

## Permittivities of 1-Alkyl-3-methylimidazolium Tetrafluoroborates and Hexafluorophosphates\*

Marek Kosmulski,<sup>a,\*\*</sup> Krystyna Marczewska-Boczkowska,<sup>a</sup> Paweł Żukowski,<sup>a</sup> Jan Subocz,<sup>b</sup> and Czesław Saneluta<sup>a</sup>

<sup>a</sup>*Faculty of Electrical Engineering and Computer Science, Lublin University of Technology, Lublin, Poland*

<sup>b</sup>*Faculty of Electrical Engineering, Szczecin University of Technology, Szczecin, Poland*

RECEIVED JUNE 14, 2006; REVISED FEBRUARY 2, 2007; ACCEPTED FEBRUARY 8, 2007

Permittivities of 1-alkyl-3-methylimidazolium tetrafluoroborates, hexafluorophosphates, and tetrafluoroborate-chloride mixtures (alkyl = butyl, hexyl, octyl or decyl) were determined from the capacitance of a specially designed capacitor, which was measured as the function of frequency over the range from 0.001 Hz to 5 MHz. The measurement setup was tested against molecular liquids. Water and methanol gave relatively stable results, which comply with the permittivities known from the literature over a frequency range from 30 kHz to 3 MHz. The apparent permittivity measured at lower frequencies was highly overestimated. With low-temperature ionic liquids, the plateau in the apparent permittivity as the function of frequency was narrower, and it was observed between 1 and 3 MHz. Yet, the apparent permittivities in the plateau region are still overestimated, at least for 1-butyl-3-methylimidazolium salts.

*Keywords*  
permittivity  
room temperature  
ionic liquids

### INTRODUCTION

Static permittivity makes it possible to quantify and compare the polarity of solvents, and thus to predict their usefulness for various applications. There are also other methods for comparing the polarities of solvents, namely, solvent scales based on solvatochromic shifts,<sup>1,2</sup> *i.e.*, solvent dependent frequency of certain bands in absorption spectra of specially designed molecules called solvatochromic probes. However, solvent polarity calculated from spectroscopic measurements refers to the cybotactic region, that is, it is influenced by the orientation of solvent molecules that solvate the solvatochromic probe, and it is not necessarily representative of the overall volume of the solvent. In mixed solvents, solva-

tochromic shifts are additionally influenced by selective solvation of the solvatochromic probe by a certain component of the mixture. Thus, the permittivity is often preferred as the quantity characterizing the solvent polarity over the solvent scales based on solvatochromic effect, especially in mixed solvents and for solvents composed of unsymmetrical molecules. The difference in polarity between the anion and the cation in the salts of 1-alkyl-3-methylimidazolium (low-temperature ionic liquids) and unsymmetrical structure of the cation are strong arguments for the static permittivity as the preferred parameter to quantify the polarity of ionic liquids. Permittivities of molecular solvents can be easily measured, and they are readily available from the literature.

\* Dedicated to Professor Nikola Kallay on the occasion of his 65<sup>th</sup> birthday.

\*\* Author to whom correspondence should be addressed. (E-mail: mkosmuls@hektor.umcs.lublin.pl)

In contrast, the permittivities of low-temperature ionic liquids are not available. Static permittivity has many applications other than selection of a solvent for certain purposes, *e.g.*, it is necessary to calculate the electrokinetic potential at the solid-liquid interface and the stability of colloids.<sup>3,4</sup> In his recent review Welton<sup>5</sup> wrote: *It is not possible to measure the dielectric constant of an ionic liquid directly.*

Such a statement is very discouraging for those interested in the permittivity of ionic liquids. As we show later, in some sense our results confirm Welton's allegation.

