This paper is published as part of a PCCP Themed Issue on: <u>Physical Chemistry of Ionic Liquids</u>

Guest Editor: Frank Endres (Technical University of Clausthal, Germany)

Editorial

Physical chemistry of ionic liquids

Phys. Chem. Chem. Phys., 2010, DOI: <u>10.1039/c001176m</u>

Perspectives

Ionicity in ionic liquids: correlation with ionic structure and physicochemical properties

Kazuhide Ueno, Hiroyuki Tokuda and Masayoshi Watanabe, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b921462n</u>

Design of functional ionic liquids using magneto- and luminescent-active anions

Yukihiro Yoshida and Gunzi Saito, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b920046k</u>

Accelerating the discovery of biocompatible ionic liquids Nicola Wood and Gill Stephens, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** 10.1039/b923429b

Ionic liquids and reactions at the electrochemical interface

Douglas R. MacFarlane, Jennifer M. Pringle, Patrick C. Howlett and Maria Forsyth, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b923053j</u>

Photochemical processes in ionic liquids on ultrafast timescales

Chandrasekhar Nese and Andreas-Neil Unterreiner, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b916799b</u>

At the interface: solvation and designing ionic liquids Robert Hayes, Gregory G. Warr and Rob Atkin, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** 10.1039/b920393a

Ionic liquids in surface electrochemistry

Hongtao Liu, Yang Liu and Jinghong Li, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b921469k</u>

Discussion

Do solvation layers of ionic liquids influence electrochemical reactions?

Frank Endres, Oliver Höfft, Natalia Borisenko, Luiz Henrique Gasparotto, Alexandra Prowald, Rihab Al-Salman, Timo Carstens, Rob Atkin, Andreas Bund and Sherif Zein El Abedin, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b923527m</u>

Papers

Plasma electrochemistry in ionic liquids: deposition of copper nanoparticles

M. Brettholle, O. Höfft, L. Klarhöfer, S. Mathes, W. Maus-Friedrichs, S. Zein El Abedin, S. Krischok, J. Janek and F. Endres, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** 10.1039/b906567a

Size control and immobilization of gold nanoparticles stabilized in an ionic liquid on glass substrates for plasmonic applications

Tatsuya Kameyama, Yumi Ohno, Takashi Kurimoto, Ken-ichi Okazaki, Taro Uematsu, Susumu Kuwabata and Tsukasa Torimoto, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b914230d</u>

Electrostatic properties of liquid 1,3-dimethylimidazolium chloride: role of local polarization and effect of the bulk

C. Krekeler, F. Dommert, J. Schmidt, Y. Y. Zhao, C. Holm, R. Berger and L. Delle Site, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b917803c</u>

Selective removal of acetylenes from olefin mixtures through specific physicochemical interactions of ionic liquids with acetylenes

Jung Min Lee, Jelliarko Palgunadi, Jin Hyung Kim, Srun Jung, Young-seop Choi, Minserk Cheong and Hoon Sik Kim, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b915989d</u>

Screening of pairs of ions dissolved in ionic liquids

R. M. Lynden-Bell, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b916987c</u>

Double layer, diluent and anode effects upon the electrodeposition of aluminium from chloroaluminate based ionic liquids

Andrew P. Abbott, Fulian Qiu, Hadi M. A. Abood, M. Rostom Ali and Karl S. Ryder, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b917351j</u>

A comparison of the cyclic voltammetry of the Sn/Sn(II) couple in the room temperature ionic liquids *N*-butyl-*N*methylpyrrolidinium dicyanamide and *N*-butyl-*N*methylpyrrolidinium bis(trifluoromethylsulfonyl)imide: solvent induced changes of electrode reaction mechanism Benjamin C. M. Martindale, Sarah E. Ward Jones and Richard G. Compton, *Phys. Chem. Chem. Phys.*, 2010, DOI: 10.1039/b920217j

Ionic liquids through the looking glass: theory mirrors experiment and provides further insight into aromatic substitution processes

Shon Glyn Jones, Hon Man Yau, Erika Davies, James M. Hook, Tristan G. A. Youngs, Jason B. Harper and Anna K. Croft, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b919831h</u>

Nitrile-functionalized pyrrolidinium ionic liquids as solvents for cross-coupling reactions involving *in situ* generated nanoparticle catalyst reservoirs

Yugang Cui, Ilaria Biondi, Manish Chaubey, Xue Yang, Zhaofu Fei, Rosario Scopelliti, Christian G. Hartinger, Yongdan Li, Cinzia Chiappe and Paul J. Dyson, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b920025h</u>

Ionic liquid as plasticizer for europium(III)-doped luminescent poly(methyl methacrylate) films

Kyra Lunstroot, Kris Driesen, Peter Nockemann, Lydie Viau, P. Hubert Mutin, André Vioux and Koen Binnemans, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b920145a</u>

Ab initio study on S_№2 reaction of methyl p-

nitrobenzenesulfonate and chloride anion in [mmim][PF_a] Seigo Hayaki, Kentaro Kido, Hirofumi Sato and Shigeyoshi Sakaki, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** 10.1039/b920190b

Influence of imidazolium bis(trifluoromethylsulfonylimide)s on the rotation of spin probes comprising ionic and hydrogen bonding groups

Veronika Strehmel, Hans Rexhausen and Peter Strauch, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b920586a</u>

Thermo-solvatochromism in binary mixtures of water and ionic liquids: on the relative importance of solvophobic interactions

Bruno M. Sato, Carolina G. de Oliveira, Clarissa T. Martins and Omar A. El Seoud, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b921391k</u>

Patterns of protein unfolding and protein aggregation in ionic liquids

Diana Constatinescu, Christian Herrmann and Hermann Weingärtner, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b921037g</u>

High vacuum distillation of ionic liquids and separation of ionic liquid mixtures

Alasdair W. Taylor, Kevin R. J. Lovelock, Alexey Deyko, Peter Licence and Robert G. Jones, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b920931j</u>

Designer molecular probes for phosphonium ionic liquids

Robert Byrne, Simon Coleman, Simon Gallagher and Dermot Diamond, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b920580b</u>

States and migration of an excess electron in a pyridiniumbased, room-temperature ionic liquid: an *ab initio* molecular dynamics simulation exploration

