluoroborate in N,N-dimethylformamide at temperatures from (283.15 to 318.15) K
IF = 2.004 MNiSW = 35p

[H3] Agnieszka Boruń*, Adam Bald, *Int. J. Electrochem. Sci.* 9 (2014) 2790-2804
Conductometric studies of 1-ethyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium tetrafluoroborate in 1-propanol at temperatures from (283.15 to 318.15) K
IF = 1.5 MNiSW = 25p

[H4] Agnieszka Boruń*, Ilona Trzcińska, Adam Bald, *Int. J. Electrochem. Sci.* 9 (2014) 7805-7818
Conductometric studies of sodium iodide, sodium tetraphenylborate, tetrabutylammonium iodide, and sodium tetrafluoroborate in 1-propanol at temperatures from (283.15 to 318.15) K
IF = 1.5 MNiSW = 25p

[H5] Agnieszka Boruń*, Carlos Fernandez, Adam Bald, *Int. J. Electrochem. Sci.* 10 (2015) 2120-2129
Conductance studies of aqueous ionic liquids solutions [emim][BF_4] and [bmim][BF_4] at temperatures from (283.15 to 318.15) K
IF = 1.692 MNiSW = 20p

[H6] Agnieszka Boruń*, Adam Bald, *J. Chem. Thermodynamics* 96 (2016) 175-180
Ionic association and conductance of [emim][BF_4] and [bmim][BF_4] in 1-butanol in a wide range of temperature
IF = 2.726 MNiSW = 30p

[H7] Agnieszka Boruń*, Adam Bald, *Ionics* 22 (2016) 859-867
Ionic association and conductance of ionic liquids in dichloromethane at temperatures from (278.15 to 303.15) K
IF = 2.062 MNiSW = 25p

[H8] Agnieszka Boruń*, Adam Bald, *Int. J. Electrochem. Sci.* 11 (2016) 7714-7725
Triple-ion formation in solutions of [emim][BF_4] and [bmim][BF_4] in dichloromethane at various temperatures. A new method of analysis of conductivity data.
IF = 1.469 MNiSW = 20p

[H9] Agnieszka Boruń*, Adam Bald, *J. Chem. Eng. Data* 61 (2016) 3788-3793
Conductance and ionic association of imidazolium-based ionic liquids in N,N-dimethylacetamide
IF = 2.323 MNiSW = 30p

[H10] Agnieszka Boruń*, *J. Mol. Liq.* 240 (2017) 717-722
Conductometric studies of [emim][BF_4] and [bmim][BF_4] in propan-2-ol. Association of ionic liquids in alcohols.
IF_{2016} = 3.648 $MNiSW_{2016}$=30p

** Corresponding author*

The Impact Factor (IF) and the MNiSW scores are given according to the year of publication.

c) description of the scientific aim and results achieved

Introduction

Ionic liquids (ILs) are a fascinating group of solvents possessing a unique combination of physicochemical properties, including extremely low vapor pressure at room temperature, low melting point, thermal and chemical stability. They also possess the ability to dissolve both polar and nonpolar organic and inorganic substances and have a wide liquid range of up to 400°C. Hence, they can replace many volatile organic solvents in various chemical processes, including synthesis, catalysis, extraction and separation. The physical and chemical properties of ionic liquids are determined by the choice of the cations and anions selected. By modifying the cations and anions, the physical properties of the IL, such as its melting point, density, viscosity, miscibility, hydrophilicity or hydrophobicity, can be customized for a particular application; therefore, ionic liquids can be designated as *designer solvents*. This tunability of their properties has aroused a great deal of interest from a wide range of researchers.

It is worth mentioning that ILs are typically not used in their pure form but as co-solvents or additives. In this role, they demonstrate improved and more desirable thermodynamic and transport properties in many processes. For this reason, a knowledge of the properties of binary mixtures of ILs is of key significance for industrial applications. Pure

ILs have a wide electrochemical window and a moderate electrolytic conductivity of between 10 and 20 $mS \cdot cm^{-1}$; this value increases in binary mixtures of ILs with molecular solvents and is comparable to those of organic solvents with an organic electrolyte [1]. This property allows them to be used as heat transfer fluids, for processing biomass and as supporting electrolytes in batteries, solar and fuel cells. The conductance of ionic liquids is the most important transport property that should be taken into consideration when devising new electrochemical applications.

Conductometry is a reliable, sensitive and widely-used electrochemical technique for investigating electrolyte solutions. Among the various techniques used for determining association constants (dielectric relaxation spectroscopy, potentiometry, spectrophotometry, ion-exchange equilibrium methods, activity coefficient measurements, spectroscopic methods), those based on conductivity measurements and thermodynamic methods are probably most accurate [2, 3]. Reliable information is obtained during investigations in dilute solutions; however, this approach requires precise measurements down to very low concentrations ($c \sim 10^{-4}$ $mol \cdot dm^{-3}$ or lower), accurately known concentrations, high quality equipment, good temperature control and high purity of solvents and solutes [4]. As can be expected, these procedures are quite time consuming.

Conductance measurements provide valuable information about ionic mobility, solvent viscosity and relative permittivity, hydrogen bonding capability and specific interactions with ions. Studies conducted at different temperatures are a source of detailed information about ion-ion and ion-solvent interactions.

Due to the presence of various interactions in ionic liquid solutions (ionic, hydrogen bonds, dipolar, π-π, van der Waals forces), their solvation behavior is unique. The ionic liquids are solvated to a different extent by the solvents, and the ionic association depends significantly on the ion solvation [5]. In turn, the physicochemical properties of solution are influenced by all the possible interactions in the solution. Solvation is one of the most important factors that determines the mechanism and rate of a number of physicochemical processes occurring in solution involving ionic species. Another extremely important phenomenon is ionic association. In non-aqueous or mixed solutions, ionic association is a very common phenomenon also for electrolytes in water which are classified as strong. Ion pairing refers to the partial association of oppositely-charged ions in electrolyte solutions to form distinct chemical species called ion pairs. In order to form the ion pair, the ions should be close enough for the Coulombic attraction energy to overcome the thermal energy that scatters them apart. The ion pair must be long-lived enough, longer than the time required for thermal motion to cause the ions to move around as separate species [2]. Ionic association influences not only the conductivity of ionic liquids, but also other properties, such as vapor pressure [6]. It also plays an important role in the mechanism of various reactions, especially in the exchange reactions, and may affect the stereochemical outcome of a chemical reaction [7].

Research objectives

Considering the ionic nature of ionic liquids, ionic association should be expected in their solutions. However, a survey of literature indicated that no systematic conductometric studies had yet been conducted on the phenomenon of ionic association and solvation in solutions of ionic liquids in various solvents, as a wide range of temperatures and low IL concentration range; the choice of ionic liquids and solvents instead seems to be rather accidental. However, it is important to emphasize the significance of the infinite-dilution limit of such data in understanding the ion-ion and ion-solvent interactions and the possibility of predicting the behavior of ILs in a specific application. Such studies are of considerable interest for the optimal use of ionic liquid solutions in high-energy batteries and other electrochemical devices, and for understanding the impact of ion pairs on the mechanisms of organic reactions.

In the light of these facts, I planned and performed research aimed at exploring the impact of temperature and solvent properties (relative permittivity, viscosity, structure, hydrogen bonds ability) on the transport properties and the association phenomenon of ionic liquid solutions. For this purpose, precise measurements of the electrical conductance of dilute solutions of imidazolium-based ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF_4] and 1-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF_4] in water **[H5]**, propan-1-ol (1-PrOH) **[H3]**, propan-2-ol (2-PrOH) **[H10]**, butan-1-ol (1-BuOH) **[H6]**, N,N-dimethylformamide (DMF) **[H1]**, N,N-dimethylacetamide (DMAc) **[H9]** and dichloromethane (DCM) **[H7, H8]** were performed in the temperature range from (283.15 to 318.15) K at 5 K intervals (in DCM from 278.15 to 303.15 K). Papers **[H2, H4]** present the results of additional conductivity measurements in DMF and 1-PrOH.

The proposed studies were mainly cognitive in nature. Their primary aim was to obtain original and highly accurate data concerning the limiting molar conductivity (Λ_o) and ionic limiting conductivity (λ_o), and the association constants (K_A) for the investigated systems. Another very important goal was to investigate the ionic association and solvation processes in the solutions and to evaluate the thermodynamics of the association. The explanation of these phenomena requires a fundamental understanding of behavior of ILs in various solvents. Such knowledge of the thermodynamics and physicochemical properties of solutions would be of great theoretical and industrial importance.
In addition, the studies on dichloromethane were mainly of a methodological character. Their aim was, among others, to develop a new method of analyzing conductivity data obtained for solutions containing free ions, ion pairs and triple ions.

Research objects

One of the most important and promising classes of ILs comprises those based on the 1-alkyl-3-methylimidazolium cation $[C_n\text{mim}]^+$. Therefore, in these studies, I chose to focus on the popular imidazolium-based salts 1-ethyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium tetrafluoroborate, which are commercially available as high-purity liquids (~99%).

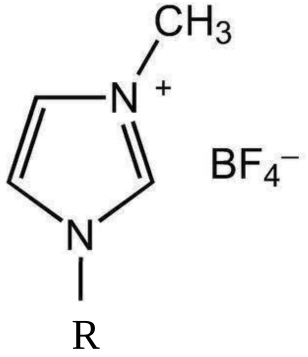

Fig. 1 1-Alkyl-3-methylimidazolium tetrafluoroborate formula

To study the solvent effect on the ionic association of the ILs, various molecular solvents were selected covering a range of relative permittivity (ε_r) and viscosity (η) ranges: i.e. 8.82 (DCM) [8] < ε_r < 78.36 (water) [9] and 0.415 (DCM) [8] < η < 2.5772 (1-BuOH) mPa·s. (this value was calculated on the basis of my density data and kinematic viscosity obtained in Ref. [10]) at 298.15 K. This group comprises a selection of relatively low and high polarity solvents, among which are aprotic polar solvents (N,N-dimethylformamide, N, N-dimethylacetamide), protic (water, alcohols) and low polarity solvent with low solvation power for the ions (dichloromethane).

Data analysis

For each system, I individually selected the range of concentrations to be measured. I conducted the measurements in very diluted solutions, ranging from about $3\cdot10^{-5}$ mol·dm^{-3} up to a maximum concentration limit depending on the relative permittivity of the solvent; this was given by Fuoss [11], $c_{\max} = 3.2\cdot10^{-7}\cdot\varepsilon_r^3$ mol·dm^{-3}.

