

Mobility of spin probes in ionic liquids

Veronika Strehmel,^{1*} André Laschewsky,² Reinhard Stoesser,³ Andrea Zehl³ and Werner Herrmann⁴

¹Institute of Chemistry, Applied Polymer Chemistry, University of Potsdam, Karl-Liebknecht-Str. 24-25, D-14476 Potsdam-Golm, Germany

²Fraunhofer Institute for Applied Polymer Research, Geiselbergstr. 69, D-14476 Potsdam-Golm, Germany

³Institute of Chemistry, Humboldt University of Berlin, Brook-Taylor-Str. 2, D-12489 Berlin, Germany

⁴Institute of Pharmaceutics, Free University of Berlin, Kelchstr. 31, D-12169 Berlin, Germany

Received 20 January 2006; revised 3 March 2006; accepted 9 March 2006

ABSTRACT: The spin probes TEMPO, TEMPOL, and CAT-1 were used to investigate microviscosity and micropolarity of imidazolium based ionic liquids bearing either tetrafluoroborate or hexafluorophosphate as anions and a variation of the substitution at the imidazolium ion. The average rotational correlation times (τ) obtained by complete simulation of the X-band ESR spectra of TEMPO, TEMPOL, and CAT-1 increase with increasing viscosity of the ionic liquid although no Stokes Einstein behavior is observed. This is caused by microviscosity effects of the ionic liquids shown by application of the Gierer–Wirtz theory. Interestingly, the jump of the probe molecule into the free volume of the ionic liquids is a nonactivated process. The hyperfine coupling constants ($A_{\text{iso}}(^{14}\text{N})$) of TEMPO and TEMPOL dissolved in the ionic liquids do not depend on the structure of the ionic liquids. The $A_{\text{iso}}(^{14}\text{N})$ values show a micropolarity of the ionic liquids that is comparable with methylenechloride in case of TEMPO and with dimethylsulfoxide in case of TEMPOL. Micropolarity monitored by CAT-1 strongly depends on structural variation of the ionic liquid. CAT-1 dissolved in imidazolium salts substituted with shorter alkyl chains at the nitrogen atom exhibits a micropolarity comparable with dimethylsulfoxide. A significant lower micropolarity is found for imidazolium salts bearing a longer alkyl substituent at the nitrogen atom or a methyl substituent at C-2. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: ionic liquids; mobility; polarity; spin probes; TEMPO; TEMPOL; CAT-1; ESR spectroscopy

INTRODUCTION

Ionic liquids based on organic cations and inorganic or organic anions are interesting materials for electrochemistry,¹ and they have become attractive solvents for reactions in organic, inorganic, and polymer chemistry as well as for separation processes recently.^{1–9} Negligible vapor pressure, high thermal stability, and nonflammability distinguish ionic liquids from common solvents and make these molten salts interesting as substitutes for conventional solvents. Variation of the cation and anion structures results in a wide variety of ionic liquids and their physicochemical properties.^{3,10–15} Macroscopic properties such as melting behavior and viscosity of ionic liquids are considered first when choosing ionic liquids as solvents. However, efficiency of ionic liquids in chemical reactions and extraction processes is strongly affected by the interactions between the ionic liquids and the molecules dissolved. Such interactions are influenced, for example, by polarity. Only a few contributions have been published regarding polarity of ionic liquids^{16–21} and mobility of molecules dissolved in ionic liquids.^{20–25}

Microscopic properties, for example, microviscosity and micropolarity can give a more detailed picture about the interactions between dissolved molecules and ionic liquids on the one hand and they may contribute to an efficient selection of ionic liquids for special applications and for a better understanding of the function of ionic liquids on the other hand. Self-diffusion processes of ionic liquids are described by electrochemical investigation^{26,27} and NMR spectroscopy.^{28–31} Polarity of ionic liquids was investigated by solvatochromic probes,^{16–19,21} spin probes,²⁰ and FTIR probes.³² Lifetime measurements of fluorescence probes^{21–23} and electron spin resonance (ESR) investigation of spin probes^{20,24,25} provide information about probe mobility in ionic liquids and polarity of the ionic liquid. Though, the information obtained depends on the nature and the structure of the probe investigated. Self-fluorescence observed in some ionic liquids results from traces of impurities that are difficult to remove from the ionic liquids. This may limit the use of fluorescence probes in an experimental window where excitation shows only negligible self-fluorescence. Low solubility of many solvatochromic dyes in the ionic liquids is another limiting factor for this method. Only a limited number of ionic liquids was investigated by ESR spectroscopy using the spin probes TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) and ATEMPO (4-amino-

*Correspondence to: V. Strehmel, Institut für Chemie, Angewandte Polymerchemie Math-Naturwissenschaftliche Fakultät, Universität Potsdam, Postfach 601553, D-14415 Potsdam, Germany.
E-mail: vstrehme@rz.uni-potsdam.de

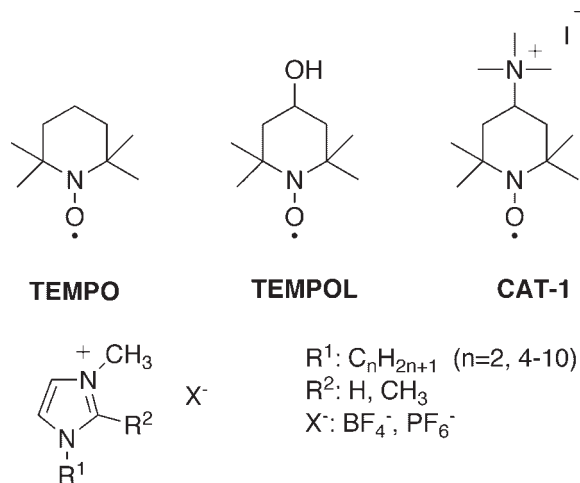


Figure 1. Chemical structures of the spin probes TEMPO, TEMPOL, CAT-1, and the imidazolium based ionic liquid