Zhiping Wang, Liang Zhang, Robert I. Cukier and Yuxiang Bu, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b921104g</u>

<u>J-aggregation of ionic liquid solutions of *meso*-tetrakis(4-<u>sulfonatophenyl)porphyrin</u></u>

Maroof Ali, Vinod Kumar, Sheila N. Baker, Gary A. Baker and Siddharth Pandey, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b920500d</u>

Spontaneous product segregation from reactions in ionic liquids: application in Pd-catalyzed aliphatic alcohol oxidation Charlie Van Doorslaer, Yves Schellekens, Pascal Mertens, Koen Binnemans and Dirk De Vos, *Phys. Chem. Chem. Phys.*, 2010, DOI: <u>10.1039/b920813p</u>

Electrostatic interactions in ionic liquids: the dangers of dipole and dielectric descriptions

Mark N. Kobrak and Hualin Li, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b920080k</u>

Insights into the surface composition and enrichment effects of ionic liquids and ionic liquid mixtures

F. Maier, T. Cremer, C. Kolbeck, K. R. J. Lovelock, N. Paape, P. S. Schulz, P. Wasserscheid and H.-P. Steinrück, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b920804f</u>

Ionic liquids and reactive azeotropes: the continuity of the aprotic and protic classes

José N. Canongia Lopes and Luís Paulo N. Rebelo, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b922524m</u>

A COSMO-RS based guide to analyze/quantify the polarity of ionic liquids and their mixtures with organic cosolvents José Palomar, José S. Torrecilla, Jesús Lemus, Víctor R. Ferro and Francisco Rodríguez, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b920651p</u>

Solid and liquid charge-transfer complex formation between 1-methylnaphthalene and 1-alkyl-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide ionic liquids

Christopher Hardacre, John D. Holbrey, Claire L. Mullan, Mark Nieuwenhuyzen, Tristan G. A. Youngs, Daniel T. Bowron and Simon J. Teat, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b921160h</u>

Blending ionic liquids: how physico-chemical properties change

F. Castiglione, G. Raos, G. Battista Appetecchi, M. Montanino, S. Passerini, M. Moreno, A. Famulari and A. Mele, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b921816e</u>

NMR spectroscopic studies of cellobiose solvation in EmimAc aimed to understand the dissolution mechanism of cellulose in ionic liquids

Jinming Zhang, Hao Zhang, Jin Wu, Jun Zhang, Jiasong He and Junfeng Xiang, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b920446f</u>

Electrochemical carboxylation of <u>#-chloroethylbenzene in</u> ionic liquids compressed with carbon dioxide

Yusuke Hiejima, Masahiro Hayashi, Akihiro Uda, Seiko Oya, Hiroyuki Kondo, Hisanori Senboku and Kenji Takahashi, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b920413j</u>

A theoretical study of the copper(I)-catalyzed 1,3-dipolar cycloaddition reaction in dabco-based ionic liquids: the anion effect on regioselectivity

Cinzia Chiappe, Benedetta Mennucci, Christian Silvio Pomelli, Angelo Sanzone and Alberto Marra, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b921204c</u>

Fragility, Stokes–Einstein violation, and correlated local excitations in a coarse-grained model of an ionic liquid

Daun Jeong, M. Y. Choi, Hyung J. Kim and YounJoon Jung, Phys. Chem. Chem. Phys., 2010, DOI: <u>10.1039/b921725h</u>

Reactions of excited-state benzophenone ketyl radical in a room-temperature ionic liquid

Kenji Takahashi, Hiroaki Tezuka, Shingo Kitamura, Toshifumi Satoh and Ryuzi Katoh, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b920131a</u>

In search of pure liquid salt forms of aspirin: ionic liquid approaches with acetylsalicylic acid and salicylic acid Katharina Bica, Christiaan Rijksen, Mark Nieuwenhuyzen and Robin D. Rogers, *Phys. Chem. Chem. Phys.*, 2010, DOI: <u>10.1039/b923855g</u>

Nanocomposites of ionic liquids confined in mesoporous

silica gels: preparation, characterization and performance Juan Zhang, Qinghua Zhang, Xueli Li, Shimin Liu, Yubo Ma, Feng Shi and Youquan Deng, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b920556j</u>

An ultra high vacuum-spectroelectrochemical study of the dissolution of copper in the ionic liquid (*N*-methylacetate)-4-picolinium bis(trifluoromethylsulfonyl)imide

Fulian Qiu, Alasdair W. Taylor, Shuang Men, Ignacio J. Villar-Garcia and Peter Licence, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b924985k</u>

Understanding siloxane functionalised ionic liquids

Heiko Niedermeyer, Mohd Azri Ab Rani, Paul D. Lickiss, Jason P. Hallett, Tom Welton, Andrew J. P. White and Patricia A. Hunt, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b922011a</u>

On the electrodeposition of tantalum from three different ionic liquids with the bis(trifluoromethyl sulfonyl) amide anion

Adriana Ispas, Barbara Adolphi, Andreas Bund and Frank Endres, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b922071m</u>

Solid-state dye-sensitized solar cells using polymerized ionic liquid electrolyte with platinum-free counter electrode

Ryuji Kawano, Toru Katakabe, Hironobu Shimosawa, Md. Khaja Nazeeruddin, Michael Grätzel, Hiroshi Matsui, Takayuki Kitamura, Nobuo Tanabec and Masayoshi Watanabe, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b920633g</u>

Dynamics of ionic liquid mediated quantised charging of monolayer-protected clusters

Stijn F. L. Mertens, Gábor Mészáros and Thomas Wandlowski, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** <u>10.1039/b921368f</u>

Influence of imidazolium bis(trifluoromethylsulfonylimide)s on the rotation of spin probes comprising ionic and hydrogen bonding groups

Veronika Strehmel,*^a Hans Rexhausen^a and Peter Strauch^b

Received 2nd October 2009, Accepted 1st December 2009 First published as an Advance Article on the web 6th January 2010 DOI: 10.1039/b920586a

