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

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

Editorial

Physical chemistry of ionic liquids
Phys. Chem. Chem. Phys., 2010, **DOI:** 10.1039/c001176m

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:** 10.1039/b921462n

Design of functional ionic liquids using magneto- and luminescent-active anions
Yukihiro Yoshida and Gunzi Saito, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** 10.1039/b920046k

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:** 10.1039/b923053j

Photochemical processes in ionic liquids on ultrafast timescales
Chandrasekhar Nese and Andreas-Neil Unterreiner, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** 10.1039/b916799b

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:** 10.1039/b921469k

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:** 10.1039/b923527m

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:** 10.1039/b914230d

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:** 10.1039/b917803c

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:** 10.1039/b915989d

Screening of pairs of ions dissolved in ionic liquids
R. M. Lynden-Bell, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** 10.1039/b916987c

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:** 10.1039/b917351j

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:** 10.1039/b919831h

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:** 10.1039/b920025h

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:** 10.1039/b920145a

***Ab initio* study on S_N2 reaction of methyl *p*-nitrobenzenesulfonate and chloride anion in [mmim][PF_6]**
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:** 10.1039/b920586a

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:** 10.1039/b921391k

Patterns of protein unfolding and protein aggregation in ionic liquids
Diana Constatinescu, Christian Herrmann and Hermann Weingärtner, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** 10.1039/b921037g

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:** 10.1039/b920931j

Designer molecular probes for phosphonium ionic liquids
Robert Byrne, Simon Coleman, Simon Gallagher and Dermot Diamond, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** 10.1039/b920580b

States and migration of an excess electron in a pyridinium-based, 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:** 10.1039/b921104g

J-aggregation of ionic liquid solutions of *meso*-tetrakis(4-sulfonatophenyl)porphyrin
Maroof Ali, Vinod Kumar, Sheila N. Baker, Gary A. Baker and Siddharth Pandey, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** 10.1039/b920500d

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:** 10.1039/b920813p

Electrostatic interactions in ionic liquids: the dangers of dipole and dielectric descriptions
Mark N. Kobrak and Hualin Li, *Phys. Chem. Chem. Phys.*, 2010, **DOI:** 10.1039/b920080k

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:** 10.1039/b920804f

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:** 10.1039/b922524m

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:** 10.1039/b920651p

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:** 10.1039/b921160h

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:** 10.1039/b921816e

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:** 10.1039/b920446f

Electrochemical carboxylation of α-chloroethylbenzene in 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:** 10.1039/b920413j

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:** 10.1039/b921204c

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:** 10.1039/b921725h

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:** 10.1039/b920131a

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:** 10.1039/b923855g

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:** 10.1039/b920556j

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:** 10.1039/b924985k

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:** 10.1039/b922011a

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:** 10.1039/b922071m

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:** 10.1039/b920633g

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:** 10.1039/b921368f

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

Jinming Zhang,[ab] Hao Zhang,[a] Jin Wu,[a] Jun Zhang,*[a] Jiasong He[a] and Junfeng Xiang*[a]

Received 1st October 2009, Accepted 4th December 2009
First published as an Advance Article on the web 19th January 2010
DOI: 10.1039/b920446f

The dissolution mechanism of cellulose in ionic liquids has been investigated by using cellobiose and 1-ethyl-3-methylimidazolium acetate (EmimAc) as a model system under various conditions with conventional and variable-temperature NMR spectroscopy. In DMSO-d_6 solution, NMR data of the model system clearly suggest that hydrogen bonding is formed between hydroxyls of cellobiose and both anion and cation of EmimAc. The CH_3COO^- anion favors the formation of hydrogen bonds with hydrogen atoms of hydroxyls, and the aromatic protons in bulky cation $[Emim]^+$, especially the most acidic H2, prefer to associate with the oxygen atoms of hydroxyls with less steric hindrance, while after acetylation of all hydroxyls in cellobiose the interactions between cellobiose octaacetate and EmimAc become very weak, implying that hydrogen bonding is the major reason of cellobiose solvation in EmimAc. Meanwhile the stoichiometric ratio of EmimAc/hydroxyl is estimated to be between 3:4 and 1:1 in the primary solvation shell, suggesting that there should be one anion or cation to form hydrogen bonds with two hydroxyl groups simultaneously. *In situ* and variable-temperature NMR spectra suggest the above mechanism also works in the real system.

Introduction

Cellulose, 1,4-β-glucan, is considered as an almost inexhaustible bio-renewable resource in the nature. It abundantly exists in the cell walls of a wide range of higher plants such as wood and cotton, and is the most important skeletal component in plants. Cellulose-based materials have been widely used in various fields of human societies. However, due to highly-developed intra- and intermolecular hydrogen bonds, cellulose is hardly soluble in water and many organic solvents, which severely limits its application.[1–3]