The presence of ions and electric conductance, which make ionic liquids substantially different from most organic solvents, do not limit the possibility of measuring the capacitance of a capacitor, upon which the permittivity calculation is based. For instance, the permittivities of up to 5 molar aqueous solutions of salts (which have molarities of the same order of magnitude as and conductivities higher by an order of magnitude than typical low-temperature ionic liquids) have been measured.<sup>6–8</sup>

The complex permittivity  $\varepsilon^*$  can be expressed as:<sup>9</sup>

$$\varepsilon^*(\nu) = \varepsilon(\infty) + \Delta\varepsilon^*(\nu) + \sigma/i\varepsilon_0\omega \quad (1)$$

where  $\varepsilon(\infty)$  is the high-frequency limit of the real part,  $\Delta\varepsilon^*(\nu)$  is the frequency-dependent part of complex permittivity,  $\sigma$  is static conductivity, and  $\varepsilon_0$  is the electric field constant. At very low frequencies, the last term on r.h.s. of Eq. (1) dominates, but at sufficiently high frequencies, the last term on r.h.s. of Eq. (1) disappears, and the effect of conductivity on the complex permittivity becomes negligible.

Thus, despite the above mentioned discouraging statement, we attempt to directly determine the permittivity of ionic liquids. Some research groups determined the permittivity of ionic liquids indirectly. Angelini *et al.*<sup>10</sup> derived an empirical equation connecting the tautomeric equilibrium constant of 2-nitrocyclohexanone and the permittivity of a solvent in a series of molecular solvents, and used their equation to calculate the relative permittivities of 1-butyl-3-methylimidazolium hexafluorophosphate, as well as of four 1-alkyl-3-methylimidazolium triflates, and the results were 10 and 16–30, respectively. Baker *et al.*<sup>11,12</sup> report values of the relative permittivity of about 10 in a few low-temperature ionic liquids, based on a correlation between certain band ratios and Stokes shifts, on the one hand, and the relative permittivity, on the other. Miscibility of low-temperature ionic liquids with organic solvents<sup>13</sup> suggests even lower relative permittivities (below 10).

Weingartner *et al.* report a permittivity of 26.2 (ethylammonium nitrate),<sup>9</sup> 11.4–12.2 (in a series of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides, alkyl = C<sub>2</sub>–C<sub>5</sub>),<sup>14</sup> and 8.9–15.2 (in a series of 1-alkyl-3-methylimidazolium tetrafluoroborates, hexafluorophos-

phates, and trifluoromethylsulfonates, alkyl = C<sub>2</sub>–C<sub>6</sub>),<sup>15</sup> obtained by means of microwave dielectric spectroscopy.

The dielectric properties of materials are represented by a complex number  $\varepsilon^*$ , whose real part  $\varepsilon'$  represents the relative permittivity, and the imaginary part  $\varepsilon''$  represents the dielectric loss (both numbers are dimensionless). The  $\varepsilon'$  is defined as:

$$\varepsilon' = C/C_0 \quad (2)$$

where  $C$  and  $C_0$  are capacitances of a capacitor filled with certain dielectric (here – ionic liquid) and the same capacitor filled with vacuum, respectively. In principle,  $\varepsilon'$  and  $\varepsilon''$  are frequency dependent, but for water and for many common molecular solvents,  $\varepsilon'$  is practically independent of frequency at frequencies < 1 GHz. This low frequency limit of  $\varepsilon'$  is the relative static permittivity in non-conductive liquids. At very low frequencies, the conductivity-dependent term in Eq. (1) prevails. Then, the choice of frequency is a compromise: high frequency is required to depress the last term on r.h.s. of Eq. (1), and low frequency is required for constant  $\varepsilon'$ . We expect that a frequency that fulfills both conditions can be found in the MHz range, at least for certain liquids.

## EXPERIMENTAL

The synthesis of ionic liquids and their properties are described elsewhere.<sup>4</sup> The 1-alkyl-3-methylimidazolium chlorides (alkyl = butyl, hexyl, octyl or decyl, abbreviated BMI, HMI, MOI, and DMI, respectively) were obtained from 1-methylimidazole (Fluka) and n-alkyl chlorides (Sigma-Aldrich). The metathesis reaction between 1-alkyl-3-methylimidazolium chlorides and ammonium tetrafluoroborate or hexafluorophosphate was carried out in acetonitrile. We also studied a few tetrafluoroborate-chloride mixtures.