The influence of the alkyl chain length in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonylimide)s is studied to explore the rotation of piperidine-1-yloxyl derivatives substituted with either hydrogen bonding hydroxy group or ionic substituents. such as the cationic trimethylammonium or the anionic sulfate group placed at the 4 position. Structural variation of the ionic liquids results in differences of their viscosity influencing the rotation of the spin probes. The size of the average rotational correlation times of the spin probes dissolved in the ionic liquids depends further on the additional substituent in 4-position at these spin probes. The rotational correlation time exhibits a linear dependence on the ionic liquid viscosity in the case of the spin probe forming hydrogen bonding with the ionic liquids. In contrast to this, a deviation from the Stokes-Einstein behavior is found in the case of rotation of the charged spin probes in the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonylimide)s substituted with a longer alkyl chain. This effect may be explained by phase separation on a molecular level between the charged part of the ionic liquid and the longer alkyl chains bound at the imidazolium ion. Although the neutral and the cationic spin probes show only a slight dependence between ionic liquid structure variation and the hyperfine coupling constants, structural effects cause changes in the hyperfine coupling constants in the case of the anionic spin probes. These probes strongly interact with the imidazolium ion.

Introduction

Ionic liquids have been new materials for various applications, such as batteries, fuel cells, solar cells, and as reaction media in inorganic, organic, and polymer synthesis.^{1–6} Among the numerous ionic liquids composed of various cations and anions, imidazolium bis(trifluoromethylsulfonylimide)s have received increased attention for some of the potential applications because of their low glass transitions, their relatively low viscosity in comparison with other ionic liquids, their hydrophobicity, and their high conductivity.⁷ Diffusion of dissolved species in the ionic liquid is highly important for many applications. Therefore, investigation of diffusion processes is necessary for the understanding of the specific function of ionic liquids and for an efficient selection of ionic liquids for the special application.

Radicals are formed as reactive species in several chemical reactions during organic and polymer synthesis. The mobility of these reactive radicals in the reaction mixture is one of the factors influencing the reaction path, and therefore, the composition of the reaction products.⁸ Investigation of reactive radicals during chemical reaction is difficult caused by their high reactivity and their low concentration in many reaction mixtures. Therefore, spin probes are employed as models for a

reactive radical in general.^{9–21} Piperidine-1-yloxyl derivatives with various substituents have been successfully investigated in ionic liquids.^{14,15,17,18–21} ESR spectroscopic investigation of spin probes in ionic liquids provides information about mobility of the stable radicals in the ionic liquids and micropolarity of the ionic liquids. Both additional substituents at the piperidine-1-yloxyl derivatives and the structure of the ionic liquid strongly influence the rotation of the spin probes in the ionic liquids.^{14,15,17,21}

One characteristic parameter obtained from the ESR spectra describing diffusion of stable radicals is the average rotational correlation time (τ). Diffusion of radicals is strongly influenced by the viscosity of the ionic liquid itself at a given temperature and by the free volume effect found in many ionic liquids.^{14,21} Furthermore, the isotropic hyperfine coupling constant related to nitrogen (A_{iso}(¹⁴N)) is a further parameter obtained from ESR spectra. This parameter sensitively probes electrostatic interactions and hydrogen bonding of the spin probe with the surrounding solvent because these interactions influence the spin density distribution of the radical electron and its interaction with the nitrogen in solution.²²

In this work, piperidine-1-yloxyl derivatives are discussed regarding their average rotational mobility in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonylimide)s at room temperature. The piperidine-1-yloxyl derivative containing a hydroxy group can form additional hydrogen bonding with the ionic liquid. Spin probes bearing an ionic substituent (sulfate group or ammonium group) strongly interact with the individual ions of the ionic liquid.

^a Institute of Chemistry, Department of Applied Polymer Chemistry, University of Potsdam, D-14476 Potsdam-Golm, Germany. E-mail: vstrehme@uni-potsdam.de; Fax: 493319775036; Tel: 493319775224

^b Institute of Chemistry, Department of Inorganic Chemistry, University of Potsdam, D-14476 Potsdam-Golm, Germany

Results and discussion

A Imidazolium bis(trifluoromethylsulfonylimide)s

1-Alkyl-3-methylimidazolium bis(trifluoromethylsulfonylimide)s are discussed containing alkyl substituents with 1–10 carbon atoms (Fig. 1). In the case of 1,3-dimethylimidazolium bis(trifluoromethylsulfonylimide), the interactions between the cation and the anion appear stronger than in the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonylimide)s substituted with a longer alkyl chain because of the higher volume of these longer alkyl substituents. This structural variation influences the physical properties of these ionic liquids, *e.g.* the viscosity.

The viscosity of ionic liquids is significantly higher than the viscosity of traditional organic solvents.²³ The viscosity of the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonylimide)s strongly depends on the length of the alkyl chain bound at one nitrogen atom of the imidazolium ring (Fig. 2). An increase in the length of the alkyl chain from an ethyl group to a decyl group bound at the imidazolium ion results in a more than three times increase in the viscosity. Interestingly, the 1,3-dimethylimidazolium bis(trifluormethylsulfonylimide) exhibits a higher viscosity than the ethyl and propyl substituted 1-alkyl-3-methylimidazolium salts. The higher viscosity of the 1,3-dimethylimidazolium bis(trifluormethylsulfonylimide) may be caused by the stronger ionic interactions between the ionic liquid cation and anion. The ionic interactions slightly decrease and van der Waals interactions tend to increase in the 1-alkyl-3-methylimidazolium salts substituted with an ethyl group or a longer alkyl chain.

The viscosity differences of the imidazolium bis(trifluoromethylsulfonylimide)s should influence rotational mobility of spin probes dissolved in these ionic liquids. This can be seen in the rotational correlation time calculated from the ESR spectra.

B Spin probes

Spin probes on the basis of piperidine-1-yloxyl derivatives bearing different substituents at the 4 position (Fig. 3) are selected for investigation of rotational mobility in ionic liquids. These substituents are a hydroxy group (1), a trimethylammonium group (2, 3), and a sulfate group (4, 5). The cationic spin probes 2 and 3 distinguish by their anions, which is iodide in the case of 2 and bis(trifluoromethylsulfonylimide) in the case of 3. The latter comprises the same anion as the ionic liquid. Although potassium is the counter ion in the anionic spin probes 4 and 5, the spin probe 5 possesses a higher molar volume because of complex formation between the potassium ion and the crown ether.