The molar conductivity (Λ) was calculated from the experimental specific conductivity (κ) and the molar concentrations of the solutions (c) using the equation $\Lambda = 1000 \cdot \kappa / c$. Many different equations are used for conductivity data analysis, for example: the Pitts equation [12], Fernandez-Print and Prue (PFPP) equation [13], Fuoss-Hsia/Fernandez-Prini (FHFP) equation [14], Fuoss equation [15, 16], and the low concentration Chemical Model (lcCM) based on the Fuoss-Justice equation [17]. It is also possible to use the Lee-Wheaton [18] and the Quint-Viallard [19] equations, which can be used for electrolytes with different types of symmetry. The different equations return nearly identical values for the limiting molar conductivity (Λ_o) however, considerably higher differences exist between the values of the ionic association constants (K_A). Therefore, all data was analyzed in the framework of the low concentration chemical model, recently applied in a number of studies, both in aqueous and non-aqueous solutions:

$$\Lambda = \alpha\,[\Lambda_o - S(\alpha c)^{1/2} + E(\alpha c)\ln(\alpha c) + J_1(\alpha c) + J_2(\alpha c)^{3/2}] \quad (1)$$

$$K_A = (1 - \alpha) / (\alpha^2 c y_\pm^2) \quad (2)$$

and

$$\ln y_\pm = -\,(A\alpha^{1/2}c^{1/2}) / (1 + BR\alpha^{1/2}c^{1/2}) \quad (3)$$

In these equations, Λ_o is the limiting molar conductance conductivity; α is the dissociation degree of an electrolyte; K_A is the ionic association constant; R is the distance parameter of ions; $y_\pm$ is the activity coefficient of ions on the molar scale; A and B are the Debye–Hückel equation coefficients. The analytical form of the parameters S, E, J_1, and J_2 was given by Barthel et al. [17]. The parameters S and E depend on the density, viscosity and relative permittivity of the solvent. The J_1 and J_2 coefficients are both functions of the distance parameter R, representing the distance up to which oppositely-charged ions can move as freely moving particles in solution. The values of Λ_o, K_A, and R were obtained using the well-known non-linear least-squares iteration method given by Fuoss [16]. The initial Λ_o value was obtained by Debye-Hückel-Onsager extrapolation of the data. The calculations were performed by finding the values for the three parameters given above which minimized the standard deviation (σ) between the calculated and the experimental conductivities for a sequence of R values. These R values were calculated independently if they could not be optimized reliably [**H7**].

It should be stressed that the calculated values of limiting molar conductivity, association constants and distance parameters for the investigated ionic liquids in various solvents and temperatures are completely new data, and have never been published in the literature.

Apart from the electrical conductance measurements, viscosimetric measurements were performed for solvents **[H1, H3]** and densimetric ones for solvents and solutions **[H1-H10]**. Density and viscosity data for the solvent was required for calculations based on lcCM, density data for solvent and solution-in order to express the concentrations on the molar scale.

Conductometric properties

The effect of structure and solvent properties on limiting molar conductivity

For comparison, Figure 2 presents the molar conductivity values of [emim][BF_4] in the investigated solvents as a function of the square root of the molar concentration at T = 298.15 K **[H1, H3, H5, H6, H7, H8, H9, H10]**. In all solvents molar conductivity decreases as the concentration of ionic liquid increases. A clear curvature of this dependency and low conductivities observed in DCM and alcohols indicate the presence of a significant ionic association in these systems. The second ionic liquid, i.e. [bmim][BF_4], has only a slightly smaller conductivity than [emim][BF_4] in the examined solvents.

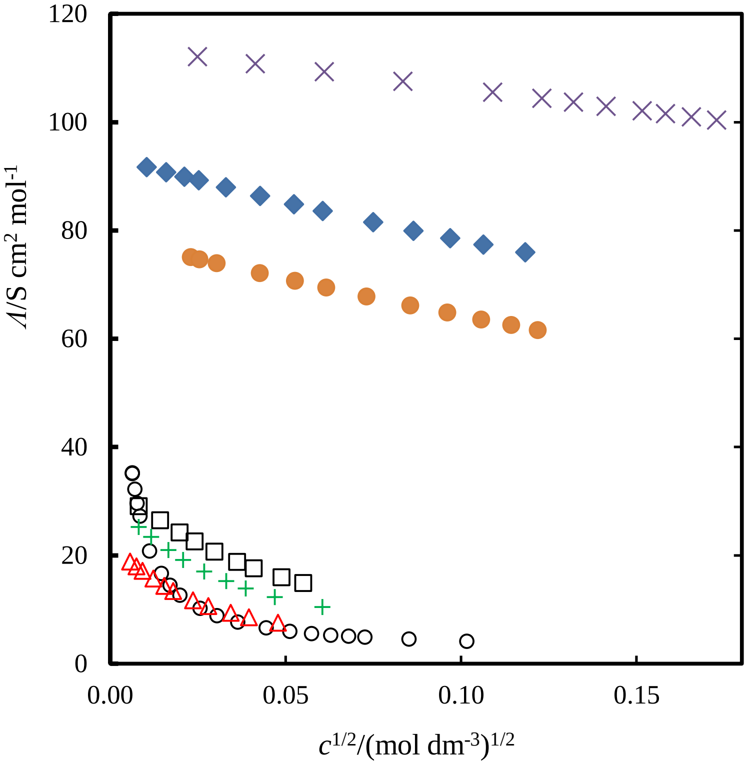

Fig. 2 Molar conductivity (Λ) of [emim]BF$_4$] versus $c^{1/2}$ in investigated solvents at 298.15 K: x water, ♦ DMF, ● DMAc, □ PrOH, + 2-PrOH, Δ BuOH, ○ DCM **[H1, H3, H5, H6, H7, H8, H9, H10]**

The properties of the solvent can have a significant impact on molar conductivities. Based on the limiting molar conductivities (Table 1) obtained for the investigated ILs in various solvents in the present study, and those reported in the literature for acetonitrile [20, 21], dimethyl sulfoxide [22] and methanol [22, 23], the limiting molar conductivity (Λ_o) was found to follow the order: acetonitrile > dichloromethane > methanol > water > N,N-dimethylformamide > N,N-dimethylacetamide > dimethyl sulfoxide > propan-1-ol > propan-2-ol > butan-1-ol. Although there is a tendency for the conductivity to increase with a decrease of solvent viscosity, this is not the case throughout the series given above. However, the findings indicate that if the protic and aprotic character of the solvent is taken into consideration, the conductivity decreases in the order MeOH > water > 1-PrOH > 2-PrOH > 1-BuOH for protic solvents, and ACN > DCM > DMF > DMAc > DMSO for aprotic solvents; this correlates very well with the increase in viscosity **[H7]**. Of course this applies to all the temperatures tested. The only example where the Λ_o values are higher than in 1-PrOH is [bmim][BF$_4$] in 2-PrOH at 313.15 K and 318.15 K; however, it is important to note that the viscosity of 2-PrOH at these temperatures is also lower than that of 1-PrOH. The branching in the alkyl chain of the alcohol (1-PrOH and 2-PrOH) appeared to cause little change in ionic mobility, and thus the molar conductivity **[H10]**.

Table 1. Comparison of the values of limiting molar conductivity (Λ_o), association constants (K_A) and Gibbs free energy of association (ΔG_A^o) for [emim][BF$_4$] and [bmim][BF$_4$] in various solvents of viscosity η and relative permittivity ε_r at 298.15 K **[H1, H3, H5, H6, H7, H9, H10]**

Solvent	η/mPa·s	ε_r	Λ_o/S·cm^2·mol^{-1}	K_A/ dm^3·mol^{-1}	ΔG_A^o / kJ·mol^{-1}	Ref.
DCM	0.415 [8]	8.82 [8]	181.07^{a}	595110^{a}	-33.0	**[H7]**
			161.08^{b}	478920^{b}	-32.4	**[H7]**
1-BuOH	2.5772^{c}	17.58 [24]	20.682^{a}	2671^{a}	-19.6	**[H6]**
			20.546^{b}	2780^{b}	-19.7	**[H6]**
2-PrOH	2.052[25]	19.45 [26]	28.285^{a}	1662^{a}	-18.9	**[H10]**
			27.881^{b}	1780^{b}	-18.6	**[H10]**
1-PrOH	1.957 **[H3]**	20.45 [9]	31.43^{a}	943^{a}	-17.0	**[H3]**
			30.29^{b}	987^{b}	-17.1	**[H3]**
MeOH	0.5438 [22]	32.63 [22]	134.0^{a}	66.1^{a}	-10.4	[23]
			121.84^{b}	37.7^{b}	-9.0	[22]
			126.9^{b}	53.7^{b}	-9.9	[23]
ACN	0.3413 [8]	35.96 [20]	197.10^{a}	15.9^{a}	-6.9	[20]
			198.3^{a}	17.9^{a}	-7.2	[21]
			189.29^{b}	15.7^{b}	-6.8	[20]
			190.3^{b}	18.2^{b}	-7.2	[21]
DMAc	0.9335^{d}	38.75^{d}	78.33^{a}	14.79^{a}	-6.7	**[H9]**
			75.04^{b}	10.24^{b}	-5.8	**[H9]**
DMF	0.8455 **[H1]**	36.81 [27]	93.47^{a}	11.30^{a}	-6.0	**[H1]**
			89.83^{b}	10.57^{b}	-5.9	**[H1]**
DMSO	1.9946 [22]	46.52 [22]				
			41.51^{b}	4.6^{b}	-3.8	[22]
Water	0.8903 [9]	78.36 [27]	114.27^{a}	0.89^{a}		**[H5]**
			107.39^{b}	016^{b}		**[H5]**

^{a} [Emim][BF$_4$], ^{b} [Bmim][BF$_4$], ^{c} this value was calculated on the basis of my density data and kinematic viscosity from Ref. [10], ^{d} interpolated data from the literature (details are given in **[H9]**)

The effect of cation of IL on limiting molar conductivity

In each studied system, the values of Λ_o (and Λ) are always slightly higher for [emim][BF$_4$] than for [bmim][BF$_4$] (Table 1). This applies to each temperature tested. This indicates that the Λ_o values decrease with increasing alkyl chain length of the ILs. The greatest differences between Λ_o values over the whole range of temperatures were observed for DCM (from about 13 to 22 S·cm^2·mol^{-1}) **[H7]**, while the smallest were seen for 1-BuOH (below 0.5 S·cm^2·mol^{-1}) **[H6]**.