2,2,6,6-tetraethylpiperidine-1-oxyl).^{20,24,25} In this work, a systematic investigation of two series of imidazolium based ionic liquids (Fig. 1 and Table 1) was carried out using three spin probes of a similar molecular skeleton containing a different polar substituent in the *p*-position to the nitroxyl group (Fig. 1) resulting in a variation of the interactions between the spin probe and the surrounding ionic liquid. Simulation of the ESR spectra using the algorithm of Budil *et al.*³³ considers static as well as dynamic spin coupling parameters. It focuses on mobility of the spin probes in the ionic liquids and polarity of these

Table 1. Chemical structure and phase transition temperatures (glass transition temperature (T_g), recrystallization temperature (T_{recryst}), and melting temperature (T_m)) of imidazolium based ionic liquids investigated using spin probes in this work, data from Refs. [34,35]

Ionic liquid	R^1	R^2	X^-	T_g ($^{\circ}\text{C}$)	T_{recryst} ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)
1a	C_2H_5	H	BF_4^-	-97.5	-67.1	16.4, 12.6
1b	C_4H_9	H	BF_4^-	-87.3	—	—
1c	C_5H_{11}	H	BF_4^-	-87.4	—	—
1d	C_6H_{13}	H	BF_4^-	-85.6	—	—
1e	C_7H_{15}	H	BF_4^-	-86	—	—
1f	C_8H_{17}	H	BF_4^-	-85.9	—	—
1g	C_9H_{19}	H	BF_4^-	-82	-58, -45, -18	-39, -7, 2
1h	$\text{C}_{10}\text{H}_{21}$	H	BF_4^-	—	—	-10, 8
1i	C_4H_9	CH_3	BF_4^-	-73	-18	39
1k	C_6H_{13}	CH_3	BF_4^-	-74	-15	2, 12
2a	C_4H_9	H	PF_6^-	-78	—	-12
2b	C_5H_{11}	H	PF_6^-	-76	—	—
2c	C_6H_{13}	H	PF_6^-	-74	—	—
2d	C_7H_{15}	H	PF_6^-	-72	—	—
2e	C_8H_{17}	H	PF_6^-	-72	-9	2
2f	C_9H_{19}	H	PF_6^-	-71	-32	3, 15
2g	$\text{C}_{10}\text{H}_{21}$	H	PF_6^-	—	—	7, 19
2h	C_4H_9	CH_3	PF_6^-	-60	1	16

solvents as a measure for interactions between the probe molecules and the ionic liquids.

EXPERIMENTAL

1-Ethyl-3-methylimidazolium tetrafluoroborate (**1a**) was purchased from Fluka. 1-Alkyl-3-methylimidazolium tetrafluoroborates (**1b–1h**) and 1-alkyl-3-methylimidazolium hexafluorophosphates (**2a–2g**) were synthesized from 1-methylimidazole and the respective alkylbromide followed by anion metathesis using hexafluorophosphoric acid or tetrafluoroboric acid.^{34–36} 1-Alkyl-2,3-dimethylimidazolium tetrafluoroborates (**1i–1k**) and 1-butyl-2,3-dimethylimidazolium hexafluorophosphate (**2h**) were synthesized from 1,2-dimethylimidazole and the respective alkylchloride followed by anion metathesis as described above.^{34,36} Water content and viscosity of the ionic liquids are described elsewhere.^{34,35} 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) and 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL) were purchased from Aldrich, and 4-trimethylammonium-2,2,6,6-tetramethylpiperidine-1-oxyl (CAT-1) was provided from the Institute of Organic Chemistry of the Russian Academy of Sciences of Novosibirsk (Russia).

ESR spectra were measured using a modified ESR 300 X-band spectrometer (ZWG and Magnetech GmbH, Adlershof, Berlin, Germany) working with a microwave power of 2 mW, a modulation frequency of 100 kHz, and a modulation amplitude of about 1/10th of the respective line width at 293 K. The slow-motion ESR spectra were analyzed using least-squares fits of model calculations based on the stochastic Liouville equation that were described by Budil *et al.*³³ The method used includes the isotropic nuclear Zeeman interaction and all three Euler angles. The latter describe the relative orientation of the *a* and *g* tensors within the molecular diffusion frame. The nitrogen isotropic hyperfine coupling constants of the spin probes were additionally determined using a computer program provided by Pfeiffer.³⁷

RESULTS AND DISCUSSION

Ionic liquids are complex solvents possessing a large variety of interactions, such as Coulomb interactions, hydrogen bonding, and van der Waals forces. The ionic liquids investigated in this work are 1-alkyl-3-methylimidazolium or 1-alkyl-2,3-dimethylimidazolium salts containing tetrafluoroborate or hexafluorophosphate as anions (Fig. 1, Table 1), which are liquid at room temperature (**1a–1h**, **1k**, **2a–2f**, **2h**) or possess a low crystallization tendency (**1i**, **2g**) after heating to a temperature higher than their melting temperature followed by cooling to room temperature. Therefore, all ionic liquids investigated in this work are viscous melts under the conditions used for ESR measurements.

Probe molecules dissolved in the ionic liquids can participate in the interactions between the individual ions

of the ionic liquids mentioned above. We chose the spin probes depicted in Fig. 1 as probe molecules for investigation of the imidazolium based ionic liquids because these probes have a similar skeleton and a different substituent in the *p*-position to the NO group resulting in a variation of interactions between these spin probes and the ionic liquids. Therefore, the spin probes can effectively describe their surrounding on a molecular level as expressed by the average rotational correlation time (τ) and the isotropic nitrogen-14 hyperfine coupling constants ($A_{\text{iso}}(^{14}\text{N})$), which were obtained by complete simulation of the ESR spectra. The τ value is obtained from the average rotational diffusion rate constant (\bar{R}) according to Eqn (1). \bar{R} is defined as the geometric mean of the rate constants for rotational diffusion about the *x*-, *y*-, and *z*-axes of the molecular diffusion frame, and it was obtained by the method of Budil *et al.*³³ The spin coupling constants ($A_{\text{iso}}(^{14}\text{N})$) are affected by interactions between the radical and the surrounding solvent including dipolar aprotic interactions, hydrogen bonding, and complex formation.^{38–45} These perturbations cause a redistribution of the π -electron charge and spin density in the probe molecules.