The piperidin-1-yloxyl derivatives interact with the individual ions of the ionic liquid *via* the radical structure. Further



Fig. 1 Chemical structure of the imidazolium bis(trifluoromethyl-sulfonylimide)s under investigation.



Fig. 2 Viscosity of imidazolium bis(trifluoromethylsulfonylimide)s at room temperature (296 K) as function of the length of the alkyl chain bound at one nitrogen atom of the imidazolium ring.



Fig. 3 Chemical structure of the piperidin-1-yloxyl derivatives 1-5.

interactions exist between the additional substituent bound at each spin probe and the ionic liquid. These are hydrogen bonding between the OH group of 1 and the ionic liquid (e.g. the acidic hydrogen atom at C-2 of the imidazolium ion or the anion of the ionic liquid). Furthermore, ionic interactions are possible between the ammonium group of the cationic spin probes 2 or 3 and the bis(trifluoromethylsulfonylimide). In addition, the sulfate group of the anionic probes 4 and 5 can interact with the imidazolium ion. The interactions of both the NO-group and the substituent at the 4 position of the piperidin-1-yloxyl derivative with the ionic liquid influence the ESR spectra, which are usually recorded as first derivative of absorbed microwave power as function of the magnetic field strength. The ESR spectra of the spin probes 1-5 consist of three lines because of a spin multiplicity of 1 for ¹⁴N. Examples of ESR spectra of the spin probes 1-5 dissolved in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonylimide) are depicted in Fig. 4.

The ESR spectra of the spin probes 1-5 show line broadening if they are dissolved in the ionic liquid (Fig. 4) in comparison with the use of a polar molecular solvent such as dimethyl sulfoxide, which causes three small lines in the ESR spectra.^{18–20} Furthermore, the ESR spectra in Fig. 4 differ in their linewidth. Especially the high field line shows significant differences between the neutral and the ionic spin probes. Hydrogen bonding interactions between the hydroxy group of the spin probe 1 and the individual ions of the ionic liquid may cause the slight line broadening in the spectrum of





Fig. 4 ESR spectra of the spin probes (a) **1**, (b) **2**, (c) **3**, (d) **4**, and (e) **5** dissolved in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonylimide) at room temperature (294 K).

the spin probe. The stronger line broadening in the ESR spectra of the ionic spin probes **2–5** dissolved in the ionic liquid may be attributed to the ionic interactions between the ionic substituents of these spin probes and the individual ions of the ionic liquid.

Furthermore, similar ESR spectra are obtained for the cationic spin probes 2 and 3 on the one hand, and for the anionic spin probes 4 and 5 on the other hand. The reason for this effect may be counter ion exchange with the anion of the ionic liquid in the case of the cationic spin probe 2 or with the cation of the ionic liquid in the case of the anionic spin probes 4 and 5. Thus, the shape of the spectra shows similar mobility of these spin probes as a result of ion exchange leading to a similar effective rotational volume. The cationic spin probe 3 bears the same anion as the ionic liquid. Moreover, cation exchange in the anionic spin probes 4 and 5 with the imidazolium ion explains the similarities in the ESR spectra although the counter ion of spin probe 5 is significantly larger because of complex formation with the crown ether. The use of the crown ether probe 5 brings the benefit of improved solubility in the ionic liquid while in a second step cation exchange occurs. Nevertheless, the broad lines in the ESR spectra of the spin probes dissolved in the ionic liquid show that the mobility of the spin probes is reduced which is caused by both the higher viscosity and the ionic nature of the ionic liquid.

C Rotational diffusion of spin probes in ionic liquids

For a more detailed discussion of the influence of the ionic liquid on the rotation of the spin probes, the alkyl chain length of the 1-alkyl-3-methylimidazolium bis(trifluoromethyl-sulfonylimide)s changes between a methyl group and a decyl group. This structural variation strongly influences the viscosity of the ionic liquid (Fig. 2). Furthermore, the structural changes additionally interfere the rotation of the spin probes. This can also be seen by comparing the ESR spectra depicted in Fig. 4–6. Moreover, the influence of the ionic liquid on the rotation of the spin probe is also dependent on the spin probe structure.

As expected, the three lines of the ESR spectra are broader in the case of the ionic spin probes 2-5 in comparison with the hydroxy substituted probe 1 in the ionic liquids (Fig. 4-6). Furthermore, a higher extent on line broadening exists in the ESR spectra of the spin probes 1-5 dissolved in 1-decyl-3bis(trifluoromethylsulfonylimide) methylimidazolium comparison with 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonylimide) and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonylimide). A quantitative description of these effects is possible using the average rotational correlation time (τ) , which is related to the rotational motion of the spin probe. A low average rotational correlation time corresponds to a high mobility of the spin probe. The average rotational



Fig. 5 ESR spectra of the spin probes (a) **1**, (b) **2**, (c) **3**, (d) **4**, and (e) **5** dissolved in 1-propyl-3-methylimidazolium bis(trifluoromethyl-sulfonylimide) at room temperature (294 K).



Fig. 6 ESR spectra of the spin probes (a) **1**, (b) **2**, (c) **3**, (d) **4**, and (e) **5** dissolved in 1-decyl-3-methylimidazolium bis(trifluoromethylsulfonylimide) at room temperature (294 K).

correlation times are calculated from the average rotational diffusion rate constants. The latter were obtained from the ESR spectra using the method of Budil et al.²⁴ In general, the average rotational correlation time exhibits the lowest values for the neutral spin probe 1 (Fig. 7a). Larger τ values are obtained for the anionic spin probes 4 and 5 (Fig. 7c). The cationic spin probes 2 and 3 result in the highest τ values (Fig. 7b). These data show a hindered rotation of the ionic spin probes 2-5 in the ionic liquids compared to the rotation of the hydroxy substituted spin probe 1. This can be explained with stronger ionic interactions in comparison with hydrogen bonding. Furthermore, the cationic spin probes 2 and 3 strongly interact additionally with the anion of the ionic liquids, which is the bis(trifluoromethylsulfonylimide), although the anionic spin probes 4 and 5 undergo additional interactions with the cation of the ionic liquids, which are the imidazolium ions substituted with alkyl chains of different lengths. The results obtained suggest to describe slightly stronger interactions of the ammonium substituent in 2 and 3 with the bis(trifluoromethylsulfonylimide) compared to interactions between the imidazolium ions of the ionic liquid and the negatively charged spin probes 4 and 5. Thus, the cationic spin probes 2 and 3 exhibit a stronger hindrance of rotation, which may be caused by the more bulky trimethylammonium substituent in comparison with the anionic spin probes 4 and 5 that may have a lower rotational volume because of the smaller volume of the sulfate group.