Room-temperature ionic liquids, defined as a class of low-melting-point organic salts, are considered as a desirable 'green', recyclable alternative to the traditional volatile organic solvents in a wide range on account of their unique physico-chemical properties such as negligible vapor pressure, high thermal stability, wide liquid range, and tunable solvation properties.[4–6] Recently, it has been reported that certain ionic liquids exhibited outstanding dissolving capability for cellulose.[7–11] However, so far the mechanism of cellulose dissolution in ionic liquids has not been thoroughly understood.[12] Especially, the conclusions on the role of cations of ionic liquids in the cellulose dissolution mechanism remain certainly inconsistent. Through ^{13}C and $^{35/37}Cl$-NMR relaxation studies, the naturally high chloride content and activity in $[C_4mim]Cl$ was suggested to be the main reason for dissolving cellulose in ionic liquids.[13,14] The non-hydrated and strongly hydrogen-bonded chloride ions were thought to disrupt the hydrogen-bonding network present in the cellulose polymer, thus facilitating its dissolution into the ionic liquid. And there were no specific interactions between the cations of ionic liquids and sugar solutes. Although the molecular simulation studies[15,16] also suggested the dominant contribution to the sugar–ionic liquid interaction energy came from favorable hydrogen bonding interactions between hydroxyls and chlorides, they simultaneously indicated that the cations formed a weak hydrogen bonding interaction and a van der Waals interaction with glucose. In our previous study,[17] through studying the dissolving process of cellulose in ionic liquid 1-allyl-3-methyl-imidazolium chloride (AmimCl), we suggested that both anion and cation of AmimCl formed strong hydrogen bonding interaction with hydroxyls of cellulose, which disrupted hydrogen bonding in cellulose and led to the dissolution. However, this assumption lacked direct experimental evidence.

In the present work, in order to clarify the mechanism of cellulose dissolution in ionic liquids, cellobiose, the repeating unit of cellulose, and low viscosity 1-ethyl-3-methylimidazolium acetate (EmimAc) are chosen as a model system (Fig. 1) and the solvation of cellobiose in EmimAc has been investigated under various conditions by conventional and variable-temperature NMR methods. The results show that the hydrogen bonding formed between hydroxyls and both anion and cation of EmimAc is the major driving force for cellulose dissolution in the ionic liquid.

[a] *Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Engineering Plastics (KLEP), Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing, 100190, China. E-mail: jzhang@iccas.ac.cn, jfxiang@iccas.ac.cn; Fax: +86 (0) 10 6261 3251; Tel: +86 (0) 10 6261 3251*
[b] *Graduate University of Chinese Academy of Sciences, Beijing, 100049, China*

† Electronic Supplementary Information (ESI) available: Additional ^1H-NMR spectra and ^{13}C-NMR spectra.

Results and discussion

Fig. 2 shows the ^{1}H-NMR spectrum of cellobiose in DMSO-d_6, which exhibits sufficient resolution to clearly identify the distinct proton signals of hydroxyls ranging from 4.5–6.8 ppm. The assignment has been done according to the literature.[18] When EmimAc is added into cellobiose/DMSO-d_6 solution, the peaks of hydroxyls merge together (Fig. 3). They are combined into three broad peaks when the molar ratio of EmimAc/cellobiose is 0.2:1. And as the amount of EmimAc increases, the peaks of hydroxyls become one broad peak and gradually move downfield (see ESI, Fig. S1).† The main reason for the significant broadening of these proton resonances of hydroxyls is that oxygen atoms of hydroxyls interact with acidic protons in the imidazolium cation so as to speed up the exchange rate of hydroxy protons,[19,20] which will further be subsequently confirmed. The downfield shift of the OH resonances is ascribed to the formation of hydrogen bonding between hydrogen atoms of hydroxyls and the acetate anion,[21–23] whereas very little change in the chemical shifts is observed for the peaks of methylene and methine in the cellobiose backbone, and only a little difference in their shape, which might be attributed to the increase of the solution viscosity. In summary, these results indicate that the hydrogen bonding is formed between the hydroxyls of cellobiose and EmimAc.

The formation of hydrogen bonding between the hydroxyl groups of cellobiose and EmimAc is expected to affect carbon atoms around the hydroxyl groups. Fig. 4 shows the chemical shift changes of all the carbon atoms in cellobiose as a function of concentration of EmimAc. It can be seen that the peaks of C-α, β-1′, C-2, C-α-2′, C-3, C-α, β-3′ and C-5 move downfield first and then become constant when the molar ratio of EmimAc/cellobiose is above 10:1 or 14:1. The peaks of C-β-2′, C-4, C-β-5′ and C-6 move upfield first and then downfield, while the peaks of C-α, β-6′, C-β-4′ and C-1 move reversely. Such a phenomenon could be interpreted as follows. The relatively small CH_3COO^- anion is a good hydrogen bond acceptor and exhibits great capability of forming hydrogen bonds, thus favors attacking hydrogen atoms of the more activated cellobiose hydroxyls, such as the anomeric hydroxyl and secondary hydroxyls. Hence, the peaks of C-α, β-1′, C-2, C-α-2′, C-3 and C-α, β-3′ move downfield.[24–28] On the other hand, the bulky cation $[Emim]^+$ prefers to associate with oxygen atoms of hydroxyls with less steric hindrance, such as primary hydroxyls and some secondary hydroxyls. Except hydrogen bonding, the aromatic ring current effect and the intermolecular steric interaction, arising from the van der Waals force between the imidazolium cation and cellobiose skeletal hydrogen, also give rise to the changes in ^{13}C chemical shift of cellobiose.[24–31] Thus, the peaks of C-β-2′, C-4, C-β-5′ and C-6 move upfield, whereas those of C-1, C-5 and C-β-4′ move downfield.

With the increase of EmimAc content, the number of both the anion and cation increases. However, because of the large volume of the cation, the increased number of the anion associated with cellobiose is larger than that of the cation. And the impact of the anion on the hydrogen bond donor is greater than that of the cation on the hydrogen bond acceptor. Therefore, some peaks move downfield persistently and then keep constant, while others move upfield first and then downfield. The main reason for the upfield movement of the peaks of C-6′ and C-β-4′ above a certain critical amount of EmimAc may be the shielding effect of the aromatic ring in the imidazolium cation, which is hustled above or below the plane of C-6′ and C-β-4′ as the number of ions around cellobiose increases. Meanwhile, the acidic aromatic hydrogen of the imidazolium cation may interact with the glycosidic linkage oxygen atom. Thereby, the peak of C-1 also moves upfield slightly when the molar ratio of EmimAc/cellobiose is above 10:1.