The effect of temperature on the limiting molar conductivity

I also investigated the effect of temperature on molar conductivity. The Λ_o values were found to increase with increasing temperature, as a result of the viscosity of the solution decreasing and the ionic mobility increasing. The radii of the solvated ions become smaller due to the interactions between IL and solvent decreasing, resulting in greater ion mobility. In addition, the greatest increase in molar conductivity with temperature was found in water **[H5]**, with only a slight increase being seen in DCM **[H7]**.

The impact of both the temperature and the type of cation of the ionic liquid on the limiting molar conductivity, taking the example of N,N-dimethylacetamide **[H9]**, is given in Figures 3 and 4, respectively.

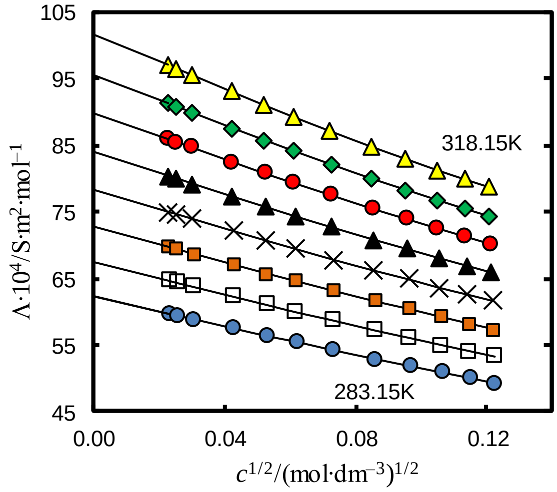

Fig. 3 Molar conductivity (Λ) of [emim][BF_4] solutions in DMAc versus $c^{1/2}$ at experimental temperatures. The lines represent the calculations according to eqs 1 through 3 **[H9]**

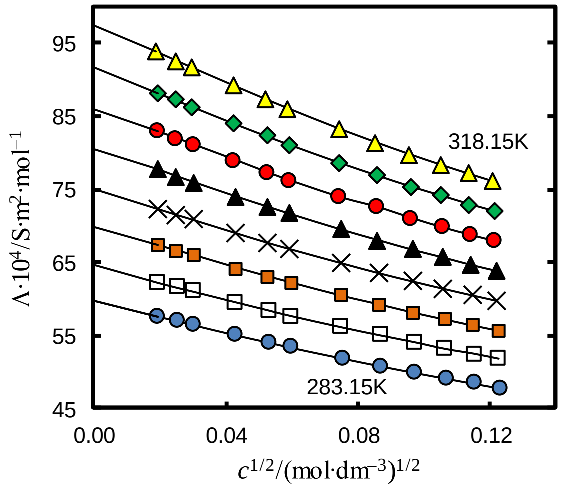

Fig. 4 Molar conductivity (Λ) of [bmim][BF_4] solutions in DMAc versus $c^{1/2}$ at experimental temperatures. The lines represent the calculations according to eqs 1 through 3 **[H9]**

Ionic association

The effect of solvent properties on the ionic association of ILs

Table 1 presents the calculated association constants for both ionic liquids in the investigated solvents at a temperature of 298.15 K. These sets of data have been supplemented with literature data available for three other solvents: MeOH, ACN and DMSO. My calculated K_A values indicated that the examined ionic liquids are strongly associated in dichloromethane **[H7]**, butan-1-ol **[H6]**, propan-2-ol **[H10]** and quite strongly in propan-1-ol **[H3]** within the investigated temperature range. The ionic association was moderate in methanol [22, 23], and slight in acetonitrile [20, 21], N,N-dimethylacetamide **[H9]**, N,N-dimethylformamide **[H1]** and dimethyl sulfoxide [22]. Water significantly promotes the dissociation of the ionic liquids **[H5]**. In this case, the association constants are practically negligible and it can be assumed that both ILs exist essentially as free ions in the water; this is probably because water forms strong hydrogen bonds with the anions and tends to separate the cations and anions in the aqueous solutions and break the aggregate structures of the ILs. These results suggest that cations and anions are less associated in the solvent, which possesses a high relative permittivity due to the independent solvation of ions. In dichloromethane, a low-permittivity solvent with low solvation power for the ions, the association is the strongest.

In alcohols, the order of the association constant values of the ILs is the reverse of that found for the Λ_o values, i.e.: 1-BuOH > 2-PrOH > 1-PrOH > MeOH, which correlates well with the observed decrease in relative permittivity of the solvent **[H10]**.

Figure 5 illustrates the dependency of log K_A versus the reciprocal relative permittivity l/ε_r; it compares the association of ionic liquids in propan-2-ol with those of the primary alcohols. The plots for both ionic liquids in propan-1-ol, propan-2-ol and butan-2-ol were found to be linear when examined according to Fuoss, who also noted a linear plot [28]. This linearity shows that in these systems, the electrostatic ionic interactions are mainly responsible for the ionic association. However, it should be noted that the slope indicating the association constants in propan-2-ol is different to those of the primary alcohols, indicating that in propan-2-ol, the association constants change in a different way with regard to relative permittivity; in this case, we can see a greater increase in K_A values with decreasing relative permittivity, and thus with increasing temperature (see Fig. 6). Figure 6 presents the predicted values of the association constants of [bmim][BF_4] in ethanol ($K_A \approx 235$ $dm^3 \cdot mol^{-1}$ at 298.15 K).

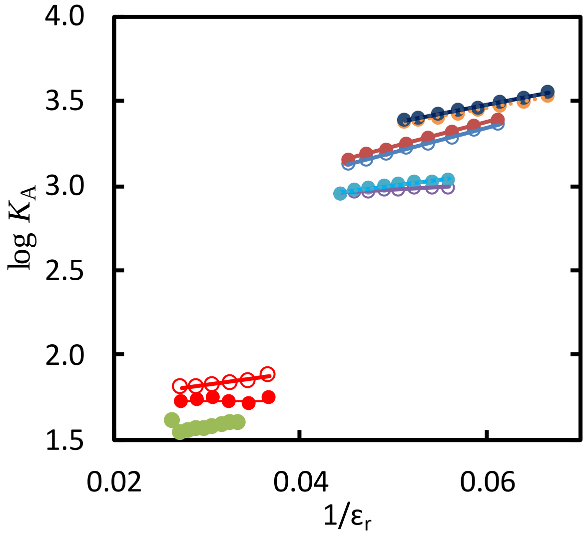

Fig. 5 The logarithm association constant (log K_A) versus the reciprocal relative permittivity ($1/\varepsilon_r$) for [emim][BF$_4$] (open circles) and [bmim][BF$_4$] (closed circles) in alcohols as a function of temperature; from the bottom ● MeOH [22], ○ and ● MeOH [23], ○ and ● 1-PrOH, ○ and ● 2-PrOH, ○ and ● 1-BuOH **[H10]**

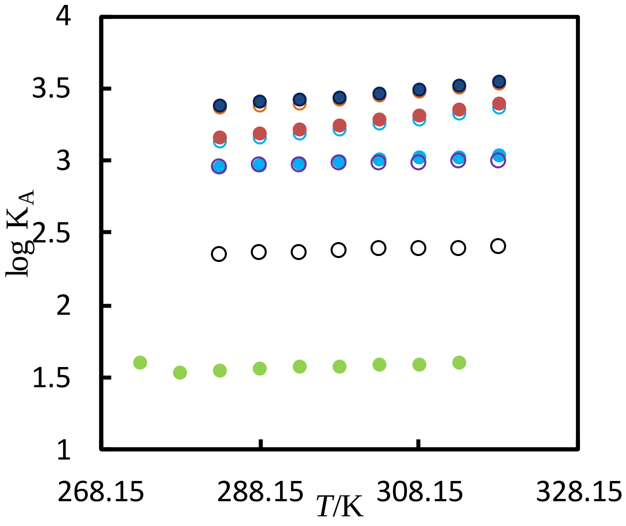

Fig. 6 Association constants (K_A) versus the temperature for [emim][BF$_4$] (open circles) and [bmim][BF$_4$] (closed circles) in alcohols; from the bottom ● MeOH [22], ○ EtOH, ○ and ● 1-PrOH, ○ and ● 2-PrOH, ○ and ● 1-BuOH **[H10]**

I noticed that branching of the alkyl chain of the alcohol causes a large increase in ionic association constants (1-PrOH and 2-PrOH) **[H10]**. This increase is approximately 49 % and 135 % at T = 283.15 K, and 58 % and 126 % at T = 318.15 K for [emim][BF$_4$] and [bmim][BF$_4$], respectively. Moreover, the primary alcohols were found to be more acidic (especially MeOH) than propan-2-ol, and consequently would be expected to bind more effectively with anions by hydrogen bonding [29, 30]. In turn, the anion solvation significantly affects the degree of ionic association. In 2-PrOH the ion pairs are less stabilized via hydrogen bonds than in 1-PrOH, which results in 2-PrOH demonstrating higher K_A values. Conversely, MeOH shows a greater tendency to form hydrogen bonds than other alcohols, which results in it demonstrating lower K_A values **[H10]**. In addition to the hydrogen bonds between the methanol OH group and the BF^- anion in methanol, or any other tested alcohol, and the ionic liquid mixture, weak interactions were also identified between the methanol OH group and the imidazolium cation, and even between the methanol alkyl (C-H) and the BF^- anion [31]. The hydrogen bonds between methanol and the BF_4^- anion are weaker than those between methanol-methanol [22]. In addition, the hydrogen bond between alcohol and the anion becomes less significant, with the interactions between the alcohol and the cation of ionic liquid increasing in importance [32]. By increasing the alkyl chain of the alcohol, the interactions with the non-polar part of the ionic liquid may increase.

The effect of temperature on the ionic association of ILs

In the studied ionic liquid-solvent systems (in alcohols, N,N-dimethylformamide, N,N-dimethylacetamide, dichloromethane) **[H1, H3, H6, H7, H9, H10],** the association constant was found to have a clear dependence on the temperature, i.e. the association constants increase with as the temperature increases; this could be due to the IL-solvent interactions decreasing with increasing temperature.