The home-made flat capacitor had passivated titanium electrodes of a surface area of 38.5 cm<sup>2</sup> each. The other elements in contact with the ionic liquids were made of Teflon, and the distance between the electrodes was adjustable (a few mm). The capacitor was designed to avoid air bubbles between the electrodes. In the frequency range 10<sup>2</sup>–5 × 10<sup>6</sup> Hz, the Helwett Packard 4284A impedance bridge was used. In the frequency range 0.001–1 Hz, we used a home-made experimental setup,<sup>16</sup> specially designed for low frequencies. The experimental setup was tested against air and molecular liquids, whose permittivities were known. The experiments were carried out at room temperature (no thermostating). The ionic liquids were dried and kept in a desiccator before the measurement, but the capacitor was filled and the measurements were carried out without special protection against atmospheric humidity.

## RESULTS AND DISCUSSION

The apparent relative permittivities of molecular liquids are shown in Figure 1. At a sufficiently high frequency, water (frequency > 3 kHz) and methanol (frequency >

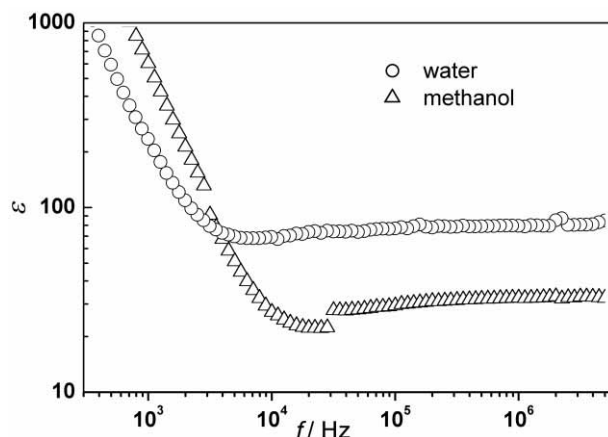


Figure 1. The apparent relative permittivity of water and methanol.

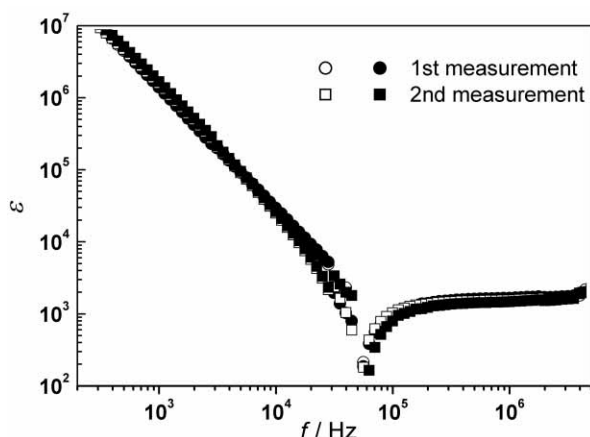


Figure 2. The apparent relative permittivity of BMIBF<sub>4</sub>. Squares and circles represent two lots of BMIBF<sub>4</sub>. Black and white represent different distances between the electrodes.

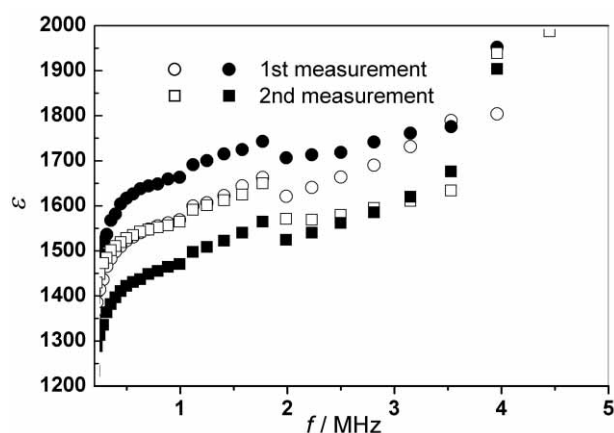


Figure 3. The same plot as Figure 2, linear scale.