From Fig. 4, it is also estimated that the stoichiometric ratio of EmimAc/cellobiose is between 6:1 and 8:1 in the primary solvation shell, that is, the ratio of EmimAc/hydroxyls is between 3:4 and 1:1. Thus, there should be one anion or cation to form hydrogen bonds with two hydroxyl groups simultaneously. A similar result has been obtained by molecular dynamics studies of glucose solvation in ionic liquid 1,3-dimethylimidazolium chloride.[15,16] From the above analysis, the possible distribution of anions and cations of EmimAc in the primary solvation shell of cellobiose is shown in Fig. 5.

The above results clearly confirm the formation of hydrogen bonding interactions between hydroxyls of cellobiose and both anion and cation of EmimAc. However, the sites of the imidazolium ring in the cation–cellobiose interactions remain unclear. For solving this problem and better understanding the interactions between cellobiose and EmimAc, the effect of cellobiose concentration on the proton chemical shift of EmimAc has been investigated. Compared to those in the pure ionic liquid, the relative changes of proton chemical shifts in EmimAc with increasing [cellobiose] are shown in Fig. 6. It can be seen that the ring protons in the imidazolium cation show a marked upfield shift, while a negligible change is observed in methyl and ethyl protons of the cation and anion, as the concentration of cellobiose increases. The greatest upfield shift is obtained for the most acidic H2 proton in the

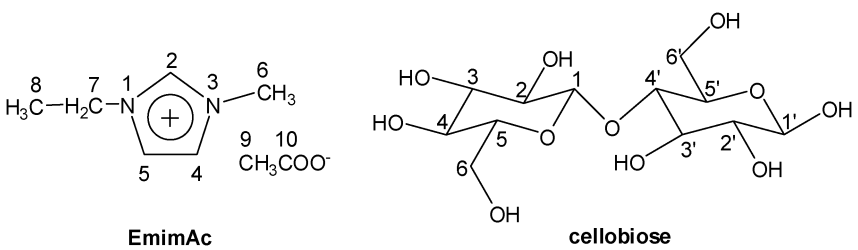

Fig. 1 Structures and numberings of EmimAc and cellobiose.

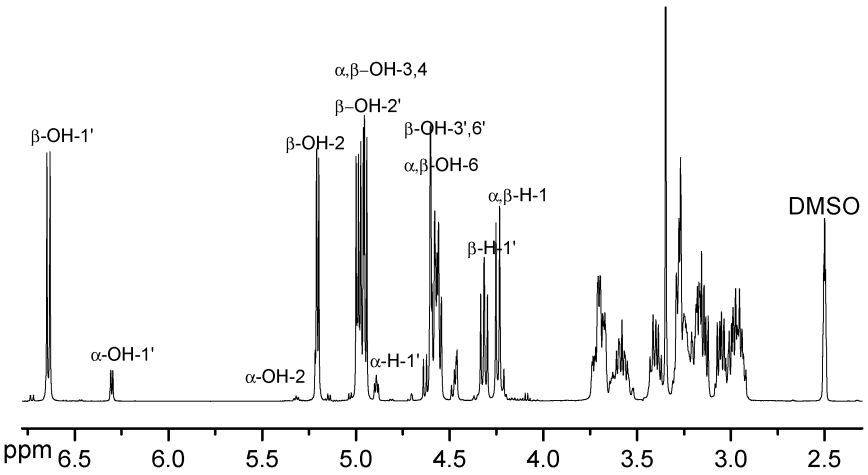

Fig. 2 The ^{1}H-NMR spectrum of cellobiose in DMSO-d_6 together with the assignment of hydroxyl groups.

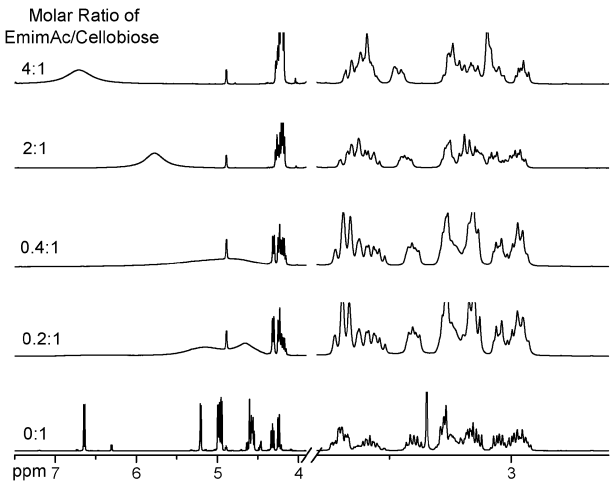

Fig. 3 The effect of molar ratios of EmimAc/cellobiose on the ^{1}H-NMR spectra for cellobiose in DMSO-d_6. (The bottom spectrum is the neat cellobiose.)