$$\tau = 10^{-\bar{R}} \quad (1)$$

Representative ESR spectra of TEMPO, TEMPOL, and CAT-1 dissolved in selected imidazolium tetrafluoroborates are shown in Fig. 2. The ESR spectra of these spin probes consist of three lines, which are due to the nitrogen-14 isotropic hyperfine splittings. However, the ESR spectra of these radicals differ significantly in their habitus and in their line widths if the three probes are dissolved in the same ionic liquid, as well as if different ionic liquids are used as solvents for the same probe. A quantitative measure for this effect can be seen in the τ values, which are given in the caption of Fig. 2. The τ values are higher for the spin probes dissolved in **1f** in comparison with the same spin probes dissolved in **1a**. Concerning the three probes, the lowest τ values are obtained for TEMPO in these ionic liquids. This is attributed to weaker interactions between TEMPO and the ionic liquids in comparison with the other spin probes bearing an OH group (TEMPOL) or an ammonium group (CAT-1) at the *p*-position to the nitroxyl group. The polar substituents cause additional interactions with the ionic liquids. Specific interactions between the OH group of TEMPOL and the ionic liquids result in higher τ values in comparison with TEMPO. However, the τ values for TEMPOL are lower than the τ values for CAT-1, which shows the highest values in these series. Thus, the specific interactions between TEMPOL and the ionic liquids may not as strongly influence the mobility of the radicals as the additional Coulomb interactions between CAT-1 and the ionic liquids.

The τ values obtained for TEMPO (Fig. 3a) and TEMPOL (Fig. 3b) dissolved in the two series of ionic

liquids investigated in this work increase with increasing viscosity (η) of the ionic liquids and level off at higher viscosities. The τ values of CAT-1 show a similar tendency if the probe is dissolved in the imidazolium tetrafluoroborates (Fig. 3c). The τ values for CAT-1 in imidazolium hexafluorophosphates were not determined because simulation of the spectra for CAT-1 in these ionic liquids was not possible because of the extreme broad high field line. Generally, higher τ values were obtained for TEMPOL in comparison with TEMPO (Fig. 3) caused by additional interactions between the OH group of TEMPOL and the ionic liquids. The highest τ values were obtained for CAT-1 (Fig. 3c). This is attributed to additional ionic interactions between this probe and the individual ions of the ionic liquids.

Moreover, no Stokes Einstein behavior is observed for the three spin probes (Fig. 3). Therefore, the mobility of the spin probes in the ionic liquids is not a simple function of macroscopic viscosity. Application of the Gierer–Wirtz theory gives information about the influence of microviscosity on the entire dynamic processes of a probe molecule in a matrix.^{46–48} The plot of η/τ as a function of η^x according to the theory of Gierer and Wirtz results in a linear function as described by Eqn (2). The exponent *x* is an expression for the function of the activation energy for the viscous flow (E_η) and the activation energy for the jump into the free volume (E_2) as shown in Eqn (3). *A* and *B* are intrinsic constants in Eqn (2).

$$\frac{\eta}{\tau} = A + B \cdot \eta^x \quad (2)$$

$$x = \frac{E_\eta - E_2}{E_\eta} \quad (3)$$

Examples of the plots are given for the radicals dissolved in imidazolium tetrafluoroborates in Fig. 4. The linear plots obtained show that both macroscopic friction and diffusion into the free volume affects the mobility of radicals in the ionic liquids independent on the substitution of the radicals investigated. The exponent *x* is about 1 for TEMPO and TEMPOL in all ionic liquids and for CAT-1 in imidazolium tetrafluoroborates (Table 2). From this one can conclude that the activation energy for the jump into the free volume (E_2) is nearly zero for TEMPO and TEMPOL in all studied ionic liquids, and for CAT-1 in imidazolium tetrafluoroborates. Therefore, the activation of the viscous flow (E_η) dominates in these systems. The influence of microviscosity on mobility of a probe molecule in a nonactivated process seems to be of general importance for ionic liquids. However, such an effect is an exception for molecular solvents.^{48–50} This result may be attributed to the special structure of the molten salts composed of positive and negative ions, which interact with the spin probes.

A further parameter that was obtained by analysis of the ESR spectra is the nitrogen isotropic hyperfine coupling