Furthermore, the average rotational correlation times of the spin probes **1–5** in the imidazolium bis(trifluoromethylsulfonylimide)s increase with the length of the alkyl chain bound at the nitrogen atom of the imidazolium ring from an ethyl to a decyl substituent (Fig. 7). This may be attributed in general to the increase in the viscosity of the ionic liquids with increasing alkyl chain lengths starting with an ethyl substituent, which is depicted in Fig. 2. Moreover, the higher viscosity of the 1,3-dimethylimidazolium ionic liquid in comparison with 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonylimide) results also in an increase in the average rotational correlation time of the ionic spin probes in the 1,3-dimethylimidazolium bis(trifluoromethylsulfonylimide) (Fig. 7).

The viscosity of the ionic liquids mainly influences the rotation of the spin probes, and thus the mobility. The straight line in the plot of the rotational correlation time of the spin probes as a function of the viscosity of the ionic liquids clearly shows Stokes–Einstein behavior (eqn (1)) in the case of the hydroxy substituted spin probe 1 (Fig. 8). The proportionality constant between the viscosity (η) and the rotational correlation time (τ) contains the rotational volume of the spin probe ($V_{\rm rot}$), the Boltzmann constant ($k_{\rm B}$) and the temperature (T).²⁵

$$\tau = \frac{V_{\rm rot} \,\pi}{k_{\rm B} \,T} \,\eta \tag{1}$$



Fig. 7 Dependence of the average rotational correlation time (τ) of the spin probes (a) 1, (b) 2 and 3, and (c) 4 and 5 from the length of the alkyl chain (*n*) bound at one nitrogen atom of the imidazolium ring at a temperature of 294 K.

However, the ionic spin probes show Stokes-Einstein behavior only in the case of imidazolium bis(trifluoromethylsulfonylimide)s substituted with an alkyl chain between an ethyl and a hexyl group. The lines of the Stokes-Einstein plot have their origin at zero as expected from the Stokes-Einstein theory (Fig. 8). The slopes of the Stokes-Einstein plot are higher for the ionic spin probes in comparison with the neutral spin probe. We obtained slopes from Fig. 8 of 0.03 ns/(mPa s) for the hydroxy substituted spin probe 1, 0.15 ns/(mPa s) for the cationic spin probe 2, 0.14 ns/(mPa s) for the cationic spin probe 3, 0.12 ns/(mPa s) for the anionic spin probe 4, and 0.11 ns/(mPa s) for the anionic spin probe 5. This follows roughly the tendency for the size of the probe indicating that the experiment discloses a higher rotational volume for the ionic spin probes compared to 1.²¹ The slope is 4 to 5 times larger for the ionic spin probes 2–5 than for the neutral spin probe 1. This is only understandable if the ionic liquid ions directly interact with the ionic probes resulting in a higher rotational volume as expected from molecular modeling calculations.²¹

The τ values of the ionic spin probes dissolved in the 1,3dimethylimidazolium bis(trifluoromethylsulfonylimide) do not fit well into the line (not shown in Fig. 8). A slightly lower rotational correlation time exists for the ionic spin probes in the 1,3-dimethylimidazolium salt as compared to the value expected from the viscosity of this ionic liquid. Presumably, microviscosity effects may explain this behavior as previously demonstrated in a distinct ionic liquid.²¹ The 1,3-dimethylimidazolium bis(trifluoromethylsulfonylimide) bears the smallest alkyl substituent at the heterocyclic ring. Therefore, it is the smallest cation in this series. This possibly leads to a different packaging in the matrix as compared to the other ionic liquids substituted with a longer alkyl chain. Thus, the spin probe mobility cannot be described according to the Stokes-Einstein theory because differences at the microscopic level are important to describe the spin probe behavior. In a previous publication we discussed that microviscosity theory might be applicable to describing such phenomena.²¹ The ionic liquid discussed in this previous publication was 1-butyl-3methylimidazolium tetrafluoroborate bearing with the tetrafluoroborate a small anion. This leads to the conclusion that small ions in the ionic liquid result in probe mobility, which can be described rather by the microviscosity theory while large ions such as the bis(trifluoromethylsulfonylimide)

favor a diffusion according to the Stokes–Einstein theory. Temperature dependent measurements on the imidazolium bis(trifluoromethylsulfonylimide)s would be necessary to underline these statements, which will be the focus of a future publication.

Moreover, the rotational correlation times of the ionic spin probes are significantly lower than expected from the viscosity of imidazolium bis(trifluoromethylsulfonylimide)s the substituted with an octyl or a decyl group. This effect may be caused by the structure of these ionic liquids. The ionic spin probes may relatively strong interact with either the bis(trifluoromethylsulfonylimide) in the case of the cationic spin probes 2 and 3 or the imidazolium ion in the case of the anionic spin probes 4 and 5. The longer alkyl substituents presumably form separate nonpolar phases on a molecular level that are not directly involved in the rotation of the ionic spin probes. In contrast to this, the hydroxy substituted spin probe 1 may not as strong interact with the individual ions of the ionic liquid as the ionic spin probes do. Therefore, the rotation of the non-charged spin probe 1 agrees with the macroscopic viscosity of the ionic liquid. Formation of such phase separation was also reported from other investigations.²⁶

D Micropolarity detected by spin probes in ionic liquids

The hyperfine coupling constants $(A_{iso}(^{14}N))$ are not influenced by the alkyl chain length bound at the imidazolium ion in the case of the hydroxy substituted spin probe 1 (Fig. 9). A similar result was observed for the nonionic spin probe 1 dissolved in 1-alkyl-3-methylimidazolium tetrafluoroborates.¹⁴ This shows that the micropolarity detected by this spin probe is similar for both the imidazolium bis(trifluoromethylsulfonylimide)s and the imidazolium tetrafluoroborates independent of the length of the alkyl chain bound at the imidazolium ion. This may be caused by weak interactions between the non-charged spin probe 1 and the individual ions of the ionic liquid. The $A_{iso}(^{14}N)$ values of the spin probe 1 in these ionic liquids are similar to the value obtained in dimethyl sulfoxide (15.9 G).¹⁴

Furthermore, the $A_{iso}(^{14}N)$ values of the cationic spin probes 2 and 3 do only slightly decrease with the length of alkyl chain bound at the nitrogen atom of the imidazolium ring (Fig. 9). This slight dependence differs from the stronger



Fig. 8 Average rotational correlation time of the spin probes 1–5 as a function of the viscosity of the ionic liquids.