The effect of other factors on the ionic association of ILs

Ion-solvent interactions may also affect the small differences between the values of K_A in DMF and DMAc **[H9]**. K_A values are higher for [emim][BF_4] in DMAc than in DMF. In turn, they were found to be slightly lower for [bmim][BF_4] in DMAc than in DMF, except for those at 313.15 and 318.15 K (11.45 and 11.96 $dm^3 \cdot mol^{-1}$ in DMF and 11.53 and 12.23 in DMAc, respectively).

My results also indicate that while [bmim][BF_4] is a more associated electrolyte than [emim][BF_4] in the investigated alcohols **[H3, H6, H10]** (see Table 1), the opposite is true in the other solvents **[H1, H7, H9]**. This confirms that the size of the alkyl substituent in the imidazolium cation and the ion-solvent interaction have a strong influence on the association constants.

My studies on dichloromethane also found that K_A values depend significantly on the adopted model of ion pairs. In the case of solvent-separated (SSIP) ion pairs, the K_A (and Λ_o) values are higher **[H7].**

My findings indicate that the process of ion pairing in the studied ionic liquid solutions depends on the properties and the relative permittivity of the solvent, which can be verified by plotting log K_A values against $1/\varepsilon_r$. An important role is also played by the ion-solvent interactions, the size of the alkyl substituent in the imidazolium cation and the temperature.

Triple ion formation. A new method of analysis of conductivity data

It is well documented that at higher concentrations or in low permittivity solvents, even at low concentrations, electrolytes can exist as ion pairs, triple ions, quadruplets and higher aggregates [33]. Triple ions may form in solvents whose relative permittivity is less than 15. Further decreases of relative permittivity to values below 10 may promote the formation of larger clusters of four, five or more ions. Conductance measurements provide direct information about the dominant species in solution. At very dilute concentrations, where free ions are dominant in solution, maximum molar conductivity can be observed. The formation of non-conducting ion pairs causes a decrease of the molar conductivity at certain concentrations depending on the solvent [34]. If triple ions form in a solution, one can expect an increase in molar conductivity; in turn, higher aggregate formation causes a reduction in conductivity (Fig. 7). The structure and stability of the aggregates depend on the ions and the solvent, Coulombic attractions, the hydrogen bonds between anion and the hydrogen atoms in the imidazolium ring of the ionic liquid [7].

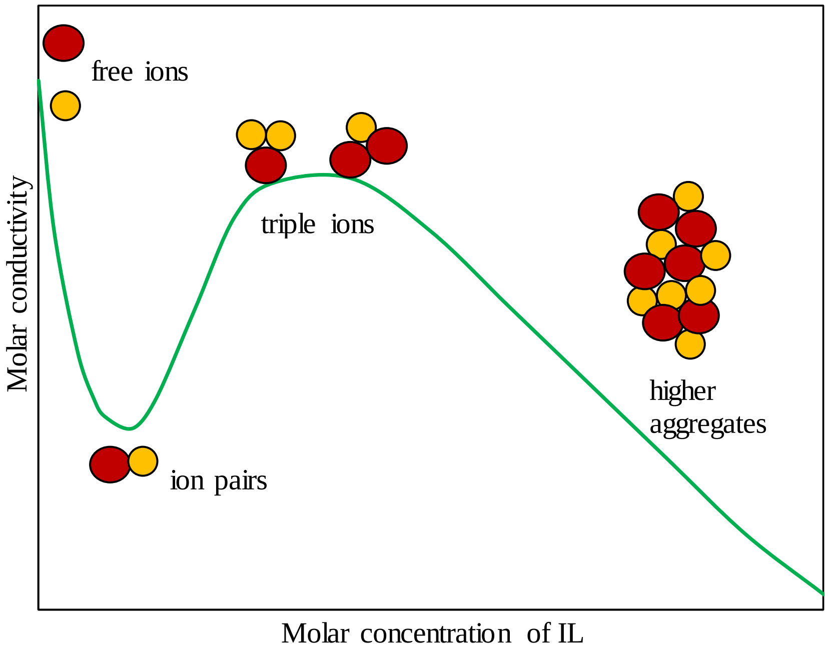

Fig. 7 Possible structures of ionic liquids aggregates in diluted and concentrated solutions

Paper **[H7]** presents conductance measurements of very dilute solutions (c = 0.4 to $4 \cdot 10^{-4}$ mol·dm^{-3}) of the studied ionic liquids [emim][BF$_4$] and [bmim][BF$_4$] in dichloromethane at T = (278.15 to 303.15) K. Paper **[H8]** reports similar results, but for higher concentrations ranging from $6 \cdot 10^{-4}$ to $1 \cdot 10^{-2}$ mol·dm^{-3}.

The results obtained in **[H7]** were analyzed on the assumption that only free ions and ion pairs were present in the investigated solutions. However, according to Fuoss [11], this assumption may not be true if the maximum concentration of the electrolyte exceeds $c_{\max} = 3.2 \cdot 10^{-7} \cdot \varepsilon_r^3$ mol·dm^{-3} (in DCM $c_{\max} = 2.3 \cdot 10^{-4}$ mol·dm^{-3}). Indeed, it turned out that for concentrations greater than c_{max}, the calculated molar conductivities (Λ_{calc}) were lower than the experimental values (Λ_{exp}) (Fig. 8). For comparison, I used the Λ_{exp} values for [emim][BF_4] and [bmim][BF_4] given in paper **[H7]** and Λ_{exp} obtained in paper **[H8]** at 298.15 K. In contrast, I obtained the values of Λ_{calc} based on the limiting molar conductivity (Λ_o) and the association constants (K_A) determined in paper **[H7]**, assuming the formation of contact ion pairs in solution. The differences between the calculated and experimental values of Λ increase together with concentration, and at $c \approx 0.01$ mol·dm^{-3}, Λ_{calc} represents about 35% and 30% of the experimental values (Λ_{exp}) for [bmim][BF_4] and [emim][BF_4], respectively. This finding suggests that with increasing concentrations of the ionic liquid above the concentration c_{max}, charge-bearing individuals, i.e. triple ions, appear in solution. The differences (Λ_{exp} - Λ_{calc}) are very significant, indicating that at higher concentrations, any analysis of molar conductivity must take into account the phenomenon of triple ion formation in solutions of [emim][BF_4] and [bmim][BF_4] in dichloromethane.

Therefore, I developed a new method of analysis of conductivity data based on the low concentration Chemical Model (lcCM) for solutions containing free ions, ion pairs and triple ions **[H8]**. This approach allowed the formation constants of triple ions (K_T) and their limiting molar conductivity values ($\Lambda_{o,T}$) to be calculated. Paper **[H8]** is the first attempt to use this model for the analysis of conductivity data in this type of solution.

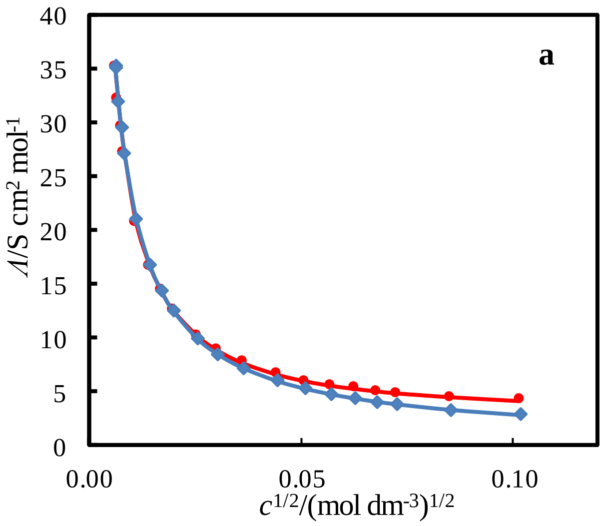

Fig. 8 Comparison of ●, experimental and ♦, calculated molar conductivities for **a.** [emim][BF_4] in DCM **[H8]**

In the electrolyte solution containing the cations C^+ and anions A^- as well as the ion pairs CA and the triple ions C_2A^+ and CA_2^- the following equilibria are established:

$$C^+ + A^- \rightleftharpoons CA \tag{4}$$

$$CA + C^+ \rightleftharpoons C_2A^+ \tag{5a}$$

$$CA + A^- \rightleftharpoons CA_2^- \tag{5b}$$

The amounts of individual ions result from the total electrolyte concentration c and the values of equilibrium constants described by the equations (6), (7a) and (7b)

$$K_A = [CA]y_{CA} / [C^+]\, y_{C^+}\, [A^-]\, y_{A^-} = [CA] / [C^+]\,[A^-]\, y_+^2 \tag{6}$$

$$K_{T_1} = [C_2A^+]y_{C_2A^+} / [CA]\,[C^+]\, y_{C^+} = [C_2A^+] / [CA]\,[C^+] \tag{7a}$$

$$K_{T_2} = [CA_2^-]y_{CA_2^-} / [CA]\,[A^-]\, y_{A^-} = [CA_2^-] / [CA]\,[A^-] \tag{7b}$$

where K_A and K_T are the ion pair and triple ion formation constants, respectively.
In the equations (6), (7a) and (7b) it was assumed that $y_{CA} = 1$, $y_{C^+} y_{A^-} = y_\pm^2$, $y_{C_2A^+} = y_{C^+}$ and $y_{CA_2^-} = y_{A^-}$.

Assuming symmetric triple ion formation, $K_{T_1} = K_{T_2} = K_T$, and $[C^+] = [A^-]$, the concentrations of individual ions can be written as

$$[C^+] = [A^-] = \beta_1 c \tag{8}$$

$$[C_2A^+] = [CA_2^-] = \beta_T c \tag{9}$$

$$[CA] = (1 - \beta_1 - 3\beta_T)\, c \tag{10}$$

From equations (6)-(10) result that

$$\beta_1 = [-1 + (1 + 4K_A c\, y_\pm^2 (1 - 3\,\beta_T))^{1/2}] / (2K_A \,c\, y_\pm^2) \tag{11}$$

$$\beta_T = K_T c\, \beta_1 (1 - \beta_1) / (1 + 3K_T \beta_1 c) \tag{12}$$

where the activity coefficient ($y_\pm$) and the ionic strength (I) of the solution are described by the equations

$$\ln y_\pm = -A\sqrt{I} / (1 + BR\sqrt{I}) \tag{13}$$

$$I = (\beta_1 + \beta_T)c \tag{14}$$

R is the distance parameter of ions, A and B are the Debye-Hückel coefficients.
For specific values of K_A and K_T, I calculated the values of β_1 and β_T coefficients for any concentration c from equations (11)-(14) using the numerical method of successive approximations.