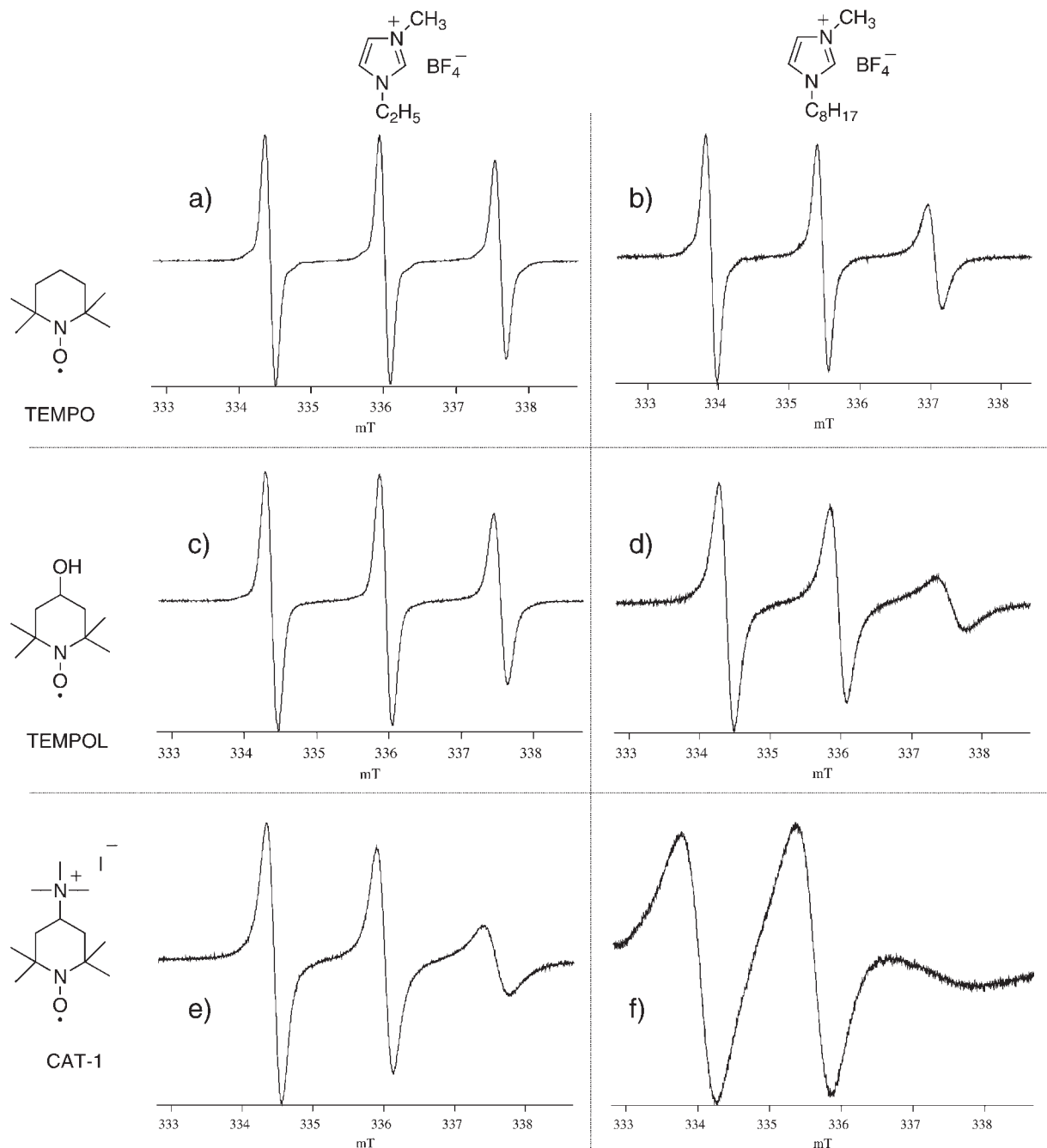


Figure 2. ESR spectra of TEMPO ((a) $\tau = 0.1$ ns, (b) $\tau = 1.8$ ns), TEMPOL ((c) $\tau = 1.1$ ns, (d) $\tau = 5.5$ ns), and CAT-1 ((e) $\tau = 4.0$ ns, (f) $\tau = 18.6$ ns) in **1a** (a, c, e) and **1f** (b, d, f) at 293 K

constant ($A_{\text{iso}}(^{14}\text{N})$), which is sensitive to electrostatic interactions and hydrogen bonding (Fig. 5).^{51–55} The $A_{\text{iso}}(^{14}\text{N})$ value is a measure for perturbations of the spin-density distribution of the radicals in solution caused by electrostatic interactions and hydrogen bonding with the solvent.^{44,56} Polar solvents should generally stabilize structures IIa and IIb resulting in an increase of $A_{\text{iso}}(^{14}\text{N})$. Solvents forming specific hydrogen bonding with the probe favor more stabilization of the structure IIb. Therefore, $A_{\text{iso}}(^{14}\text{N})$ should be higher for solvents

undergoing hydrogen bonding with the probe than for other polar solvents. Nevertheless, the hyperfine coupling constant ($A_{\text{iso}}(^{14}\text{N})$) reports about the polarity of the environment, which is sensed by the probe.

The $A_{\text{iso}}(^{14}\text{N})$ values obtained for TEMPO and TEMPOL in ionic liquids are not dependent on the structure of the ionic liquid in case of both imidazolium tetrafluoroborates (Fig. 6) and imidazolium hexafluorophosphates ($A_{\text{iso}}(^{14}\text{N})$ values are 1.58–1.59 mT for TEMPO in **2a–2g** and 1.57–1.59 mT for TEMPOL in

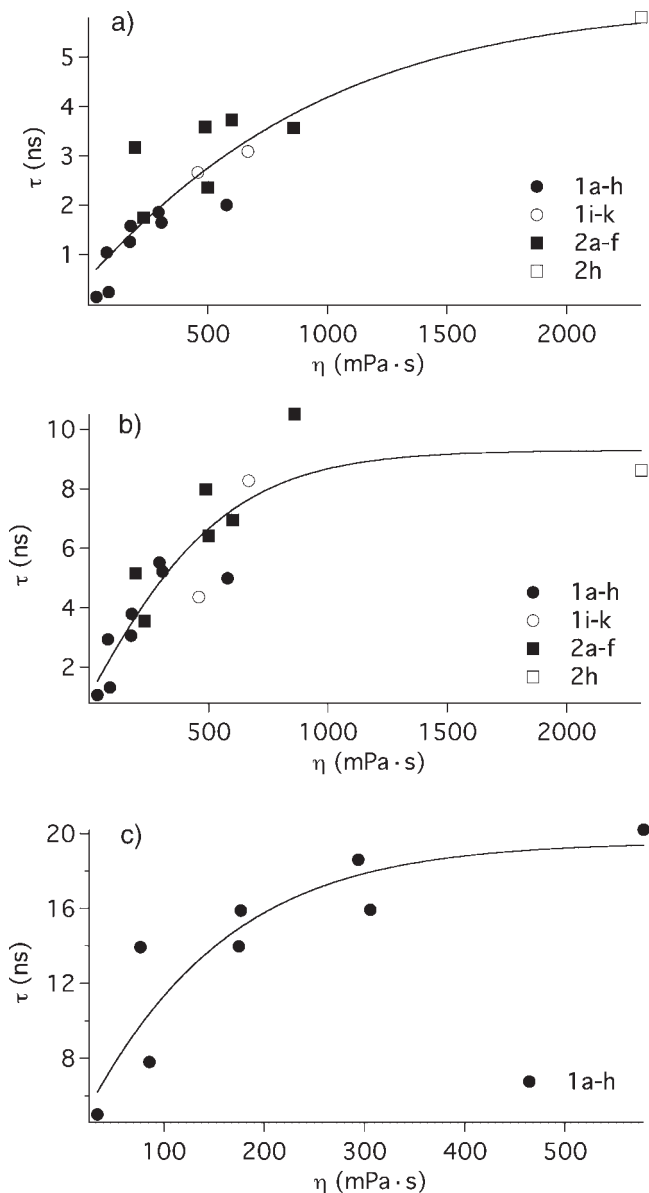


Figure 3. Rotational correlation time (τ) for TEMPO (a), TEMPOL (b), and CAT-1 (c) dissolved in the imidazolium salts **1a–k** and **2a–h** as function of the viscosity of the solvents at 293 K