30 kHz) gave relatively stable results, which comply with the permittivities known from the literature, but the apparent permittivity was severely overestimated at lower frequencies. Apparently, in water and methanol, even

without addition of salt, the conductivity dependent term in Eq. (1) prevails when the frequency is sufficiently low. The experimental setup applied in the present study produces reliable values of static permittivity of water and methanol over a frequency range from 30 kHz to 3 MHz, and we hypothesize that also for ionic liquids such plateaus exist, and that these plateaus represent static permittivity, although they may occur at higher frequencies since the conductivity of ionic liquids is higher than that of water or methanol (Eq. (1)). For low-temperature ionic liquids studied in the present paper, the apparent relative permittivity assumed very high values (even  $> 10^6$ ) at frequencies below 1 kHz (Figure 2), and the behavior was more complicated than for molecular liquids. Figure 2 presents the apparent permittivity of BMIBF<sub>4</sub> over the frequency range  $10^2 - 5 \times 10^6$  Hz on the log-log scale. Different shapes of symbols represent two series of measurements (two lots of BMIBF<sub>4</sub>) and different colors represent two different distances between the electrodes. The outstanding results at  $f > 3$  MHz are due to the frequency limit of the bridge rather than to the properties of the ionic liquid, and similar behavior was observed for water (Figure 1). On the log-log scale, the permittivity at  $f = 1-3$  MHz seems to be relatively stable. A closer look at the same results (Figure 3, linear scale) indicates that even over a relatively narrow frequency range, from  $10^6$  to  $3 \times 10^6$  Hz, the apparent permittivity of BMIBF<sub>4</sub> is not as stable as demonstrated in Figure 1 for molecular liquids, yet it is stable within about 10 %, and the scatter between different experiments and different electrode distances within the same experiment is in the range of 20 %. Thus, the present method gives only a rough estimate of the apparent permittivity. The results for water and methanol obtained by means of the same experimental setup are more reproducible. Air bubbles and determination of the distance between the electrodes are probably the main error sources. The former is more significant for ionic liquids, which have high viscosity. Figure 4 presents apparent permittivities for a series of 1-alkyl-3-methylimidazolium tetrafluoroborates. Unlike BMIBF<sub>4</sub> (Figure 3), which shows irregular variation of the apparent permittivity as the function of frequency, the other 1-alkyl-3-methylimidazolium tetrafluoroborates show a systematic increase in the apparent permittivity as the frequency increases, and the slope increases as the chain length in the substituent in the imidazolium ring increases. Nevertheless, the results shown in Figure 4 are stable enough to estimate permittivity. The apparent relative permittivity of 1600 (BMIBF<sub>4</sub>, Figures 2 and 3) is higher by an order of magnitude than the highest permittivities observed for molecular solvents. Relative permittivities of the other 1-alkyl-3-methylimidazolium tetrafluoroborates (Figure 4), 170–190 (hexyl), 30–40 (octyl), and 7–12 (decyl), fall in the range encountered with molecular liquids and are comparable with N-methylformamide (189), methanol (33), and 1-octanol (10.3), respectively.<sup>17</sup>

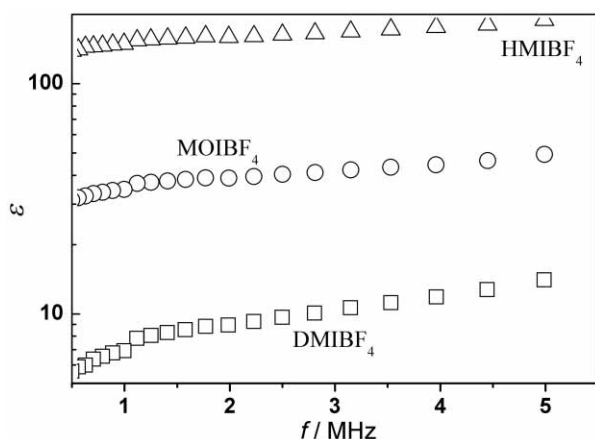


Figure 4. The apparent relative permittivity of  $\text{HMIBF}_4$ ,  $\text{MOIBF}_4$ , and  $\text{DMIBF}_4$ .