In the case where triple ions are present in the solution, the molar conductivity of the electrolyte is described by the following equation [33, 35]

$$\Lambda = \beta_1 \Lambda_1 + \beta_T \Lambda_T \tag{13}$$

where Λ_1 is the conductance of the electrolyte in the form of ions C^+ and A^-, Λ_T is the conductance of an electrolyte consisting of the ions C_2A^+ and CA_2^-.
In the case of extremely low electrolyte concentrations, the limiting molar conductivity parameters Λ_o and $\Lambda_{o,T}$ were used to describe the respective values of Λ_1 and Λ_T [33, 36]. The low concentration Chemical Model was used for the analysis of the molar conductivity parameters Λ_1 and Λ_T, and the conductivity was calculated using the following equations

$$\Lambda_1 = \Lambda_o - S_{(1)}\sqrt{I} + E_{(1)} I \ln I + J_{1(1)} I + J_{2(1)} I^{3/2} \tag{16}$$

$$\Lambda_T = \Lambda_{o,T} - S_{(T)}\sqrt{I} + E_{(T)} I \ln I + J_{1(T)} I + J_{2(T)} I^{3/2} \tag{17}$$

In the case of triple ions in solutions, the analysis of the relationship between molar conductivity and molar concentration requires the values of four parameters to be determined: Λ_o, $\Lambda_{o,T}$, K_A, and K_T. The values of Λ_o and K_A were determined in paper **[H7]**. In this case, only the values of $\Lambda_{o,T}$ and K_T need to be determined, or only one parameter of K_T if the specified value of $\Lambda_{o,T}/\Lambda_o$ is used. However, a significant aspect of this paper is that it attempts to simultaneously determine the values of $\Lambda_{o,T}$ and K_T in a wide range of temperatures from 278.15 to 303.15 K. Furthermore, it identifies the most real value of the quotient of $\Lambda_{o,T}/\Lambda_o$. The calculated values of $\Lambda_{o,T}$ and K_T are collected in Table 2. Part (a) of Table 2 includes the values of $\Lambda_{o,T} = \Lambda_o/3$ and the optimized K_T values, while part (b) includes the results of the simultaneous optimization of $\Lambda_{o,T}$ and K_T values. All the calculations were performed using the parameter of the closest approach of the ions (R) corresponding to the contact ion pairs.

Table 2. The limiting molar conductivities of the triple ions ($\Lambda_{o,T}$), formation constants of the triple ions (K_T), and standard deviations $\sigma(\Lambda_{o,T})$ for the investigated electrolytes in DCM at different temperatures **[H8]**

T/K	$\Lambda_{o,T}$/S·cm^2·mol^{-1}	K_T/dm^3·mol^{-1}	$\sigma(\Lambda_{o,T})$	$\Lambda_{o,T}$/S·cm^2·mol^{-1}	K_T/dm^3·mol^{-1}	$\sigma(\Lambda_{o,T})$
	(a)			(b)		
			[emim][BF$_4$]			
278.15	49.91	197.5	0.009	48.51	205.6	0.025
283.15	52.13	198.5	0.028	51.80	200.3	0.010
288.15	54.85	200.1	0.028	54.04	204.2	0.017
293.15	57.50	200.2	0.031	58.33	196.3	0.023
298.15	60.35	199.3	0.013	58.86	205.8	0.023
303.15	63.54	199.4	0.013	63.24	200.6	0.024
			[bmim][BF$_4$]			
278.15	45.50	189.6	0.022	47.04	180.9	0.022
283.15	47.41	190.9	0.022	49.38	180.3	0.031
288.15	49.31	191.1	0.026	50.75	183.6	0.036
293.15	51.67	195.1	0.027	53.34	186.7	0.029
298.15	53.69	190.7	0.063	53.69	188.2	0.053
303.15	56.17	193.8	0.020	57.61	187.2	0.019

As seen from Table 2, the values of $\Lambda_{o,T}$ obtained by the optimization method were surprisingly close to the values resulting from the assumption of $\Lambda_{o,T} = \Lambda_o/3$ used earlier by several other authors [33, 36, 37]; in addition, the values of K_T obtained using these two methods were also very similar. I concluded, therefore, that this assumption can be successfully used in the studied systems to determine the formation constants of the triple ions.

Paper **[H8]** uses K_T values to calculate the thermodynamic functions of triple ion formation, which suggests that spontaneous triple ion formation is a process mainly driven by entropy. In turn, the values for the activation enthalpy of charge transport determined from the temperature dependence of $\Lambda_{o,T}$ are higher for [emim][BF$_4$] than for [bmim][BF$_4$], and are practically the same as observed for the electrolyte consisting of simple ions.

Ion transport

Λ_o values taken at various temperatures were used to calculate the Eyring activation enthalpy of charge transport($\Delta H_\lambda^\ddagger$) [38]

$$\ln \Lambda_o + 2/3 \ln \rho_o = - \Delta H_\lambda^\ddagger / RT + D \qquad (18)$$

where D is an empirical constant. The $\Delta H_\lambda^\ddagger$ values presented in Table 3 were obtained from the slope of the linear dependencies of ln Λ_o + $2/3$ ln ρ_o versus the inverse of the temperature ($1/T$),.

Table 3. Eyring activation enthalpy of charge transport ($\Delta H_\lambda^\ddagger$) for [emim][BF$_4$] and [bmim][BF$_4$] in the investigated solvents **[H1, H3, H5, H6, H7, H9, H10]**

	$\Delta H_\lambda^\ddagger$ / J·mol^{-1}	
solvent	[emim][BF$_4$]	[bmim][BF$_4$]
DCM	6138	5257
DMF	8541	8669
DMAc	9922	9959
Water	16078	16727
1-PrOH	16335	16665
BuOH	18623	18674
2-PrOH	20698	20798

The positive $\Delta H_\lambda^\ddagger$ values suggest that the solvated ion pairs have a less stable arrangement than the solvated ions, which means that the ion pair-solvent interactions are weaker than the ion-solvent interactions [39]. In the investigated solvents, the values of $\Delta H_\lambda^\ddagger$ are higher for [bmim][BF$_4$] than [emim][BF$_4$]; this is a result of the presence of a larger substituent in the [bmim]$^+$ cation than the [emim]$^+$ cation. It seems that this conclusion applies to both protic and aprotic solvents. Only in the case of dichloromethane is the value of $\Delta H_\lambda^\ddagger$ for [emim][BF$_4$] higher than for [bmim][BF$_4$]. This may suggest that in DCM, [emim]$^+$ has a greater effective ionic radius than [bmim]$^+$.

It was concluded that the obtained values for the Eyring activation enthalpy of charge transport depend mainly on the type of solvent and the ability of hydrogen bonds to form between solvent molecules. Therefore, these values are almost twice as high, or more so, in protic solvents than in aprotic solvents.

More detailed information on the mobility of ions in terms of ion-solvent interactions can be obtained on the basis of their limiting ionic conductivity ($\lambda_\pm^o$). Therefore, additional conductometric measurements were proposed for NaBPh$_4$, Bu$_4$NBr and NaBF$_4$ in N,N-dimethylformamide **[H2],** as well as for NaI, NaBPh$_4$, Bu$_4$NI and NaBF$_4$ in propan-1-ol **[H4],** in the temperature range from 283.15 to 318.15 K. The main reason for choosing these electrolytes was the fact that $NaBPh_4$, Bu_4NI, Bu_4NBr and NaI can be used to split the values for limiting molar conductivity into their ionic components; for this purpose, I used the Fuoss-Hirsch assumption about the equality of ionic mobilities for Bu_4N^+ and BPh_4^- [40]. The limiting molar conductivity of $NaBF_4$ was needed to split the Λ_o values for the studied ionic liquids. The calculated values of limiting ionic conductivities in DMF and 1-PrOH are presented in Tables 4 and 5, respectively.

Table 4. Limiting ionic conductivities ($\lambda_{\pm}^{o}$) in DMF **[H2]**

			$\lambda_{\pm}^{o}\cdot10^{4}/S\cdot m^{2}\cdot mol^{-1}$			
T/K	BPh_4^- = Bu_4N^+	Na^+	Br^-	BF_4^-	$[emim]^+$	$[bmim]^+$
283.15	19.91	24.29	43.67	44.33	32.38	28.79
288.15	21.52	26.03	46.98	47.76	34.45	30.94
293.15	23.15	27.81	50.31	51.23	36.57	33.03
298.15	24.91	29.70	53.57	54.67	38.81	35.17
303.15	26.70	31.61	56.85	58.16	41.09	37.29
308.15	28.55	33.58	60.13	61.68	43.46	39.42
313.15	30.46	35.59	63.41	65.25	45.83	41.47
318.15	32.43	37.66	66.69	68.82	48.31	43.53

Table 5. Limiting ionic conductivities ($\lambda_{\pm}^{o}$) in 1-PrOH **[H4]**

			$\lambda_{\pm}^{o}\cdot10^{4}/S\cdot m^{2}\cdot mol^{-1}$			
T/K	BPh_4^- = Bu_4N^+	Na^+	I^-	BF_4^-	$[emim]^+$	$[bmim]^+$
283.15	7.60	7.26	9.36	9.75	12.00	11.39
288.15	8.65	8.15	10.61	10.73	13.98	12.77
293.15	9.75	9.24	12.08	11.77	16.14	15.21
298.15	10.94	10.48	13.72	12.87	18.56	17.43
303.15	12.45	11.64	15.37	14.21	21.01	19.71
308.15	13.96	13.07	17.28	15.51	23.85	22.27
313.15	15.58	14.61	19.37	16.93	26.79	25.02
318.15	17.23	16.37	21.71	18.32	30.24	28.14

Both papers **[H2, H4]** present the ionic association constants, limiting molar conductivities, Eyring's activation enthalpy of charge transport and thermodynamic functions of association for the investigated electrolytes. However, the most interesting observations and conclusions concern the limiting ionic conductivity and solvation process.

The large organic ions, i.e. BPh_4^- and Bu_4N^+, have low conductivity and high activation enthalpy values of charge transport, both in DMF and 1-PrOH. The low conductivity and high activation enthalpy of the Na^+ ion result from its strong interaction with

DMF and 1-PrOH attributable to its high surface charge density. As a result of these interactions, the effective radius of the sodium ion is comparable with that of the radius of large organic ions; however, the limiting ionic conductivities for these ions are definitely higher in DMF.