2a–2g). Furthermore, the $A_{\text{iso}}(^{14}\text{N})$ values for TEMPO ($A_{\text{iso}}(^{14}\text{N})$ is about 1.59 mT for TEMPO in **1i** and 1.58 mT in **1k**, and about 1.57 mT in **2h**) and TEMPOL ($A_{\text{iso}}(^{14}\text{N})$ is about 1.56 mT for TEMPOL in **1i** and **1k**, and about 1.52 mT in **2h**) measured in imidazolium salts methyl substituted at C-2 of the imidazolium ring are similar to or slightly lower than those obtained in imidazolium salts unsubstituted at this position (Fig. 6). Therefore, the $A_{\text{iso}}(^{14}\text{N})$ values of TEMPO and TEMPOL cannot distinguish between micropolarity of imidazolium salts methyl substituted or unsubstituted at C-2. The latter shows only a low C–H acidity.^{36,57} Furthermore, these probes are also not sensitive enough to detect the influence of the alkyl chain length at the nitrogen atom on micropolarity

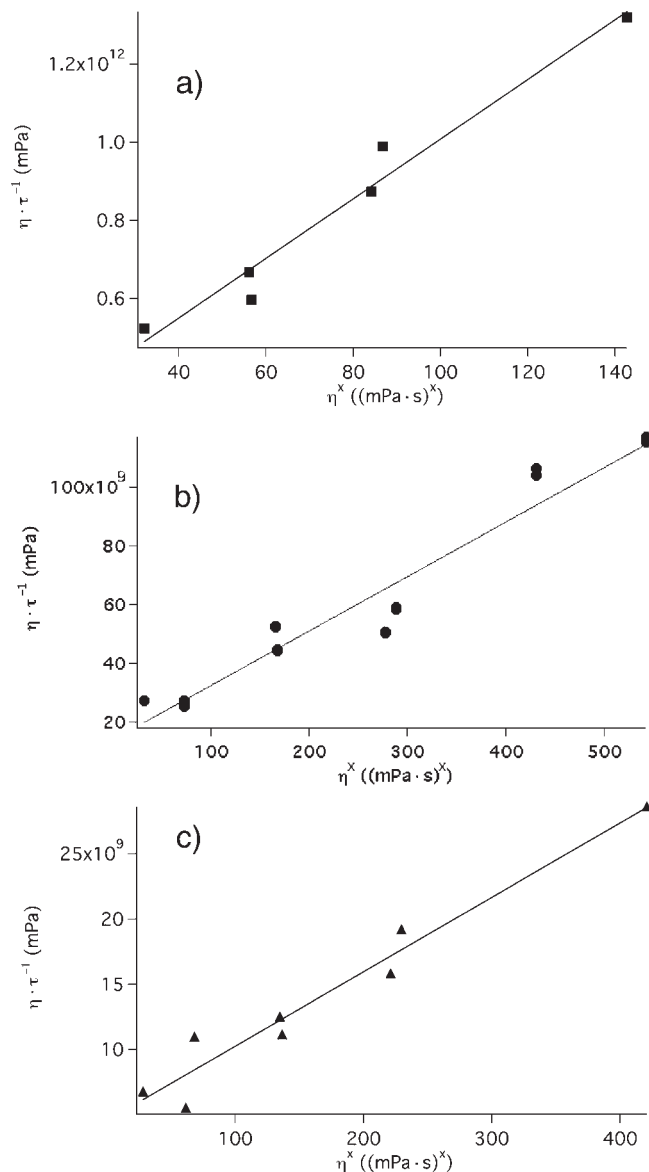


Figure 4. Plot of η/τ as function of η^x (Eqn (2)) for TEMPO (a), TEMPOL (b), and CAT-1 (c) dissolved in **1a–h** at 293 K

of the ionic liquids. Moreover, the $A_{\text{iso}}(^{14}\text{N})$ values obtained for TEMPO are comparable with the value found in methylenechloride ($A_{\text{iso}}(^{14}\text{N})$: 1.58 mT), and TEMPOL shows an $A_{\text{iso}}(^{14}\text{N})$ value similar to that obtained in dimethylsulfoxide ($A_{\text{iso}}(^{14}\text{N})$: 1.59 mT). This suggests a

Table 2. Exponent x from Eqn (2) obtained for TEMPO and TEMPOL in imidazolium tetrafluoroborates and hexafluorophosphates, and for CAT-1 in imidazolium tetrafluoroborates