Fig. 9 Hyperfine coupling constants $(A_{iso}(^{14}N))$ of the spin probes 1, 2, 3, 4, and 5 dissolved in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonylimide)s determined from ESR spectra at room temperature (294 K).

decrease of the hyperfine coupling constants with increasing alkyl chain length of the imidazolium tetrafluoroborates in the case of the spin probe 2 and may be caused by differences in the interactions between the cationic spin probe with tetrafluoroborate or bis(trifluoromethylsulfonylimide).¹⁴

Moreover, the Aiso(14N)-values are higher for the anionic spin probes than for the cationic spin probes. This may be explained with the preference of the ionic structure of the NO group in comparison with its neutral structure resulting in higher spin density at the nitrogen atom in the case of the anionic spin probes. Thus, the free electron at the nitrogen radical results in higher hyperfine coupling constants. Furthermore, the hyperfine coupling constants of anionic spin probes 4 and 5 increase with increasing alkyl chain length of imidazolium bis(trifluoromethylsulfonylimide)s substituted with alkyl chains containing between 2 and 10 carbon atoms. Although the polarity of imidazolium bis(trifluoromethylsulfonylimide)s should decrease with increasing alkyl chain length, the opposite result is obtained in the experiments. Indeed, the hyperfine coupling constants of 5 are lower in the case of lower polar solvents, e.g. A_{iso}(¹⁴N) is 15.1 G for tert-butyl methyl ether, 15.7 G for dimethyl sulfoxide, 16.0 G for ethanol, and 16.9 G for water.²⁰ This would indicate micropolarity of the imidazolium bis(trifluoromethylsulfonylimide)s increasing from ethanol to water with increasing alkyl chain length, which contradicts the experience. Therefore, a further factor of influence must be taken into consideration, which is the preferred place of residence for the anionic spin probe. The increase in the hyperfine coupling constants indicates a preference of the ionic structure of the NO group resulting in stronger interactions with the imidazolium ion. Furthermore, the increased tendency of the ionic liquids to separate into polar and nonpolar domains on a molecular level with increasing alkyl chain length at the nitrogen atom may be discussed as one reason for the increase of the $A_{iso}(^{14}N)$ values. Heterogeneities in ionic liquids at the nano-scale are also discussed in literature based on simulation techniques and experimental methods such as dynamic light scattering or X-ray diffraction.²⁶ This must lead to different mobility as shown for the rotational mobility and different polarity at the microscopic level. The probe reports about the environment around it that it feels by itself. The anionic spin probes show strong interactions with the imidazolium ion, which may undergo an increased phase separation tendency with longer alkyl chains on a molecular level. Interestingly, the hyperfine coupling constant is higher for the anionic spin probe 4 in 1,3-dimethylimidazolium bis(trifluoromethylsulfonylimide) in comparison with the use of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonylimide) substituted with an ethyl, propyl, or butyl group at one nitrogen atom of the imidazolium ring. This shows that the 1,3-dimethylimidazolium based ionic liquid is something special in comparison with the other ionic liquids. The small methyl substituents enable stronger electrostatic interactions between the anionic spin probe and the 1,3-dimethylimidazolium ion in comparison with 1-alkyl-3-methylimidazolium ions substituted with a longer alkyl chain. The stronger ionic interactions between the anionic spin probe 4 and the 1,3-dimethylimidazolium ion relative to the other imidazolium cations bearing a longer alkyl chain

may cause an increase in the electrostatic interactions, and therefore, an increase in the hyperfine coupling constant relative to the other ionic liquids. These results show the complex relation between the hyperfine coupling constant of spin probes and discussion of micropolarity. Micropolarity discussion is strongly coupled on the spin probe structure and on the interactions with the ionic liquid on a molecular level.

Conclusions

Viscosity measurements of 1-alkyl-3-methylimidazolium bis-(trifluoromethylsulfonylimide)s show an increase in the viscosity from the ethyl substituted to the decyl substituted imidazolium salt that is caused by an increase in the size of the cation. In contrast to this, the viscosity of the 1,3-dimethylimidazolium salt is also higher in comparison with the 1-ethyl or the 1-propyl substituted ionic liquid. From this we can conclude that the stronger ionic interactions between the cation and the anion of the ionic liquid make the 1,3-dimethylimidazolium salt to some special ionic liquid relative to those with longer alkyl chains.

Similar to the viscosity of the ionic liquids, the rotational correlation times of the ionic spin probes show qualitatively the same tendency in their dependence on the length of the alkyl chain bound at the imidazolium ion. Viscosity dependence of the rotational correlation times indicates Stokes-Einstein behavior only up to a hexyl substituent at the imidazolium ion in the case of the ionic spin probes. Longer alkyl substituents at the imidazolium ion result in a deviation from the Stokes-Einstein behavior that may be caused by phase separation on a molecular level between the charged part of the ionic liquid and the longer alkyl chains. In contrast to this, the rotation of the neutral spin probe shows Stokes-Einstein behavior also in the case of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonvlimide)s substituted with a longer alkyl chain. From this we can conclude that the ionic interactions between the individual ions of the ionic liquids and the ionic spin probes strongly influence the rotation of the ionic spin probes in the ionic liquids. However, the neutral spin probe does not as strong interact with the ionic liquid as the ionic spin probes. Therefore, the rotation of the neutral spin probe is less influenced by the individual ions of these ionic liquids.