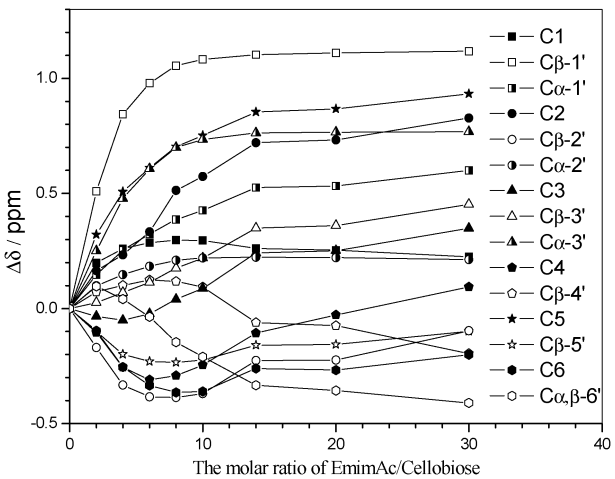

Fig. 4 The effect of molar ratios of EmimAc/cellobiose on the chemical shift difference of carbons in the ^{13}C-NMR spectra of cellobiose in DMSO-d_6 ($\Delta\delta = \delta - \delta_{neat}$).

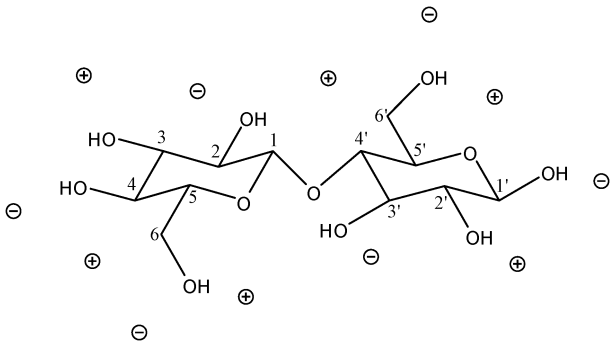

Fig. 5 The possible distribution of anions and cations of EmimAc in the primary solvation shell of cellobiose.

imidazolium cation followed by H4 and H5 protons. This seems a little surprising, since the formation of a hydrogen bond will cause a downfield shift of a proton resonance. However, these results should be reasonable, if we consider the existence of the hydrogen bonding between cations and anions in ionic liquids themselves, which have been proven by computer simulations and experimental measurements in several previous studies.[21,32–36] In pure 1,3-dialkylimidazolium ionic liquid, the cation and anion connect with each other to form an interionic hydrogen-bonded network. The strongest hydrogen bonding always involves the most acidic H2 of the imidazolium cation (pK_a = 22.1 for the 1,3-dimethylimidazolium cation), followed by the other two hydrogens (H4 and H5) of the imidazolium nucleus.[35–37] Introduction of other molecules such as water and dichloromethane would disrupt the interionic hydrogen bond network and form the intermolecular hydrogen bonds.[21,34] Therefore, the observed obvious changes in the ^{1}H chemical shift of EmimAc with increasing [cellobiose] could be explained as follows. Because the hydrogen atoms in hydroxyls are stronger hydrogen bonding donors than the protons of the imidazolium cation,[38] the acetate anions prefer to form stronger hydrogen bonding with the hydrogen atoms in cellobiose hydroxyls, therefore disrupting the interaction between the anion and the aromatic protons of the cation. Subsequently, the hydroxyls replace the acetate

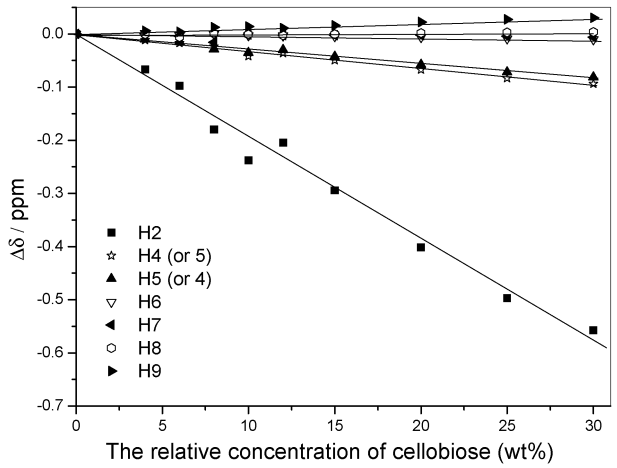

Fig. 6 The changes of proton chemical shift difference in EmimAc with increasing [cellobiose] in DMSO-d_6 ($\Delta\delta = \delta - \delta_{neat}$).

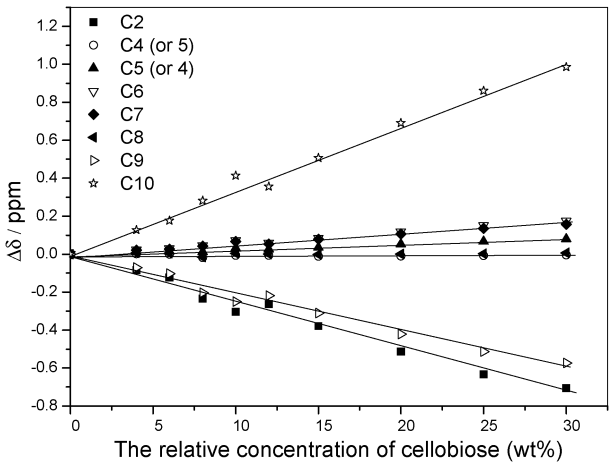

Fig. 7 Changes of carbon chemical shift difference in EmimAc with increasing [cellobiose] in DMSO-d_6 ($\Delta\delta = \delta - \delta_{neat}$).