Ionic liquids	x		
	TEMPO	TEMPOL	CAT-1
1a–1h	0.88	0.99	0.97
2a–2f	1.0	0.99	—

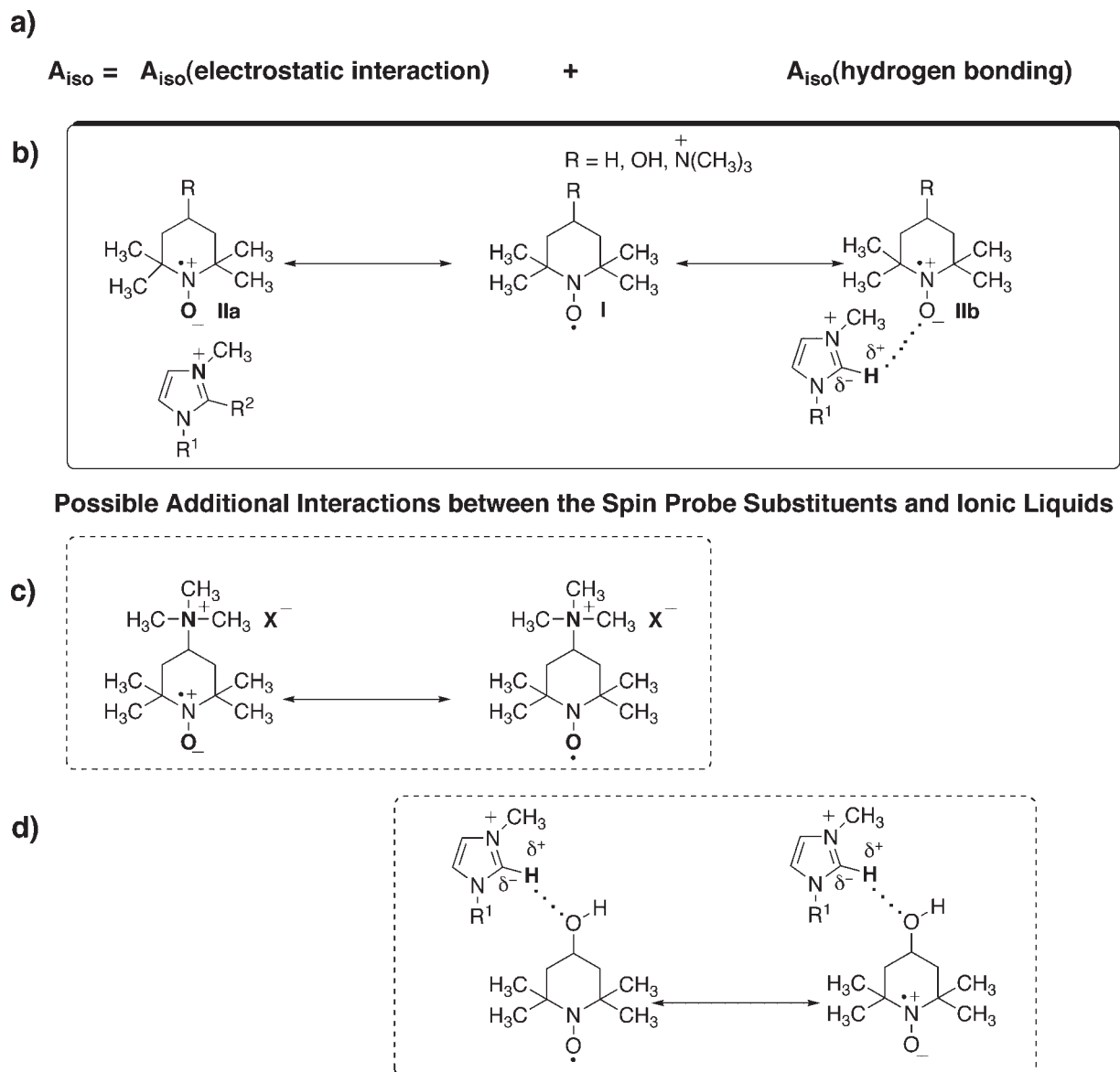


Figure 5. Schematic presentation of electrostatic interactions and hydrogen bonding between the spin probes (TEMPO, TEMPOL, CAT-1) and an ionic liquid that may influence the nitrogen isotropic hyperfine coupling constants ($A_{\text{iso}}(^{14}\text{N})$) of the spin probes. a: Simplified scheme summarizing different contributions to the nitrogen isotropic hyperfine structure. b: Radical (I) and ionic (II) structures of the spin probes; IIa: ionic interactions between the imidazolium ion and the NO-group; IIb: hydrogen bonding between the hydrogen at C-2 of the imidazolium ion and the NO-group. c: Electrostatic interactions between the ammonium substituent at CAT-1 and the anion of the ionic liquid. d: Hydrogen bonding between the hydrogen at C-2 of the imidazolium ion and the OH group of TEMPOL.

micropolarity of ionic liquids similar to methylenechloride for nonpolar solutes, and similar to dimethylsulfoxide for solutes that can form hydrogen bonding to the ionic liquids. This result is supported by other results published in literature that show a probe dependent micropolarity of the ionic liquids.⁵⁸ However, this discussion bases on a simplification of the microstructure of ionic liquids.

Interestingly, $A_{\text{iso}}(^{14}\text{N})$ values for CAT-1 are lower than for TEMPO and TEMPOL, and they depend on the structure of the imidazolium salt (Fig. 6). The positive charge of the substituent at CAT-1 may cause the lower nitrogen isotropic hyperfine coupling constant in com-

parison with TEMPO. The decrease of the $A_{\text{iso}}(^{14}\text{N})$ values for CAT-1 with increasing alkyl chain length at the nitrogen atom of imidazolium tetrafluoroborates indicates a decrease in micropolarity with increasing alkyl chain length bound at the nitrogen atom of the imidazolium ring (Fig. 6). The $A_{\text{iso}}(^{14}\text{N})$ values for CAT-1 in **1a–1e** are comparable with the value determined in dimethylsulfoxide ($A_{\text{iso}}(^{14}\text{N})$): 1.58 mT) indicating a similar micropolarity as this molecular solvent. The $A_{\text{iso}}(^{14}\text{N})$ values for **1f–h** indicate a significantly lower polarity caused by the longer alkyl chain. Although CAT-1 is insoluble in nonpolar solvents such as toluene it can be dissolved in