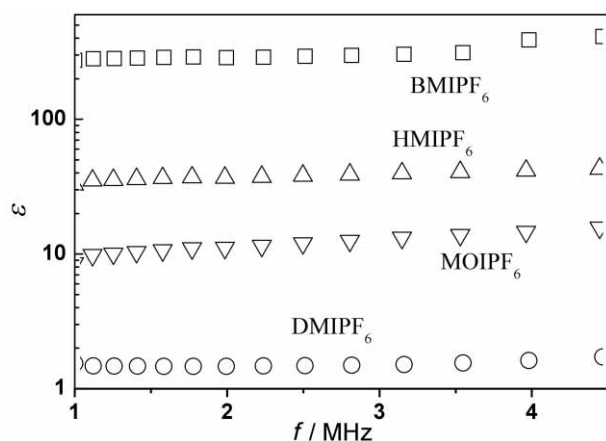


Figure 5. The apparent relative permittivity of  $\text{BMIPF}_6$ ,  $\text{HMIPF}_6$ ,  $\text{MOIPF}_6$ , and  $\text{DMIPF}_6$ .

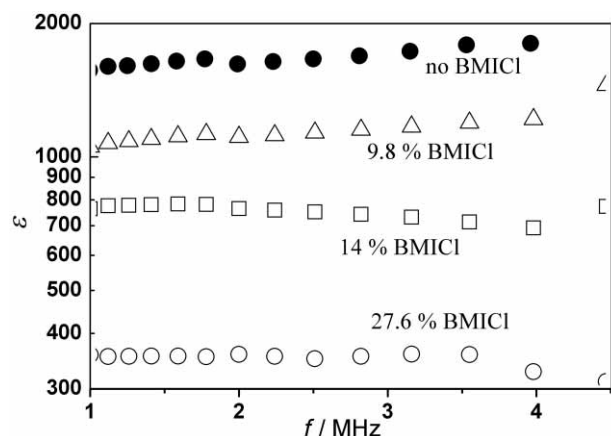


Figure 6. The apparent relative permittivity of  $\text{BMIBF}_4$ - $\text{BMICI}$  mixtures.

In the series of 1-alkyl-3-methylimidazolium hexafluorophosphates (Figure 5), the permittivity decreases when the chain length of the substituent in the «1» position increases from 250 (butyl) to 35–40 (hexyl), 10–15 (octyl),

and 1.5 (decyl, overcooled liquid). Finally, in the series of mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate and chloride (Figure 6), the permittivity decreases when the mass fraction of 1-butyl-3-methylimidazolium chloride increases from 1600 (no chloride) to 1100 (9.75 %  $\text{BMICI}$ ), 700 (14 %  $\text{BMICI}$ ), and 330 (27.6 %  $\text{BMICI}$ ).

Trends in the apparent permittivity in the series of 1-alkyl-3-methylimidazolium tetrafluoroborates and hexafluorophosphates as the function of the chain length of the substituent in the «1» position are qualitatively correct, that is, the permittivity decreases when the chain length increases. Qualitatively similar trends were found in other series of homologs (alcohols, organic acids),<sup>17</sup> but the effects of the chain length were less significant than those presented in Figures 3–5. Also, the numerical values of the apparent permittivities presented in Figures 3–6, at least for the 1-butyl-3-methylimidazolium salts, are too high to be realistic. The apparent permittivities are correlated with the third power of reciprocal viscosities of ionic liquids. The viscosity  $\eta$ , apparent permittivity  $\epsilon$ , and the product  $\eta^3\epsilon$  (which assumes similar values for all ionic liquids studied) are summarized in Table I. Since the molarity of all systems of interest is similar, the reciprocal viscosity is roughly proportional to the conductivity (Walden product). Literature data on the conductivity of ionic liquids is limited, while the viscosities are easily available,<sup>18</sup> and this is why we used viscosity rather than conductivity in the present correlation. The viscosity of tetrafluoroborate-chloride mixtures was estimated from the results presented in Ref. 19. The number of experimental data points in Ref. 19 is limited, and we could only roughly estimate the viscosity. Probably, the apparent permittivities of short-chain 1-alkyl-3-methylimidazolium salts obtained in the present study represent a sum of actual permittivity and a term proportional to the third power of conductivity. Interestingly, this term is rather insensitive to the frequency in the MHz range. On the other hand, the results obtained for long-chain components may very well represent actual permittivities. These values (except for  $\text{C}_{10}\text{MIPF}_6$ ) are high compared to the above discussed results from the literature.