anions to form hydrogen bonding with the aromatic protons in the imidazolium cation, especially for the most acidic H2. The weaker hydrogen bonding acceptor ability of the hydroxyl causes an upfield shift for the aromatic protons.[39,40] A similar trend of ^{7}Li-NMR has been observed by Morgenstern *et al.*[41] for cellulose dissolved in LiCl/DMAc. It has been interpreted as an exchange of DMAc in the lithium co-ordination sphere by cellulose hydroxyl groups, which have stronger shielding effect than DMAc. A similar interpretation has also been given by Erica Brendler *et al.* for cellulose dissolved in inorganic molten salt hydrates.[42,43] Therefore, the sites of imidazolium cation–cellobiose interaction are the aromatic protons in the imidazolium rings, especially H2. It can be expected that if H2 is substituted by other groups, the dissolving capability of ionic liquids for cellulose will decrease. This hypothesis has been supported by the observations of Barthel *et al.*[44]

The effect of cellobiose concentration on the ^{13}C chemical shifts of EmimAc has been investigated as well. The results are summarized in Fig. 7. The signal of the carboxyl moves downfield significantly, indicating that the acetate anions create stronger hydrogen bonding with hydrogens of hydroxyl groups.[28] Thus, the hydrogen bonding between the cation and anion in EmimAc is disrupted. Simultaneously, the cellobiose hydroxyl groups replace the acetate anions and form weaker hydrogen bonding with the ring protons in the imidazolium cation, therefore all carbon signals in the imidazolium cation (C2, C4 and C5) should remarkably move upfield.[21] The peak of C2 indeed shows a pronounced upfield change. However, because H4 and H5 are less acidic and weaker hydrogen bonding donors than H2, the hydrogen bonding interactions of H4 and H5 with the acetate anion are essentially weak in EmimAc/DMSO-d_6 solutions. Therefore, adding cellobiose into EmimAc/DMSO-d_6 solutions has a negligible impact on the chemical shifts of C4 and C5. These results further confirm the formation of hydrogen bonding between the hydroxyl groups and EmimAc. The upfield change of C9 is mainly attributed to the increase of electron density around the C9 nucleus, because the stronger hydrogen bonding between the carboxyl and hydroxyl groups causes electronic distribution of the acetate anion.

Based on the above results, we conclude that the hydrogen bonding is the main driving force for cellobiose dissolution into EmimAc. Therefore, if all hydroxyls of cellobiose were acetylated, there would be almost no chance for the hydrogen bonding between EmimAc and the acetylated cellobiose, *i.e.* cellobiose octaacetate (COA). Hence, COA could not be possibly dissolved in EmimAc. Actually, our experimental results prove our conjecture, showing that COA is hardly soluble in EmimAc even at high temperature, say 100 °C. Simultaneously, no change of both ^{1}H-NMR and ^{13}C-NMR spectra of COA is observed with the increase of EmimAc in DMSO-d_6 solutions (see Fig. 8 and ESI, Fig. S3),† implying the hydrogen bonding between hydroxyl groups of cellobiose and the anion and cation of EmimAc is the major driving force in the dissolution of cellobiose in EmimAc.

Since in DMSO-d_6 solution the hydrogen bonding between cellobiose and EmimAc is the major driving force in dissolving cellobiose into EmimAc, one may wonder if this mechanism would really work in the real system. In order to answer this question, we have measured NMR spectra of cellobiose and

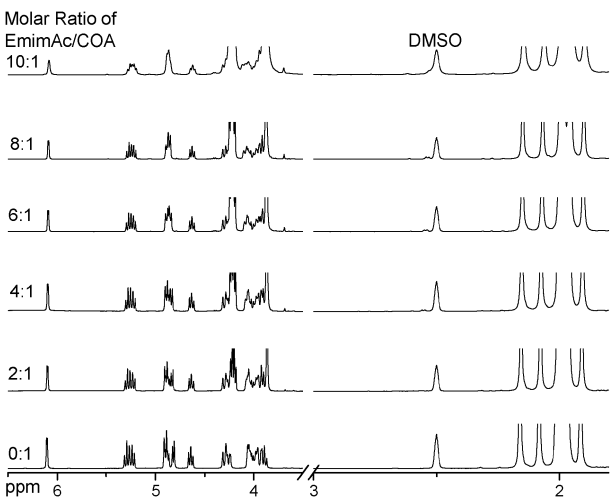

Fig. 8 Effect of molar ratios of EmimAc/COA on the ^{1}H-NMR spectra for COA in DMSO-d_6. (The bottom spectrum is the neat COA.)

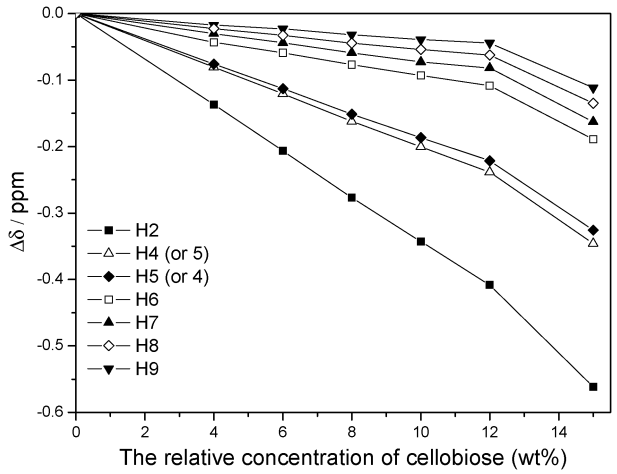

Fig. 9 [Cellobiose]-dependent chemical shift difference of protons in *in situ* ^{1}H-NMR of EmimAc ($\Delta\delta = \delta - \delta_{neat}$).