In the $[emim]^+$ and $[bmim]^+$ cations, the positive charge localized on the nitrogen atom is covered by a $-CH_3$ group, which hinders cation solvation. In propan-1-ol, these cations have the highest conductivity among the investigated ions, which means that they are less solvated by propan-1-ol molecules, but definitely more strongly than by DMF molecules (see Table 4 and 5). The ionic conductivity of $[emim]^+$ is greater than $[bmim]^+$, due to the differences in the sizes of ethyl and butyl group occurring in these cations.

The analysis of limiting ionic conductivities and crystallographic radii indicate that Br^-, BF_4^- , $[emim]^+$, and $[bmim]^+$ ions are poorly solvated by DMF molecules. In turn, in 1-PrOH, I^- and BF_4^- are less solvated than Na^+, and the organic ions BPh_4^- and Bu_4N^+ are poorly solvated (or unsolvated). The BF_4^- anion possesses small values of activation enthalpy of charge transport; this may confirm that it interacts with propan-1-ol molecules by a different model to that used by the more polarizable iodide anion, which has a similar crystallographic radius.

All discussed interactions are probably weakened by a temperature increase: the effective size of the ions slightly decreases, causing an additional increase in the conductivity.

On the basis of the calculated association constants, the electrolytes can be ordered as follows, from the least to the most strongly associated in propan-1-ol: $NaBPh_4$ (K_A = 62.7 $dm^3 \cdot mol^{-1}$ at 298.15 K) < NaI < Bu_4NI < $NaBF_4$ (K_A = 906.5 $dm^3 \cdot mol^{-1}$ at 298.15 K). In DMF, all examined electrolytes are weakly associated at the experimental temperatures.

Information concerning the ion-solvent interaction in solution is also provided by the Walden product. Simple hydrodynamic models assume that the values of the Walden product ($\Lambda_o\eta$) depend on changes in temperature to a very small degree. The values presented in Table 6 show that the Walden rule is well fulfilled in the examined solvents **[H3, H5, H10]** for both ionic liquids. The same simple thermodynamic models assume that the $\Lambda_o\eta$ values are reciprocally proportional to the effective size of the ions according to the equation

$$\Lambda_o\eta = 8.204 z_i^2/r_s \qquad (19)$$

where r_s is the effective solvated radius (Stokes radius), z_i is the charge number of the ion, η is the dynamic viscosity of solvent.

Therefore, when analyzing the Walden products in DMF and propan-1-ol in paper **[H3]**, the effective size of the ions was assumed to be much greater in 1-PrOH than in DMF; this is due to the poor solvation of BF_4^- anions in the aprotic DMF compared with the protic 1-PrOH. Although the crystallographic radius of the BF_4^- ion is slightly larger than that of Br^- and Cl^-, these ions have very similar limiting molar conductivities in DMF (Table 4). The fact that the poorly-polarized anions are poorly solvated in dipolar aprotic solvents seems to be fairly well substantiated [41-44]. The data presented in Tables 4, 5 and 6, indicates that the limiting ionic conductivities (λ_o^+), and thus ionic Walden products ($\lambda_o^+\eta$), for $[emim]^+$ are higher than those for $[bmim]^+$, both in 1-PrOH and in DMF **[H3]**. From Table 6, it follows that the differences between the values of $\lambda_o^+\eta$ for $[emim]^+$ and $[bmim]^+$ increase slightly with increasing temperature in the case of 1-PrOH (from 0.017 to 0.026), and decrease slightly (from 0.035 to 0.030) in the case of DMF.

The values of the Walden products for [emim][BF_4] and [bmim][BF_4] in water are analyzed in paper **[H5]**. When applying equation (19), the temperature change in the used range was assumed to not practically affect the effective size of ions, and that the effective size of the ion $[bmim]^+$ was larger than that of the ion $[emim]^+$ over the range of temperatures tested. I also noticed that the Walden products in water, DMF and propan-1-ol satisfy the following relations: $\Lambda_o\eta$ [emim][BF_4] > $\Lambda_o\eta$ [bmim][BF_4] and $\Lambda_o\eta$ (water) > $\Lambda_o\eta$ (DMF) > $\Lambda_o\eta$ (1-PrOH). The first relationship suggests that the ion $[bmim]^+$ has a greater effective radius, which corresponds well with the fact that it also has a greater Eyring activation enthalpy of charge transfer.

In my last article **[H10],** I also analyzed the changes of Walden products in alcohols. I noticed that the values of $\Lambda_o\eta$ at a given temperature change in the same order as the values of limiting molar conductivity, these being highest in methanol and lowest in butan-1-ol; this confirms the predominance of Λ_o over η. The effective size of the ions in butan-1-ol is obviously greater than in methanol. I also noted that the mobility of the ions at infinite dilution is controlled mainly by the bulk viscosity, and a weak solvation of ions is expected. A detailed analysis of solvation processes on the basis of limiting ionic conductivities and Stokes radii in methanol [22, 23], propan-1-ol [**H4**, 45] and butan-1-ol [45] confirms that $[emim]^+$ and $[bmim]^+$ are weakly solvated by the alcohol molecules. The ion-solvent interactions of the BF_4^- anion are also weak, but a little stronger than for the large organic cations of ILs.

Table 6. Comparison of the Walden products ($\Lambda_o\eta$) as a function of temperature for [emim][BF_4] and [bmim][BF_4] in various solvents **[H3, H5, H10]**

T/K	$10^{-2}\cdot\Lambda_o\eta$/S·cm²·mol⁻¹·mPa·s					
	DMF	Water	MeOH^a	1-PrOH	2-PrOH	1-BuOH
			[emim][BF_4]			
283.15	0.747	1.035		0.617	0.570	0.532
288.15	0.748	1.028		0.616	0.582	0.531
293.15	0.748	1.022		0.615	0.576	0.531
298.15	0.746	1.017		0.615	0.580	0.533
303.15	0.745	1.014		0.609	0.581	0.521
308.15	0.742	1.011		0.607	0.576	0.529
313.15	0.740	1.011		0.604	0.574	0.525
318.15	0.739	1.013		0.600	0.568	0.523
			[bmim][BF_4]			
273.15			0.683			
278.15			0.677			
283.15	0.712	0.977	0.673	0.600	0.558	0.525

288.15	0.716	0.963	0.670	0.597	0.573	0.524
293.15	0.718	0.958	0.666	0.594	0.567	0.526
298.15	0.717	0.956	0.663	0.593	0.572	0.530
303.15	0.716	0.958	0.659	0.586	0.571	0.517
308.15	0.713	0.964	0.656	0.583	0.568	0.523
313.15	0.711	0.971	0.652	0.579	0.565	0.520
318.15	0.709	0.983		0.574	0.561	0.518

[a] Walden product calculated on the basis of data in Ref. [22].

Thermodynamics of association

One of the goals of my research was to investigate the thermodynamic properties of the association process **[H1, H3, H6, H7, H9, H10]**. To calculate the Gibbs free energy of ion association (ΔG_A^o) I used the temperature dependence of the association constants

$$\Delta G_A^o(T) = -RT \ln K_A(T) \tag{20}$$

$\Delta G_A^o(T)$ can also be expressed by the polynomial

$$\Delta G_\mathrm{A}^o\ (T) = A + B\,T + C\,T^2 \tag{21}$$

The entropy and enthalpy of ion association are defined as

$$\Delta S_\mathrm{A}^o = -(\partial \Delta G_\mathrm{A}^o / \partial T)_p = -B - 2CT \tag{22}$$

$$\Delta H_\mathrm{A}^o = \Delta G_\mathrm{A}^o + T\ \Delta S_\mathrm{A}^o = A - CT^2 \tag{23}$$

The thermodynamic functions of the ion pair formation ($\Delta G_\mathrm{A}^o, \Delta S_\mathrm{A}^o, \Delta H_\mathrm{A}^o$) at different temperatures are presented in Figs. 9, 10, and 11, respectively, with the example of propan-2-ol.

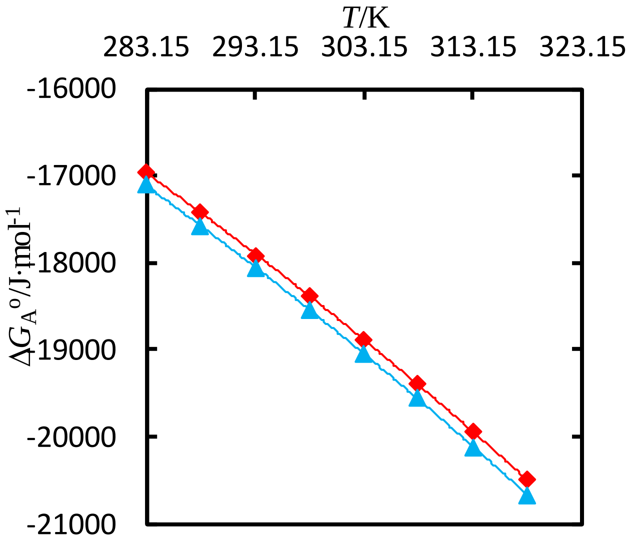

Fig. 9 Variation of Gibbs free energy of association (ΔG_A^o) as a function of temperature T of ♦ [emim][BF$_4$] and ▲ [bmim][BF$_4$] in 2-PrOH

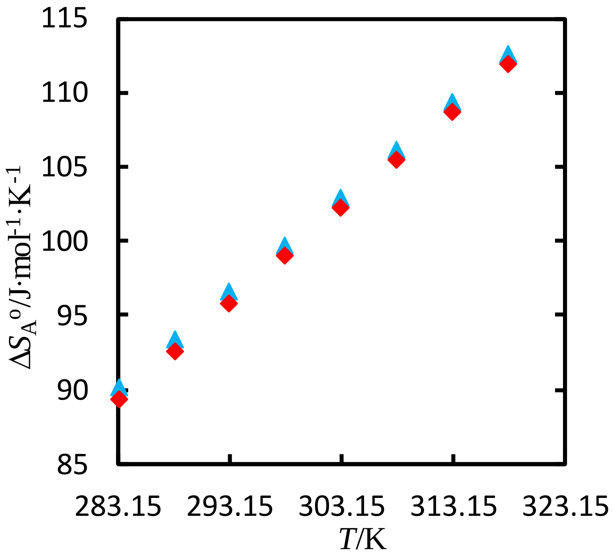

Fig. 10 Variation of entropy of association (ΔS_A^o) as a function of temperature of ♦ [emim][BF_4] and ▲ [bmim][BF_4] in 2-PrOH