The structural variation of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonylimide)s influences the hyperfine coupling constants ($A_{iso}(^{14}N)$) significantly only in the case of the anionic spin probe. This shows that electrostatic interactions between the anionic spin probe and the imidazolium ion are necessary to describe the differences in the spin density at the nitrogen of the spin probe dissolved in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonylimide)s.

Experimental

Materials

1-Alkyl-3-methylimidazolium bis(trifluoromethylsulfonylimide)s are prepared in a two step synthesis. In the first step, 1-alkyl-3methylimidazolium iodides or chlorides are synthesized followed by anion metathesis with lithium bis(trifluoromethylsulfonylimide)s. 1-Alkyl-3-methylimidazolium iodides substituted with a methyl or ethyl group are synthesized from 1-methylimidazole and the corresponding alkyl iodide using a 25 wt% excess on the alkyl halogenide at room temperature. *tert*-Butyl methyl ether is used as solvent in the case of methyl iodide and ethyl iodide because of the high exothermic reaction in these examples. The volume ratio of the solvent to the alkyl iodide is 1:1. The 1-propyl-3-methylimidazolium iodide is synthesized using a 5 wt% excess of the propyl iodide in bulk. 1-alkyl-3methylimidazolium chlorides substituted with a butyl, hexyl, octvl or decvl chain are synthesized from 1-methylimidazole and the corresponding alkyl chloride in bulk at 65 °C in the case of butyl chloride and hexyl chloride and at 70 °C in the case of octyl chloride and decyl chloride using 5 wt% excess on the alkyl chloride. 1-Alkyl-3-methylimidazolium halogenide obtained and lithium bis(tifluoromethylsulfonylimide) from Iolitec are separately dissolved in water. The amount of each starting material is 1 g per 1 ml water. A 5 wt% excess of the lithium bis(trifluoromethylsulfonylimide) relative to the necessary stoichiometric amount is used for anion metathesis. The water solutions are unified under stirring and kept further stirring for 18 h. After stirring, ethyl acetate or methylene chloride (500 ml solvent relative to 70 g of the imidazolium iodide) is added to the water solution. Both solvents result in similar products. Methylene chloride is preferred because of phase inversion in the case of ethyl acetate. The organic phase is separated, washed 8 times with 300 ml water each, and filtered over sodium sulfate. The solvent is evaporated from the organic solution in vacuo. The remaining ionic liquid is dried in vacuo (1-4 mbar) at a temperature between 70 and 90 °C for 3 days. No remaining halide was detected after addition of a solution of AgNO3 dissolved in a water-acetone mixture. The water content of these ionic liquids is lower than 1000 ppm.

The nonionic spin probe 1 was purchased from Sigma-Aldrich and used as obtained. Synthesis of the spin probes 2-5 is described elsewhere.^{18–20}

Measurements

ESR spectra of 0.05 wt% of each spin probe dissolved in the ionic liquids were measured in X-band with a CW spectrometer ELEXSYS E500 (Bruker) at 9.4 GHz. Rotational correlation time (τ) was calculated from the average rotational diffusion rate constant, which was determined using the method of Budil *et al.* using the model of isotropic viscosity for the fitting procedure.²⁴ This procedure comprises an experimental error of about ± 5 –10% depending on the quality of the ESR signal. Furthermore, shear rate viscosity measurements on ionic liquids were carried out using shear rates between 0.1 s⁻¹ and 800 s⁻¹ at 296 K. Data are given at a shear rate of 10 s⁻¹ because viscosity of all ionic liquids investigated is independent on the shear rate at 10 s⁻¹.

Acknowledgements

We gratefully acknowledge A. Laschewsky for the use of laboratory equipment, H. Wetzel (Fraunhofer Institute of Applied Polymer Research) for water analysis using the Karl Fischer Method, and E. Görnitz and K. Blümel (Fraunhofer Institute of Applied Polymer Research) for support during viscosity measurements. Furthermore, V.S. and H.R. gratefully acknowledge the DFG for financial support within the priority program SPP 1191.