The high electrophoretic mobility of colloidal particles observed in the low-temperature ionic liquids<sup>4</sup> is an argument in favor of high permittivities. The  $\zeta$ -potentials of anatase calculated from experimental data by means of the Smoluchowski equation with various values of permittivity are summarized in Table II. The  $\zeta$ -potentials calculated with  $\epsilon = 10$  (typical value reported in the literature) are unrealistically high compared to the  $\zeta$ -potentials of anatase and other mineral oxides in aqueous solutions of comparable molarity.<sup>20</sup> The absolute value of the  $\zeta$ -potential in aqueous medium decreases when the ionic strength increases,<sup>3</sup> so high values are expected at low ionic strengths, and low values are expected at high ionic strengths. This is because the thickness of the diffuse layer of the countercharge around the particles is



TABLE I. Correlation between apparent permittivity and viscosity. Viscosities at 20 °C were taken from Ref. 18 except for C<sub>10</sub>MIPF<sub>6</sub> (estimated from data in Ref. 18) and chloride-tetrafluoroborate mixtures (estimated from data in Ref. 19). *n* is the chain length of the longer substituent in the imidazolium ring

Substance	<i>n</i>	$\eta/\text{Pa s}$	apparent $\epsilon$	$\eta^3\epsilon$
C <sub><i>n</i></sub> MIBF <sub>4</sub>	4	0.154	1600	5.8
	6	0.314	180	5.6
	8	0.439	35	3
	10	0.928	10	8
C <sub><i>n</i></sub> MIPF <sub>6</sub>	4	0.371	250	12.8
	6	0.69	38	12.5
	8	0.866	12	7.8
	10	1.55	1.5	5.6
90.2 % BMIBF <sub>4</sub> + 9.8 % BMICl		0.2	1100	8.8
86.0 % BMIBF <sub>4</sub> + 14.0 % BMICl		0.26	700	12.3
72.4 % BMIBF <sub>4</sub> + 27.6 % BMICl		0.6	330	71.3

TABLE II. The  $\zeta$ -potential of anatase in low-temperature ionic liquids calculated with different relative permittivity values

	BMIPF <sub>6</sub>	HMIPF <sub>6</sub>	BMICF <sub>3</sub> SO <sub>3</sub>	Ref.
Mobility / 10 <sup>-10</sup> m <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup>	-0.65	-0.55	-0.98	4
Viscosity / mPa s	124	440	85	4,18,4
$\zeta$ / mV (calculated for $\epsilon = 10$ )	-81	-242	-83	this work
$\zeta$ / mV (calculated for $\epsilon = 100$ )	-8.1	-24.2	-8.3	this work

proportional to the reciprocal root of ionic strength. In aqueous medium, the  $\zeta$ -potentials of about 80 mV (*cf.* Table II) are observed at ionic strengths of about 0.001 mol dm<sup>-3</sup>, that is, lower by 3 orders of magnitude than the ionic strength in ionic liquids, and  $\zeta$ -potentials in excess of 200 mV are not observed at all. Thus, the values of  $\zeta$ -potentials calculated with  $\epsilon = 10$  are at least surprising. On the other hand, the  $\zeta$ -potentials calculated with  $\epsilon = 100$  (the order of magnitude of apparent permittivities found in the present study) are similar to the  $\zeta$ -potentials of anatase and other mineral oxides in aqueous solutions at comparable concentrations of inorganic 1–1 electrolytes,<sup>20</sup> that is, 10–20 mV.

## CONCLUSIONS

Apparent permittivity of low-temperature ionic liquids obtained from direct measurements of capacity is substantially higher than that determined from the correlations between the permittivity and the solvatochromic shifts. A plateau in the apparent permittivity as the function of frequency is observed over a frequency range about 1 MHz. Although we were not particularly succes-

ful in determining reliable values of permittivity, our work shows specific limitations and directions for future work. The electrometric method is more suitable for ionic liquids, which have viscosities in the range of 1 Pa s rather than for less viscous ionic liquids (the lowest viscosities are on the order of 0.01 Pa s), and a plateau in the apparent permittivity *vs.* frequency plots is expected in the range 1 MHz–1 GHz.