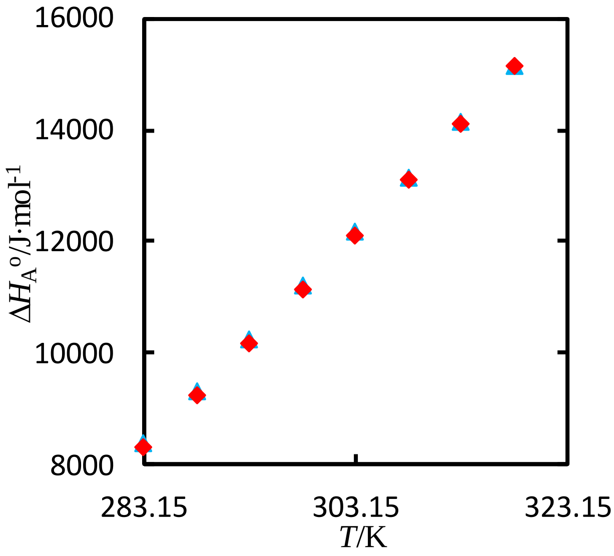

Fig. 11 Variation of enthalpy of association (ΔH_A^o) as a function of temperature of ♦ [emim][BF_4] and ▲ [bmim][BF_4] in 2-PrOH

The Gibbs free energy values of the ILs in all solvents (DMF, 1-PrOH, 1-BuOH, DCM, DMAc, 2-PrOH and MeOH, ACN, DMSO; see Table 1) are negative and become more negative as temperature increases **[H1, H3, H6, H7, H9, H10]**. This behavior indicates that the formation of ion pairs is a spontaneous process and its spontaneity increases at high temperatures. This is due to a reduction in the preferential solvation of ions by temperature, i.e. the interactions between the IL and the solvent become weaker with increasing temperature. The values of $\Delta G_{\mathrm{A}}^{\mathrm{o}}$ also indicate that the two ionic liquids demonstrate comparable spontaneity of ion pair formation in the investigated solvents.

In turn, both the entropy and enthalpy of association values are positive and increase with increasing temperature for both tested electrolytes. The fact that the entropy values are positive confirms that the transition from the free solvated ions into ion pairs causes the system to become less ordered, which is related to the partial desolvation of ions prior to the formation of an ion pair. In addition, I noticed that the examined alcohols can be organized in the same order with regard to their $\Delta S_{\mathrm{A}}^{\mathrm{o}}$ and $\Delta H_{\mathrm{A}}^{\mathrm{o}}$ values, i.e. 2-PrOH > 1-BuOH > 1-PrOH, with the system showing the smallest arrangement in 2-PrOH. The positive values of $\Delta H_{\mathrm{A}}^{\mathrm{o}}$ indicate that the ion pair formation processes are endothermic. From eq. (24)

$$\Delta G_{\mathrm{A}}^{\mathrm{o}}(T) = \Delta H_{\mathrm{A}}^{\mathrm{o}}(T) - T\,\Delta S_{\mathrm{A}}^{\mathrm{o}}(T) \qquad (24)$$

it follows that entropic effects seem to dominate over the enthalpic effects: the Gibbs free energy $\Delta G_{\mathrm{A}}^{\mathrm{o}}$ is negative, and thus the ion pair formation is exoergic for [emim][BF_4] and [bmim][BF_4] in the investigated solvents **[H1, H3, H6, H7, H9, H10]**.

Main achievements

1. I determined the molar conductivity values of dilute solutions of 1-ethyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium tetrafluoroborate in various molecular solvents such as water **[H5]**, propan-1-ol **[H3]**, propan-2-ol **[H10]**, butan-1-ol **[H6]**, N,N-dimethylformamide **[H1]**, N,N-dimethylacetamide **[H9]** and dichloromethane **[H7, H8]** over a wide range of temperatures.

2. I calculated the values of limiting molar conductivities and association constants for the ionic liquids in various solvents and temperatures. Based on the calculated K_A values, I concluded that the examined ionic liquids are strongly associated in dichloromethane **[H7, H8]**, butan-1-ol **[H6]**, propan-2-ol **[H10]** and quite strongly in propan-1-ol **[H3]** within the investigated temperature range. Moderate ionic association occurs in N,N-dimethylacetamide **[H9]** and N,N-dimethylformamide **[H1],** in turn water promotes the significant dissociation of the ionic liquids **[H5]**. The ionic association of the ionic liquids in all investigated solvents increases with temperature.

3. I demonstrated and discussed the effect of structure and solvent properties, type of ionic liquid cation and temperature on the limiting molar conductivity of ionic liquids in the investigated solvents **[H1, H3, H5, H6, H7, H9, H10]**.

4. I demonstrated and discussed the effect of solvent properties, ion-solvent interactions, size of the alkyl substituent in the imidazolium cation and temperature on the ionic association of [emim][BF_4] and [bmim][BF_4] **[H1, H3, H6, H7, H9, H10]**.

5. I developed a new method of analysis of conductivity data which can be applied for solutions containing free ions, ion pairs, and triple ions **[H8]**; this method allows the triple ion formation constants (K_T) and the limiting molar conductivities of triple ions $\Lambda_{o,T}$ to be calculated.

6. I described the ion transport processes in the examined systems. In this order I calculated and analyzed the Eyring activation enthalpy of charge transport ($\Delta H_{\lambda}^{\ddagger}$) **[H1, H3, H5, H6, H7, H9, H10]**, the Walden product ($\Lambda_o\eta$) **[H3, H5, H10]** and the values of the limiting ionic conductivity ($\lambda_{\pm}^{o}$) for BPh_4^-, Bu_4N^+, Na^+, Br^-, I^-, BF_4^-, $[emim]^+$ and $[bmim]^+$ in DMF and 1-PrOH at various temperatures **[H2, H4]**.

7. I determined the limiting molar conductivities and association constants of $NaBPh_4$, Bu_4NBr and $NaBF_4$ solutions in N,N-dimethylformamide **[H2]** and NaI, $NaBPh_4$, Bu_4NI, and $NaBF_4$ in propan-1-ol **[H4]** in the temperature range 283.15 to 318.15 K.

8. I characterized the thermodynamic properties of the ion pairing process (Gibbs free energy, enthalpy and entropy) for $[emim][BF_4]$ and $[bmim][BF_4]$ in the investigated solvents **[H1, H3, H6, H7, H9, H10]**.

The research I conducted offers a new insight into the conductometric and thermodynamic properties of imidazolium-based IL solutions, and into the mechanism and extent of ion-ion and ion-solvent interactions.

These studies revealed that in dilute solutions, the investigated ionic liquids behave like classical electrolytes with an organic cation.

References

[1] M. Anouti, Room-temperature molten salts: protic ionic liquids and deep eutectic solvents as media for electrochemical application, in: A.A.J Torriero (Ed), Electrochemistry in Ionic Liquids: Volume 1: Fundamentals. Springer International, Cham, Switzerland, 2015, p.225

[2] Y. Marcus, G. Hefter, Ion Pairing, Chem. Rev. 2006, 106, 4585-4621

[3] G. Hefter When spectroscopy fails: The measurement of ion pairing. Pure Appl. Chem. 2006, 78, 1571-1586

[4] R.K. Srour, L.M. McDonald, Solution properties of inorganic contamination in mixed solvents: theory, progress, and limitations. Crit. Rev. Env. Sci. Technol. 2011, 41, 521–621

[5] H. Wang, J. Wang, S. Zhang, Y. Pei, K. Zhuo, Ion association of the ionic liquids $[C_4mim][BF_4]$, $[C_4mim][PF_6]$, and $[C_nmim]Br$ in molecular solvents, ChemPhysChem 2009, 10, 2516-2523.

[6] C.A. Angell, N. Byrne, J.P. Belieres, Parallel developments in aprotic and protic ionic liquids: Physical chemistry and applications. Acc. Chem. Res. 2007, 40, 1228−1236.

[7] H.K. Stassen, R. Ludwig, A. Wulf, J. Dupont, Imidazolium salt ion pairs in solution, Chem. Eur. J. 2015, 21, 8324-8335

[8] M. Bešter-Rogač, J. Hunger, A. Stoppa, R. Buchner, 1-Ethyl-3-methylimidazolium ethylsulfate in water, acetonitrile, and dichloromethane: molar conductivities and association constants, J. Chem. Eng. Data 2011, 56, 1261-1267

[9] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents. Wiley, New York, 1986

[10] http://www.ddbst.com/en/EED/PCP/VSK_C39.php

[11] R.M. Fuoss, Conductance-concentration function for associated symmetrical electrolytes, J. Phys. Chem. 1975, 79, 525-540.