EmimAc *in situ*. The results are summarized in Fig. 9 and 10, which are similar to those in DMSO-d_6 solutions. As the cellobiose concentration is increased, the aromatic protons in the imidazolium cation show a pronounced upfield change in the chemical shift. The carbon signal of the carboxyl significantly moves downfield, while the carbon signal of C2 remarkably moves upfield. And the change trends of all signals are more prominent than those in DMSO-d_6 solutions. These phenomena suggest that the above mechanism model is quite suitable for the real system.

It is well known that hydrogen bonding will be broken as temperature increases, so temperature-dependent ^{1}H-NMR spectra of the cellobiose/EmimAc solution are also measured. By taking a cellobiose/EmimAc solution containing 15% cellobiose as an example (see ESI Fig. S4),† it can be clearly seen that the peaks of protons of cellobiose hydroxyls overlap each other, change into one unresolved broad peak and move downfield by 8.0 ppm at ambient temperature. This behavior is similar to the result observed in DMSO-d_6 solutions and indicates the hydrogen bonding is formed between hydroxyls of cellobiose and EmimAc at room temperature. As temperature

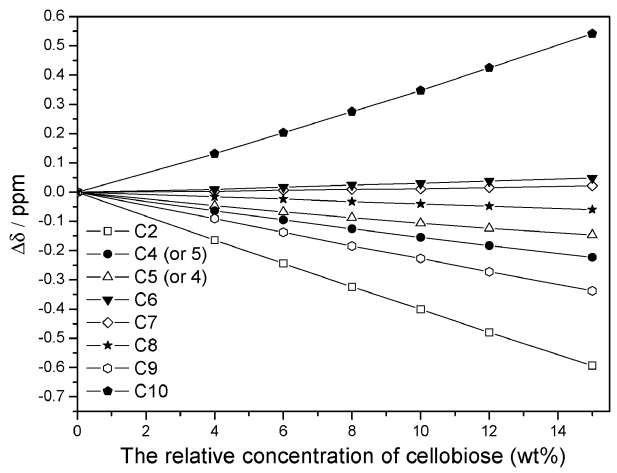

Fig. 10 [Cellobiose]-dependent chemical shift difference of carbons in *in situ* ^{13}C-NMR of EmimAc ($\Delta\delta = \delta - \delta_{neat}$).

increases, most of the NMR signals shift downfield. However, the overlapped peak of cellobiose hydroxy protons does not change. This phenomenon implies the hydrogen bonding between hydroxyls and EmimAc becomes weak, which offsets the temperature effect on the chemical shift change of hydroxy protons. The signals of protons in the cellobiose backbone become clear and exhibit good resolution at higher temperatures, mainly due to the decrease of solution viscosity and the dissociation and gradual solvation of cellobiose aggregates in EmimAc. Therefore, with the increase of temperature, there are two pairs of competition: the destruction *vs.* the formation of hydrogen bonding between cellobiose and EmimAc, and the formation of hydrogen bonding between cellobiose and EmimAc *vs.* the destruction of hydrogen bonding in cellobiose. Chemical shifts of protons in EmimAc are also affected as the increase of temperature. H8, which is affected mainly by the temperature, moves downfield significantly, while the extent of downfield shift of H2, H4 and H5 is lower than that of H8 (see ESI, Fig. S5).† This is because, except temperature, the hydrogen bonding between hydroxyls and EmimAc, which becomes weak as temperature increases, also affects the chemical shift of H2, H4 and H5. However relatively strong hydrogen bonding interactions still exist even at higher temperatures.

From the above results, we conclude that the hydrogen bonding between hydroxyls and cation and anion of EmimAc is the major reason responsible for the cellulose dissolution in the ionic liquid. The process of cellulose dissolving in EmimAc can be described as follows. Due to hydrogen bonding interaction, Coulomb interaction and π–π interaction, the pure ionic liquid exists mainly in the form of supramolecular aggregates, while a small amount of ionic liquid is in the form of free ions and tight ion pairs, which plays a pioneering role in cellulose dissolution in EmimAc. When cellulose is added into the ionic liquid, the relatively small free acetate anion, acting as a good hydrogen bond acceptor, first attacks the hydrogen atoms of the cellulose hydroxyls; then the bulky cation $[Emim]^{+}$ quickly associates with the oxygen atoms of the cellulose hydroxyls. After opening up the gap on the surface of cellulose, the anion and cation progressively attack the cellulose hydroxyls, disrupt hydrogen bonding in cellulose and lead to the dissolution of cellulose.

Therefore, in order to dissolve cellulose, the ionic liquid should satisfy at least three conditions: (1) the anion must be a good hydrogen bond acceptor; (2) the cation should be a moderate hydrogen bond donor, *i.e.* the cation has the moderate activated hydrogen for forming hydrogen bonding with oxygen atoms of hydroxyls of cellulose; and (3) the size of the cation is not too large.