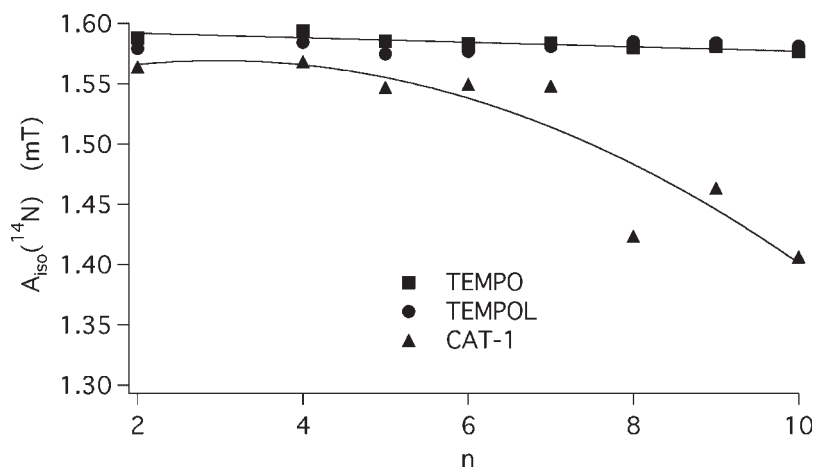


Figure 6. Nitrogen isotropic hyperfine coupling constants ($A_{\text{iso}}(^{14}\text{N})$) for imidazolium tetrafluoroborates (**1a–1h**) as function of the alkyl chain length at the nitrogen atom of the imidazolium salt

ionic liquids bearing longer alkyl chains and indicates a low micropolarity of these solvents.

Moreover, the $A_{\text{iso}}(^{14}\text{N})$ values for CAT-1 in **1i** ($A_{\text{iso}}(^{14}\text{N})$: 1.36 mT) and **1k** ($A_{\text{iso}}(^{14}\text{N})$: 1.37 mT), which bear a methyl substituent at C-2, are lower in comparison with the imidazolium salts unsubstituted at C-2 (**1b** and **1d**) containing the same substituents at the nitrogen atoms (Fig. 6). This indicates a lower micropolarity of **1i** and **1k** relative to **1b** and **1d** that is attributed to the methyl substituent at C-2 in **1i** and **1k**. The higher $A_{\text{iso}}(^{14}\text{N})$ values for CAT-1 in **1b** and **1d** may be caused by the C–H acidity of the imidazolium ion⁵⁴ resulting in additional hydrogen bonding, and therefore, in an increase in micropolarity of the imidazolium salts unsubstituted at C-2. The ionic structure of CAT-1 makes this probe more sensitive than TEMPO and TEMPOL to detect differences in micropolarity between the imidazolium salts.

CONCLUSION

Investigation of the spin probes TEMPO, TEMPOL, and CAT-1 in imidazolium based ionic liquids shows an influence of microviscosity of the ionic liquid on mobility of all probes investigated. The effect is higher for TEMPOL and it is strongest for CAT-1. Hydrogen bonding in case of TEMPOL and ionic interactions between CAT-1 and the individual ions of the ionic liquids may be discussed as responsible parameter describing this phenomenon. However, motion into the free volume of the ionic liquid becomes a non-activated process, and it seems to be typical for these molten salts whereas this phenomenon is an exception for molecular solvents. Furthermore, micropolarity of the ionic liquids described by the nitrogen hyperfine coupling constant ($A_{\text{iso}}(^{14}\text{N})$) is not only dependent on the probe investigated. The $A_{\text{iso}}(^{14}\text{N})$ values of CAT-1 show also an influence of the

substituents at the imidazolium ion on micropolarity of the ionic liquids. Microviscosity and micropolarity are very important for application of ionic liquids as solvents for reactions in organic, inorganic, and polymer chemistry. Furthermore, micropolarity is crucial for selection of ionic liquids for special separation processes. Moreover, the spin probes can function as models for radicals formed during radical polymerization. The lower mobility of the radicals caused by the higher viscosity of the ionic liquids and the free volume effects may affect radical polymerization. The results obtained for solute dependent micropolarity may be useful for selection of monomers and ionic liquids for an efficient copolymerization in the ionic liquids.

REFERENCES

- Rogers RD, Seddon KR. *Ionic Liquids Industrial Applications to Green Chemistry*; ACS Symp. Ser. 2002; 818 American Chemical Society: Washington DC.
- Rogers RD, Seddon KR, Kubisa P. *Ionic Liquids as Green Solvents*; ACS Symp. Ser. 2003; 856 American Chemical Society: Washington DC.
- Wasserscheid P, Welton T. *Ionic Liquids in Synthesis*. Wiley-VCH: Weinheim, 2003.
- Rogers RD, Brazel CS. *Ionic Liquids in Polymer Systems*; ACS Symp. Ser. 2005; 913; American Chemical Society: Washington, DC.
- Welton T. *Chem. Rev.* 1999; **99**: 2071–2083.
- Wasserscheid P, Keim W. *Angew. Chem.* 2000; **112**: 3927–3945.
- Zhao H, Malhotra SV. *Aldrichimica Acta* 2002; **35**: 75–83.
- Dupont J, de Souza RF, Suarez PAZ. *Chem. Rev.* 2002; **102**: 3667–3692.
- Kubisa P. *Progr. Polym. Sci.* 2004; **29**: 3–12.
- Tokuda H, Hayamizu K, Ishii K, Susan MABH, Watanabe M. *J. Phys. Chem. B* 2004; **108**: 16593–16600.
- Tokuda H, Hayamizu K, Ishii K, Susan MABH, Watanabe M. *J. Phys. Chem. B* 2005; **109**: 6103–6110.
- Rebelo LPN, Lopes JNC, Esperanca JMSS, Filipe E. *J. Phys. Chem. B* 2005; **109**: 6040–6043.
- Zhou ZB, Matsumoto H, Tatsumi K. *ChemPhysChem* 2005; **6**: 1324–1332.