Notes and references

- H. Ohno, Electrochemical Aspects of Ionic Liquids, John Wiley & Sons Inc., Hoboken, New Jersey, 2005; W. A. Henderson, M. Herstedt, V. G. Young, S. Passerini, H. C. De Long and P. C. Trulove, *Inorg. Chem.*, 2006, **45**, 1412–1414; S.-L. Chou, J.-Z. Wang, J.-Z. Sun, D. Wexler, M. Forsyth, H.-K. Liu, D. R. MacFarlane and S.-X. Dou, *Chem. Mater.*, 2008, **20**, 7044–7051.
- 2 S. S. Sekhon, B. S. Lalia, J.-S. Park, C.-S. Kim and K. Yamada, J. Mater. Chem., 2006, 16, 2256–2265.
- 3 Z.-S. Wang, N. Koumura, Y. Cui, M. Miyashita, S. Mori and K. Hara, *Chem. Mater.*, 2009, **21**, 2810–2816; N. Cai, J. Zhang, D. Zhou, Z. Yi, J. Guo and P. Wang, *J. Phys. Chem. C*, 2009, **113**, 4215–4221; A. Mishra, M. K. R. Fischer and P. Bauerle, *Angew. Chem., Int. Ed.*, 2009, **48**, 2474–2499.
- 4 F. Endres, S. Zein, El Abedin, A. Y. Saad, E. M. Moustafa, N. Borissenko, W. E. Price, G. G. Wallace, D. R. MacFarlane, P. J. Newman and A. Bund, *Phys. Chem. Chem. Phys.*, 2008, 10, 2189–2199; H. Itoh, K. Naka and Y. Chujo, *J. Am. Chem. Soc.*, 2004, 126, 3026–3027; L. Ren, L. Meng, Q. Lu, Z. Fei and P. J. Dyson, *J. Colloid Interface Sci.*, 2008, 323, 260–266; R. Böck, *Materialwiss. Werkstoffiech.*, 2008, 39(12), 901–906; R. G. Reddy, *J. Phys.: Conf. Ser.*, 2009, 165, 012076, DOI: 10.1088/1742-6596/165/1/012076.
- 5 P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, 2003; C. E. Song, *Chem. Commun.*, 2004, 1033–1043; N. Paape, W. Wei, A. Bösmann, C. Kolbeck, F. Maier, H.-P. Steinrück, P. Wasserscheid and P. S. Schulz, *Chem. Commun.*, 2008, 3867–3869; D. Saha, A. Saha and B. C. Ranu, *Green Chem.*, 2009, **11**, 733–737.
- 6 P. Kubisa, Prog. Polym. Sci., 2004, 29, 3-12; C. S. Brazel and R. D. Rogers, Ionic Liquids in Polymer Systems, ACS Symp. Ser., 913, American Chemical Society, 2005; V. Strehmel, A. Laschewsky, H. Wetzel and E. Görnitz, Macromolecules, 2006, 39, 923-930; Y. S. Vygodskii, O. A. Melnik, I. Lozinskaya, A. S. Shaplov, I. A. Malyshkina, D. Gavrilova, K. A. Lyssenko, M. Y. Antipin, E. N. D. G. Golovanov, A. A. Korlyukov, N. Ignatev and U. Welz-Biermann, Polym. Adv. Technol., 2007, 18, 50-63; V. Strehmel, H. Wetzel, A. Laschewsky, E. Moldenhauer and Т Klein, Polym. Adv. Technol., 2008, 19, 1383-1390; Strehmel, E. Reynaud, H. Wetzel, E. Görnitz and V. A. Laschewsky, Macromol. Symp., 2009, 275-276, 242-249.
- 7 C. P. Fredlake, J. M. Crosthwaite, D. G. Hert, S. N. V. K. Aki and J. F. Brennecke, J. Chem. Eng. Data, 2004, 49, 954–964; H. Tokuda, K. Hayamizu, K. Ishii, Md. A. B. H. Susan and M. Watanabe, J. Phys. Chem. B, 2005, 109, 6103–6110; J. M. S. S. Esperanca, Z. P. Visak, N. V. Plechkova, K. R. Seddon, H. J. R. Guedes and L. P. N. Rebelo, J. Chem. Eng. Data, 2006, 51, 2009–2015.
- T. Linker and M. Schmittel, *Radikale und Radikalionen in der* organischen Synthese, Wiley VCH, 1998; R. G. W. Norrish and R. R. Smith, *Nature*, 1942, **150**, 336–337; E. Trommsdorff, H. Köhle and P. Lagally, *Makromol. Chem.*, 1948, **1**, 169–198; M. L. Coote, T. P. Davis, B. Klumperman and M. J. Monteiro, J. M. S. Rev. Macromol. Chem. Phys. C, 1998, **38**, 567–593.
- 9 M. A. M. Noel, R. D. Allendoerfer and R. A. Osteryoung, J. Phys. Chem., 1992, 96, 2391–2394.
- 10 A. Kawai, T. Hidemori and K. Shibuya, *Chem. Lett.*, 2004, 33, 1464–1465.
- 11 R. G. Evans, A. J. Wain, C. Hardacre and R. G. Compton, *ChemPhysChem*, 2005, 6, 1035–1039.
- 12 A. Kawai, T. Hidemori and K. Shibuya, *Chem. Phys. Lett.*, 2005, **414**, 378–383.
- 13 A. Kawai, T. Hidemori and K. Shibuya, *Mol. Phys.*, 2006, 104, 1573–1579.

- 14 V. Strehmel, A. Laschewsky, R. Stoesser, A. Zehl and W. Herrmann, J. Phys. Org. Chem., 2006, 19, 318–325.
- 15 R. Stoesser, W. Herrmann, A. Zehl, V. Strehmel and A. Laschewsky, *ChemPhysChem*, 2006, 7, 1106–1111.
- 16 G. Grampp, D. Kattnig and B. Mladenova, Spectrochim. Acta, Part A, 2006, 63, 821–825.
- 17 R. Stoesser, W. Herrmann, A. Zehl, A. Laschewsky and V. Strehmel, Z. Phys. Chem., 2006, 220, 1309–1342.
- 18 V. Strehmel, H. Rexhausen and P. Strauch, *Tetrahedron Lett.*, 2008, **49**, 586–588.
- 19 V. Strehmel, H. Rexhausen and P. Strauch, *Tetrahedron Lett.*, 2008, **49**, 3264–3267.
- 20 V. Strehmel, H. Rexhausen and P. Strauch, *Tetrahedron Lett.*, 2008, **49**, 7143–7145.
- 21 V. Strehmel, H. Rexhausen, P. Strauch and B. Strehmel, *ChemPhysChem*, 2008, 9, 1294–1302.
- 22 R. Owenius, M. Engström, M. Lindgren and M. Huber, J. Phys. Chem. A, 2001, 105, 10967–10977; G. A. A. Saracino, A. Tedeschi,

G. D'Errico, R. Improta, L. Franco, M. Ruzzi, C. Corvaia and V. Barone, J. Phys. Chem. A, 2002, **106**, 10700–10706.

- 23 J. Zhang, W. Wu, T. Jiang, H. Gao, Z. Liu, J. He and B. Han, J. Chem. Eng. Data, 2003, 48, 1315–1317.
- 24 D. E. Budil, S. Lee, S. Saxena and J. H. Freed, J. Magn. Reson., Ser. A, 1996, 120, 155–189.
- 25 A. Einstein, Z. Electrochem., 1908, 14, 235; P. Debye, Trans. Elektrochem. Soc., 1942, 82, 205; G. Stokes, Trans. Cambridge Phil. Soc., 1956, 9, 5.
- 26 Y. Wang and G. A. Voth, J. Am. Chem. Soc., 2005, 127, 12192–12193; Q. Kuang, J. Zhang and Z. Wang, J. Phys. Chem. B, 2007, 111, 9858–9863; A. Trido, O. Russina and H.-J. Bleif, J. Phys. Chem. B, 2007, 111, 4641–4644; W. Yanting, J. Chem. Phys., 2008, 129, 194501–194515; T. Köddermann, R. Ludwig and D. Paschek, ChemPhysChem, 2008, 9, 1851–1858; W. Jiang, Y. Wang, T. Yan and G. A. Voth, J. Phys. Chem. C, 2008, 112, 1132–1139; Y. Wang, J. Phys. Chem. B, 2009, 113, 11058–11060.