The above results could explain several experimental phenomena such as the influence of co-solvents in ionic liquids on the solubility of cellulose. Because water is not only a better hydrogen bond donor than hydroxyls but also a good hydrogen bond acceptor, it could form strong hydrogen bonding with the free anion and cation of ionic liquids. As a result, the small amount of water (> 1 wt%) will solvate free ions in the ionic liquid and seriously impair the dissolving capability of the ionic liquid for cellulose.[8] In contrast to H_2O, the solvent dimethyl sulfoxide (DMSO) slightly strengthens the

interactions between cations and anions, because this solvent is a weak hydrogen bond acceptor and not a hydrogen bond donor. Thus, DMSO has a negligible effect on the dissolution of cellulose in ionic liquids.[37,45]

Conclusions

The present results provide direct evidence to confirm that the hydrogen bonding of hydroxyls with the acetate anion and imidazolium cation of EmimAc is the major force for cellulose dissolution in the ionic liquid. The relatively small acetate anion favors the formation of a hydrogen bond with the hydrogen atoms of the hydroxyls, whiles the aromatic protons in the bulky cation imidazolium, especially H2, prefer to associate with the oxygen atoms of hydroxyls with less steric hindrance. Hence, the ionic liquid capable of dissolving cellulose should be a good hydrogen bond acceptor, a moderate hydrogen bond donor with a high enough dissociation degree. The observed stoichiometric ratio of EmimAc/hydroxyl is between 3:4 and 1:1 in the primary solvation shell, implying that there should be one anion or cation to form hydrogen bonding with two hydroxyl groups simultaneously.

The effect of the structure of ionic liquids on the dissolution of cellulose will be discussed in another paper.

Experimental

Material

Cellobiose was obtained from Sinopharm Chemical Reagent Co. Ltd, China, and cellobiose octaacetate was supplied by BJ-MDS Biochem-Pharm Co. Ltd., China. They were dried at 80 °C in vacuum for 2 h prior to use. EmimAc was synthesized according to a previous literature source and dried under high vacuum at 80 °C for 2–3 days to remove water as much as possible. The water content in the ionic liquid was less than 300 ppm, determined using Karl Fischer analysis. DMSO-d_6 (99.9%, D), containing TMS (0.03%, v/v), was purchased from Cambridge Isotope Laboratories, Inc., USA.

Conventional NMR sample preparation

In order to observe the changes in ^{1}H and ^{13}C chemical shifts of cellobiose with increasing EmimAc concentration, samples of Series I (the molar ratios of EmimAc/cellobiose: 0:1, 0.2:1, 0.4:1, 0.8:1, 1:1, 2:1, 4:1, 6:1, 8:1, 10:1, 14:1, 20:1 and 30:1) were prepared by adding different amounts of EmimAc into solutions of 0.5 ml DMSO-d_6 and 30 mg cellobiose. In order to investigate the effect of cellobiose concentration on the proton and carbon chemical shifts of EmimAc, samples of Series II (cellobiose concentrations in EmimAc: 0, 4, 6, 8, 10, 12, 15, 20, 25, and 30 wt%) were prepared by adding different weights of cellobiose into the solution of 0.5 ml DMSO-d_6 and 100 mg EmimAc with constant stirring. Upon dissolution, these samples were transferred into 5 mm NMR tubes. For observing changes in ^{1}H and ^{13}C chemical shifts of cellobiose octaacetate with increasing EmimAc, samples of Series III (the molar ratios of EmimAc/cellobiose octaacetate: 0:1, 2:1, 4:1, 6:1, 8:1 and 10:1) were prepared by adding different amounts of EmimAc into the solution of 0.5 ml DMSO-d_6 and 30 mg cellobiose octaacetate. The DMSO-d_6 provided lock frequency. Both DMSO-d_6 and TMS were used as an internal reference in NMR spectra.

In situ NMR sample preparation

Samples of Series IV (cellobiose concentrations in EmimAc: 0, 4, 6, 8, 10, 12 and 15 wt%) were prepared by adding a known weight of cellobiose into EmimAc at 60 °C with constant stirring. After complete dissolution, the samples were transferred into 5 mm NMR tubing with coaxial capillary inserts containing $CDCl_3$ for ^{13}C-NMR or D_2O for ^{1}H-NMR, which provided a field-frequency lock and NMR external standards.

NMR instrumentation and experiments

The NMR spectra of samples in Series I, Series II and Series III were acquired on a Bruker AV 400 spectrometer with 16–32 scans for ^{1}H-NMR and 500–3000 scans for ^{13}C-NMR measurements at room temperature.

NMR spectroscopy tests of samples in Series IV 1–3 (neat EmimAc and 4–6 wt% solutions of cellobiose in EmimAc) were performed at 298 K, while those in Series IV 4–7 (8–15 wt% solutions of cellobiose in EmimAc) at temperatures ranging from 298 to 398 K. All experiments were measured on a Bruker AV 600 spectrometer.

Acknowledgements

The authors thank the National Natural Science Foundation of China (No. 50873111), the Chinese Academy of Sciences (No. KJCX.YW.H16), and the National Key Technology R&D Program (No. 2006BAC02A10) for financial support.