14. Gu Z, Brennecke JF. *J. Chem. Eng. Data* 2002; **47**: 339–345.
15. Fredlake CP, Crosthwaite JM, Hert DG, Aki SNVK, Brennecke JF. *J. Chem. Eng. Data* 2004; **49**: 954–964.
16. Carmichael AJ, Seddon KR. *J. Phys. Org. Chem.* 2000; **13**: 591–595.
17. Muldoon MJ, Gordon CM, Dunkin IR. *J. Chem. Soc., Perkin Trans.* 2001; **2**: 433–435.
18. Aki SNVK, Brennecke JF, Samanta A. *Chem. Commun.* 2001; 413–414.
19. Karmakar R, Samanta A. *J. Phys. Chem. A* 2002; **106**: 6670–6675.
20. Kawai A, Hidemori T, Shibuya K. *Chem. Lett.* 2004; **11**: 1464–1465.
21. Ingram JA, Moog RS, Ito N, Biswas R, Maroncelli M. *J. Phys. Chem. B* 2003; **107**: 5926–5932.
22. Ito N, Arzhantsev S, Maroncelli M. *Chem. Phys. Lett.* 2004; **396**: 83–91.
23. Ito N, Arzhantsev S, Heitz M, Maroncelli M. *J. Phys. Chem. B* 2004; **108**: 5771–5777.
24. Noel MAM, Allendoerfer RD, Osteryoung RA. *J. Phys. Chem.* 1992; **96**: 2391–2394.
25. Evans RG, Wain AJ, Hardacre C, Compton RG. *ChemPhysChem* 2005; **6**: 1035–1039.
26. Bonhôte P, Dias AP, Papageorgiou N, Kalyanasundaram K, Grätzel M. *Inorg. Chem.* 1996; **35**: 1168–1178.
27. Evans RG, Klymenko OV, Price PD, Stephen GD, Hardacre C, Compton RG. *ChemPhysChem* 2005; **6**: 526–533.
28. Campbell JLE, Johnson KE, Torkelson JR. *Inorg. Chem.* 1994; **33**: 3340–3345.
29. Noda A, Hayamizu K, Watanabe M. *J. Phys. Chem. B* 2001; **105**: 4603–4610.
30. Tokuda H, Hayamizu K, Ishii K, Susan MABH, Watanabe M. *J. Phys. Chem. B* 2004; **108**: 16593–16600.
31. Tokuda H, Hayamizu K, Ishii K, Susan MABH, Watanabe M. *J. Phys. Chem. B* 2005; **109**: 6103–6110.
32. Tao G, Zou M, Wang X, Chen Z, Evans D, Kou Y. *Austr. J. Chem.* 2005; **58**: 327–331.
33. Budil DE, Lee S, Saxena S, Freed JH. *J. Magnet. Res. A* 1996; **120**: 155–189.
34. Strehmel V, Laschewsky A, Kraudelt H, Wetzel H, Görnitz E. In *Ionic Liquids in Polymer Solvents*, Ed. Brazel CS, Rogers RD; ACS Symp. Ser. 2005; 913 American Chemical Society, Washington DC, 17–36.
35. Strehmel V, Laschewsky A, Wetzel H, Görnitz E. *Macromolecules* 2006; **39**: 932–939.
36. Huddleston JG, Visser AE, Reichert WM, Willauer HD, Broker GA, Rogers RD. *Green Chem.* 2001; **3**: 156–164.
37. Pfeiffer D. *Programme "Isotrop"*. Federal Institute for Materials Research and Testing: Berlin, Germany.
38. Hoffman BM, Eames TB. *J. Amer. Chem. Soc.* 1969; **91**: 5168–5170.
39. Hoffman BM, Eames TB. *J. Amer. Chem. Soc.* 1969; **91**: 2169–2170.
40. Lim YY, Drago RS. *J. Amer. Chem. Soc.* 1971; **93**: 891–894.
41. Cohen AH, Hoffman BM. *J. Amer. Chem. Soc.* 1973; **95**: 2061–2062.
42. Cohen AH, Hoffman BM. *J. Phys. Chem.* 1974; **78**: 1313–1320.
43. Whisnant CC, Ferguson S, Chesnut DB. *J. Phys. Chem.* 1974; **78**: 1410–1415.
44. Stout G, Engberts JBFN. *J. Org. Chem.* 1974; **39**: 3800–3802.
45. Reddoch AH, Konishi S. *J. Chem. Phys.* 1979; **70**: 2121–2130.
46. Spornol A, Wirtz K. *Z. Naturf.* 1953; **8A**: 522–532.
47. Gierer A, Wirtz K. *Z. Naturf.* 1953; **8A**: 532–538.
48. Strehmel B, Strehmel V, Younes M. *J. Polym. Sci. Polym. Phys. Ed.* 1999; **37**: 1367–1386.
49. Vogel M, Rettig W. *Ber. Bunsen-Gesellschaft* 1987; **91**: 1241–1247.
50. Strehmel B. Fluorescence Probes for Material Science. In *Advanced Functional Molecules and Polymers, Vol 3, Electronic and Photonic Properties*, Nalwa HS (ed.). Gordon and Breach Science Publishers: 2001; 299–384.
51. Saracino GAA, Tedeschi A, D'Errico GD, Improta R, Franco L, Ruzzi M, Corvaia C, Barone V. *J. Phys. Chem. A* 2002; **106**: 10700–10706.
52. Knauer BR, Napier JJ. *J. Amer. Chem. Soc.* 1976; **98**: 4395–4400.
53. Katritzky AR, Fara DC, Yang H, Tamm K, Tamm T, Karelson M. *Chem. Rev.* 2004; **104**: 175–198.
54. Owenius R, Engström M, Lindgren M, Huber M. *J. Phys. Chem. A* 2001; **105**: 10967–10977.
55. Griffith OH, Dehlinger PJ, Van SP. *J. Membr. Biol.* 1974; **15**: 159–192.
56. Dodd GH, Barratt MD, Rayner L. *FEBS Lett.* 1970; **8**: 286–288.
57. Amyes TL, Driver ST, Richard JP, Rivas FM, Toth K. *J. Amer. Chem. Soc.* 2004; **126**: 4366–4374.
58. Fletcher KA, Storey IA, Hendricks AE, Pandey S, Pandey S. *Green Chem.* 2001; **3**: 210–215.