## REFERENCES

1. C. Reinhardt, *Chem. Rev.* **94** (1994) 2319–2358.
2. Y. Marcus, *Chem. Soc. Rev.* **22** (1993) 409–416.
3. M. Kosmulski, *Chemical Properties of Material Surfaces*, Dekker, New York, 2001.
4. M. Kosmulski, J. Gustafsson, and J. B. Rosenholm, *J. Colloid Interface Sci.* **275** (2004) 317–321.
5. T. Welton, *Coord. Chem. Rev.* **248** (2004) 2459–2477.
6. R. Buchner, G. T. Hefter, and P. M. May, *J. Phys. Chem. A* **103** (1999) 1–9.
7. Y. Chen, G. T. Hefter, and R. Buchner, *J. Phys. Chem. A* **107** (2003) 4025–4031.

8. A. S. Lileev, Z. A. Filimonova, and A. K. Lyashchenko, *J. Mol. Liq.* **103–104** (2003) 299–308.
9. H. Weingartner, A. Knocks, W. Schrader, and U. Kaatze, *J. Phys. Chem. A* **105** (2001) 8646–8650.
10. G. Angelini, C. Chiappe, P. De Maria, A. Fontana, F. Gasparrini, D. Pieraccini, M. Pierini, and G. Siani, *J. Org. Chem.* **70** (2005) 8193–8196.
11. S. N. Baker, G. A. Baker, M. A. Kane, and F. V. Bright, *J. Phys. Chem. B* **106** (2001) 9663–9668.
12. K. A. Fletcher, S. N. Baker, G. A. Baker, and S. Pandey, *New J. Chem.* **27** (2003) 1706–1712.
13. P. Bonhote, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram, and M. Gratzel, *Inorg. Chem.* **35** (1996) 1168–1178.
14. C. Daguinet, P. J. Dyson, I. Krossing, A. Oleinikova, J. Slattery, C. Wakai, and H. Weingartner, *J. Phys. Chem. B* **110** (2006) 12682–12688.
15. C. Wakai, A. Oleinikova, M. Ott, and H. Weingartner, *J. Phys. Chem. B* **109** (2005) 17028–17030.
16. J. Subocz, *Wybrane zagadnienia przewodnictwa i relaksacji dielektrycznej w aspekcie diagnostyki izolacji kompozytowej*, Prace Naukowe Politechniki Szczecińskiej, Instytut Elektrotechniki, Szczecin, 2003.
17. *CRC Handbook of Chemistry and Physics, 79th edition*, Boca Raton 1998–1999.
18. K. R. Seddon, A. Stark, and M. J. Torres, *ACS Sym. Ser.* **819** (2002) 34–49.
19. K. R. Seddon, A. Stark, and M. J. Torres, *Pure Appl. Chem.* **72** (2000) 2275–2287.
20. M. Kosmulski and J. B. Rosenholm, *Adv. Colloid Interface Sci.* **112** (2004) 93–107.

---

## SAŽETAK

### Permitivnosti 1-alkil-3-metilimidazolijevih tetrafluoroborata i heksafluorofosfata

M. Kosmulski, K. Marczevska-Boczkowska, P. Żukowski, J. Subocz i C. Saneluta

Iz kapaciteta posebno dizajniranih kondenzatora, mjerenih kao funkcija frekvencije u području od 0,001 Hz do 5 MHz, određivane su permitivnosti 1-alkil-3-metilimidazolijevih tetrafluoroborata i heksafluorofosfata, kao i smjese 1-alkil-3-metilimidazolijevih tetrafluoroborata i klorida (alkil = butil, heksil, oktil ili decil). Mjerni sustav testiran je pomoću molekulskih tekućina. Razmjerno stabilni rezultati dobiveni su u pokusima s vodom i metanolom, što se slaže s podacima iz literature za područje frekvencija od 30 kHz do 3 MHz. Permitivnost mjerena pri nižim frekvencijama bila je izrazito veća od realne. U slučaju niskotemperaturnih ionskih tekućina, plato pri prikazu ovisnosti permitivnosti o frekvenciji je uža i nalazi se u području od 1 do 3 MHz. Permitivnosti u području platoa su i u tom slučaju veće od realnih što se posebno odnosi na 1-butil-3-metilimidazolijeve soli.