References and notes

1 D. Klemm, B. Heublein, H. P. Fink and A. Bohn, *Angew. Chem., Int. Ed.*, 2005, **44**, 3358–3393.
2 T. Heinze and T. Liebert, *Prog. Polym. Sci.*, 2001, **26**, 1689–1762.
3 T. Heinze, *Macromol. Chem. Phys.*, 1998, **199**, 2341–2364.
4 P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772–3789.
5 R. D. Rogers and K. R. Seddon, *Ionic Liquids: Industrial Applications for Green Chemistry*, American Chemical Society, Washington, DC, 2002.
6 O. A. El Seoud, A. Koschella, L. C. Fidale, S. Dorn and T. Heinze, *Biomacromolecules*, 2007, **8**, 2629–2647.
7 C. Graenacher, *Cellulose Solution*, US patent, 1943176, 1934.
8 R. P. Swatloski, S. K. Spear, J. D. Holbrey and R. D. Rogers, *J. Am. Chem. Soc.*, 2002, **124**, 4974–4975.
9 J. Wu, J. Zhang, H. Zhang, J. S. He, Q. Ren and M. L. Guo, *Biomacromolecules*, 2004, **5**, 266–268.
10 Y. Fukaya, A. Sugimoto and H. Ohno, *Biomacromolecules*, 2006, **7**, 3295–3297.
11 H. Zhao, G. A. Baker, Z. Y. Song, O. Olubajo, T. Crittle and D. Peters, *Green Chem.*, 2008, **10**, 696–705.
12 T. Liebert and T. Heinze, *BioResources*, 2008, **3**, 576–601.
13 R. C. Remsing, R. P. Swatloski, R. D. Rogers and G. Moyna, *Chem. Commun.*, 2006, 1271–1273.
14 R. C. Remsing, G. Hernandez, R. P. Swatloski, W. W. Massefski, R. D. Rogers and G. Moyna, *J. Phys. Chem. B*, 2008, **112**, 11071–11078.
15 T. G. A. Youngs, J. D. Holbrey, M. Deetlefs, M. Nieuwenhuyzen, M. F. Costa Gomes and C. Hardacre, *ChemPhysChem*, 2006, **7**, 2279–2281.
16 T. G. A. Youngs, C. Hardacre and J. D. Holbrey, *J. Phys. Chem. B*, 2007, **111**, 13765–13774.

17 H. Zhang, J. Wu, J. Zhang and J. S. He, *Macromolecules*, 2005, **38**, 8272–8277.
18 B. Bernet and A. Vasella, *Helv. Chim. Acta*, 2000, **83**, 2055–2071.
19 N. F. Chamberlain, *The Practice of NMR Spectroscopy, with Spectra-Structure Correlations for Hydrogen-1*, Plenum Press, New York, 1974.
20 N. X. Wang, *Nuclear Magnetic Resonance Spectroscopy —Applications in Organic Chemistry*, Chemical Industry Press, Beijing, 2006.
21 A. G. Avent, P. A. Chaloner, M. P. Day, K. R. Seddon and T. Welton, *J. Chem. Soc., Dalton Trans.*, 1994, 3405–3413.
22 E. Yashima, C. Yamamoto and Y. Okamoto, *J. Am. Chem. Soc.*, 1996, **118**, 4036–4048.
23 C. L. McCormick, P. A. Callais and B. H. Hutchinson, *Macromolecules*, 1985, **18**, 2394–2401.
24 S. N. Vinogradov and R. H. Linnell, *Hydrogen Bonding*, Van Nostrand Reinhold Company, New York, 1971.
25 D. Hadži and H. W. Thompson, *Hydrogen Bonding*, Symposium Publications Division Pergamon Press, Now York, 1959.
26 G. E. Maciel and D. D. Traficante, *J. Am. Chem. Soc.*, 1966, **88**, 220–223.
27 E. Breitmaier and G. Bauer, *Pharm. Unserer Zeit*, 1976, **5**, 97–123.
28 R. Hagen and J. D. Roberts, *J. Am. Chem. Soc.*, 1969, **91**, 4504–4506.
29 D. E. Dorman and J. D. Roberts, *J. Am. Chem. Soc.*, 1971, **93**, 4463–4472.
30 D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, 1972, **94**, 5318–5324.
31 E. Breitmaier and W. Voelter, *Carbon-13 NMR Spectroscopy: High Resolution Methods and Applications in Organ. Chemistry and Biochemistry*, 3rd completely revised edition, VCH, Weinheim, 1987.
32 K. Dong, S. J. Zhang, D. Wang and X. Q. Yao, *J. Phys. Chem. A*, 2006, **110**, 9775–9782.
33 K. M. Dieter, C. J. Dymek, N. E. Heimer, J. W. Rovang and J. S. Wilkes, *J. Am. Chem. Soc.*, 1988, **110**, 2722–2726.
34 T. Singh and A. Kumar, *J. Phys. Chem. B*, 2007, **111**, 7843–7851.
35 J. Dupont, *J. Braz. Chem. Soc.*, 2004, **15**.
36 A. D. Headley and N. M. Jackson, *J. Phys. Org. Chem.*, 2002, **15**, 52–55.
37 Y. Chu, H. Deng and J. P. Cheng, *J. Org. Chem.*, 2007, **72**, 7790–7793.
38 S. T. Handy and M. Okello, *J. Org. Chem.*, 2005, **70**, 1915–1918.
39 H. Shimura, M. Yoshio, K. Hoshino, T. Mukai, H. Ohno and T. Kato, *J. Am. Chem. Soc.*, 2008, **130**, 1759–1765.
40 M. R. Chierotti and R. Gobetto, *Chem. Commun.*, 2008, 1621–1634.
41 B. Morgenstern, H. W. Kammer, W. Berger and P. Krabal, *Acta Polym.*, 1992, **43**, 356–357.
42 E. Brendler, S. Fischer and H. Leipner, *Cellulose*, 2001, **8**, 283–288.
43 S. Fischer, H. Leipner, K. Thümmler, E. Brendler and J. Peters, *Cellulose*, 2003, **10**, 227–236.
44 S. Barthel and T. Heinze, *Green Chem.*, 2006, **8**, 301–306.
45 R. C. Remsing, Z. W. Liu, I. Sergeyev and G. Moyna, *J. Phys. Chem. B*, 2008, **112**, 7363–7369.