[12] E. Pitts, An Extension of the Theory of the Conductivity and Viscosity of Electrolyte Solutions, Proc. Roy. Soc. London, 1953, 217A, 43-70

[13] R. Fernandez-Prini, J.E. Prue, Z. Phys. Chem. Leipzig, A comparison of conductance equations for unassociated electrolytes, 1965, 227, 373-379

[14] R. Fernandez-Prini, Conductance of electrolyte solutions. A modified expression for its concentration dependence, Trans. Faraday Soc. 1969, 65, 3311-3313

[15] R.M. Fuoss, Paired ions: Dipolar pairs as subset of diffusion pairs, Proc. Natl. Acad. Sci. USA 1978, 75, 16-20

[16] R.M. Fuoss, Conductance-concentration function for the paired ion model, J. Phys. Chem., 1978, 82, 2427-2440

[17] M.G. Barthel, H. Krienke, W. Kunz, Physical chemistry of electrolyte solutions: modern aspects, Springer, New York, 1998

[18] W.H. Lee, R.J. Wheaton, Conductance of symmetrical, unsymmetrical and mixed electrolytes. Part 1.- Relaxation terms, J. Chem. Soc., Faraday Trans. 2, 1978, 74, 743-766

[19] J. Quint, A. Viallard, Electrical conductance of electrolyte mixtures of any type, J. Solution Chem. 1978, 7, 533-548

[20] M. Bešter-Rogač, A. Stoppa, R. Buchner, Ion association of imidazolium ionic liquids in acetonitrile, Phys. Chem. B 2014, 118, 1426-1435

[21] O.N. Kalugin, I.V. Voroshylova, A.V. Riabchunova, E.V. Lukinova, V.V. Chaban, Conductometric study of binary systems based on ionic liquids and acetonitrile in a wide concentration range, Electrochim Acta 2013, 105, 188-199

[22] M. Bešter-Rogač, J. Hunger, A. Stoppa, R. Buchner, Molar conductivities and association of 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium tetrafluoroborate in methanol and DMSO, J. Chem. Eng. Data 2010, 55, 1799-1803

[23] I.V. Voroshylova, S.R. Smaga, E.V. Lukinova, V.V. Chaban, O.N. Kalugin, Conductivity and association of imidazolium and pyridinium based ionic liquids in methanol, J. Mol. Liq. 2015, 203, 7-15

[24] K. Klimaszewski, A. Boruń, A. Bald, R. J. Sengwa J. Chem. Eng. Data 2012, 57, 3164-3170

[25] S. Paez, M. Contreras, Densities and viscosities of binary mixtures of 1-propanol and 2-propanol with acetonitrile, J. Chem. Eng. Data 1989, 34, 455-459

[26] C.M. Kinart, W.J. Kinart, A. Kolasiński, A. Ćwiklinska, T. Dzikowski, Studies on associated solutions. Part II. Physicochemical properties of acetonitrile-propan-2-ol mixtures, Phys. Chem. Liq. 2000, 38, 695-704

[27] G.A. Krestov, V. N. Afanas’ev, L. S. Efremova Fizikokhimicheskie svoistva binarnykh rastvoritelei (Physicochemical properties of binary solvents), Khimiya, Leningrad, 1988

[28] R.M. Fuoss, F. Accascina, Electrolytic conductance, Interscience Publishers, Inc., New York, 1959

[29] D.F. Evans, S.M.A. Matesich, Ionic association in hydrogen-bonding solvents. J. Solution Chem. 1973, 2, 193-216

[30] M.A. Matesich, J.A. Nadas, D.F. Evans, Transport processes in hydrogen-bonding solvents. V. Conductance of tetraalkylammonium salts in 2-propanol, J. Phys. Chem. 1970, 74, 4568-4573

[31] G. Gonfa, M.A. Bustam, Z. Man, M. I. Abdul Mutalib, Unique structure and solute–solvent interaction in imidazolium based ionic liquids: a review, Asian Trans. Eng. 2011, 1, 24-34

[32] J.M. Crosthwaite, S.N.V.K. Aki, E.J. Maginn, J.F. Brennecke, Liquid phase behavior of imidazolium-based ionic liquids with alcohols: effect of hydrogen bonding and non-polar interactions, Fluid Phase Equilib. 2005, 228–229, 303-309

[33] R.A. Robinson, R.H. Stokes, Electrolyte Solutions, 2nd edn, Dover, Publications INC, Mineola, New York, 2002

[34] D.R. MacFarlane, M. Forsyth, E. I. Izgorodina, A.P. Abbott, G. Annat, K. Fraser, On the concept of ionicity in ionic liquids, Phys. Chem. Chem. Phys. 2009, 11, 4962−4967

[35] M. Hojo, T. Ueda, H. Hamada, Z. Chen and S. Umetani, Condutometric studies on higher ion-aggregation from lithium fluoroalkanoates in propylene carbonate and N,N-dimethylformamide, J. Mol. Liq. 2009, 145, 24-32

[36] R. M. Fuoss and C. A. Kraus Properties of Electrolytic Solutions. IV. The Conductance Minimum and the Formation of Triple Ions Due to the Action of Coulomb Forces, J. Am. Chem. Soc. 1933, 55, 2387-2399

[37] M. Hojo, Y. Miyauchi, A. Tanio and Y. Imai, Specific interactions between anions and cations in protophobic aprotic solvents. Triple-ion and higher aggregate formation from lithium and tributylammonium thiocyanates, J. Chem. Soc., Faraday Trans. 1991, 87, 3847-3852

[38] S.B. Brummer, G.J. Hills, Kinetics of ionic conductance. 1. Energies of activation and the constant volume principle, J. Chem. Soc., Faraday Trans. 1961, 57, 1816-1822

[39] I. Shehata, Thermodynamics of ion-pair association. Part 1. Conductance of sodium tetraphenylborate in 1-alkanols, Thermochim. Acta 1994, 239, 243-251

[40] R.M. Fuoss, E. Hirsch, Single ion conductances in non-aqueous solvents, J. Am. Chem. Soc. 1960, 82, 1013-1017

[41] A.K. Covington, T. Dickinson, Physical chemistry of organic solvent systems, Plenum Press, London, New York, 1973

[42] J.E. Gordon, The organic chemistry of electrolyte solutions, Wiley, New York, 1975

[43] A.J. Parker, The effects of solvation on the properties of anions in dipolar aprotic solvents, Quart. Rev. 1962, 16, 163-187

[44] B.G Cox, G.R. Hedwig, A.J. Parker and D.W. Watts, Solvation of ions. XIX. Thermodynamic properties for transfer of single ions between protic and dipolar aprotic solvents, Austr. J. Chem., 1974, 27, 477-501

[45] M.Ch. Roy, M.N. Roy, Conductometric investigation of ion-solvent interactions of an ionic liquid {[emim]CH3SO3} in pure n-alkanols. J. Mol. Liq. 2014, 195, 87-91

5. *Other research achievements*

It is important to emphasize that it was only when I started working in the Department of Physical Chemistry of Solutions in 2008 that I was able to fully devote my time to scientific research in the field of Physical Chemistry. Before this time, I previously worked in the Department of Chemical Didactics, where I was mainly involved in didactic activity, after completing my Doctoral studies in 2002.

My other scientific achievements have been published in 14 articles from peer-reviewed journals listed in Journal Citation Reports. My research interests are focused on the physicochemical studies of electrolytes in water, organic and aqueous-organic solvents. They concern mainly the conductometric, volumetric, viscosimetric and dielectric properties of electrolyte solutions. I have determined the values of many physicochemical parameters and identified many of the processes taking place in solutions at the molecular level. In the last year, the purchase of new instruments, including an Anton Paar DSA 5000M density and sound velocity meter and a KRÜSS BP50 Bubble pressure tensiometer, have also enabled me to study the sound velocity and surface tension of ionic liquid solutions.

I have demonstrated that the phenomenon of ionic association should be taken into account when analyzing the viscosimetric data of weak electrolytes. I also developed a method of analyzing the viscosimetric data of solutions of weak electrolytes with different types of symmetry, assuming incomplete dissociation. My studies also derived equations describing the viscosity of solutions with regard to two things: the dimerization of the non-dissociated part of the electrolyte, based on the example of carboxylic acids, and the hydrolysis phenomenon, based on the example of carboxylic acid salts [articles 2, 3, 5, 6, appendix 4, point II).

Articles [8, 9, 11] concern the conductometric properties of NaCl, KCl, NaBr, NaI, $NaBPh_4$, Bu_4NI and $NaClO_4$ in water + 2-methoxyethanol, water + 2-ethoxyethanol and water + 2-butoxyethanol mixtures containing from 0.01 to 0.2 mole fraction of alkoxyethanols at 298.15 K. I determined the limiting molar conductivities, association constants and Walden products, as well as the limiting ionic conductivities values and ionic Walden products. I demonstrated that the salts were not associated in the mixed solvent media, across the examined composition range, and the values of Λ_o decrease significantly during the addition of alkoxyethanol to water. I have discussed in detail the process of solvation in the studied systems, and demonstrated that, in the investigated composition range, the slight addition of 2-alkoxyalcohol to water did not cause any significant changes in the hydration shells of ions. I conducted similar studies for KI, LiBr, $LiNO_3$, $AgNO_3$, Et_4NI, $NaBPh_4$, Bu_4NI, NaI, NaCl and NaBr in water + propan-1-ol mixtures at 298.15 K [articles 4, 13]. These allowed me to fully characterize the solvation processes in the tested mixtures. I described the changes in effective size of ions occurring as a result of variations in the composition of water + propan-1-ol mixed solvent and devised a probable explanation of these variations. I showed the dissimilarity between small inorganic cations and large organic cations in terms of their interactions with the solvent. In addition, I conducted similar conductometric and potentiometric investigations for NaI in water + butan-1-ol mixtures [article 1].

I performed dielectric studies of binary mixtures of alcohols over their entire composition range at different temperatures [articles 7, 12]. I analyzed the relationships of the relative permittivity, the relative temperature coefficients, and their excess values as the function of their composition, and demonstrated that these values, associated with intermolecular H-bond interactions, depend on the carbon chain length of the mixture constituents and on the type of alcohol added (primary, secondary, or tertiary).

I also determined the excess molar volumes and excess thermal expansion coefficients of binary alcohol mixtures by investigating their densities [article 10].

I was also involved in cyclic voltammetry studies of the electrochemical behavior of paracetamol on screen-printed graphene electrodes [article 14]. These electrodes displayed exceptional electrocatalytic activity for paracetamol. The proposed method demonstrated for the first time the successful application of screen-printed graphene electrodes for the determination of paracetamol in pharmaceutical products as well as in human oral fluid samples with excellent sensitivity and selectivity.

I actively develop and continue cooperation with foreign scientific centers. Publications [12, 13, 14] and **[H5]** were created in collaboration with scientists from foreign centers (Dr Carlos Fernandez, Robert Gordon University, School of Pharmacy and Life Sciences, Aberdeen, UK; Prof. dr Ram Jeewan Sengwa, JNV University, Jodhpur, Department of Physical and Theoretical Chemistry, India; Prof. dr Jan Benko, Comenius University, Faculty of Natural Science, Bratislava, Slovakia). In 2016 I participated in an international project on the physicochemical properties of ionic liquids within the framework of COST Action CM1206. As part of the ERASMUS program I have also established didactic and scientific cooperation with Prof. dr Renato Tomaš (University of Split, Faculty of Chemistry and Technology, Department of Physical Chemistry, Croatia) on the viscosimetric, volumetric and acoustic investigations of solutions of ionic liquids. I am currently involved in this research.

For my scientific achievements I received team awards from the Rector of the University of Łódź for a cycle of publications on two occasions (2012 and 2016).

Boruń Agnieszka