Dissolution, regeneration and ion-gel formation of agarose in room-temperature ionic liquids

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The suitability of several ionic liquids, containing imidazolium or pyridinium cations with different alkyl chains and anions ranging from small hydrogen-bond acceptors to those of a large and non-coordinating nature, has been tested for solubilization of a widely used biopolymer, agarose. The solubility of agarose was found to depend on both the nature of anion and amphiphilicity of the cation. Dissolved agarose was regenerated using methanol, and ionic liquids were recovered and recycled for different experiments. Regenerated agarose largely maintained the features of native agarose in terms of molecular weight, polydispersity, thermal stability and crystallinity but varied slightly in conformation preferences. Subsequently, agarose-based highly conducting soft ion-gels having small thermal hysteresis were prepared and characterized. Such ion-gels have possible applications as electrochemical devices.

Introduction

The biopolymer agarose, an algal polysaccharide comprising of alternating D-galactose and 3,6-anhydro-L-galactose repeating units, is essentially uncharged, and is often used as a model system in gelation. Hot-water agarose sols form thermoreversible hydrogels which find numerous applications in various fields such as food industry, pharmaceutical formulations, electrophoresis, tissue engineering or as a matrix for soft-matter organic devices.[1–3] However, the large number of hydroxyl groups makes agarose insoluble in cold water and many common organic solvents. Also, the high temperature solubility of agarose in water creates difficulties in functionalization of agarose and limits its applications. Therefore it is imperative to search for alternative media that can dissolve agarose effectively without degrading the material property, and from which the material can be regenerated in adequate yields.

Room-temperature ionic liquids (RTILs), owing to their unique physical and chemical properties, are emerging as alternative solvents for various chemical processes. One can finely tune the desired properties such as polarity, viscosity, thermal stability, conductivity and solvent capacity in RTILs by making a judicious choice of cations and anions.[4–10] RTILs can also be considered as somewhat greener than the conventional volatile organic solvents in terms of their very low vapour pressure and high thermal stability, and ease of recycling without much deterioration in their physical properties. In recent years the role of RTILs as a potential media for dissolution and blending of a variety of bio-macromolecules (mainly cellulose) has been investigated by various research groups. Rogers and co-workers, as pioneers, carried out the dissolution and processing of cellulosic materials in RTILs to obtain carbohydrate-free lignin- and cellulose-rich materials.[11–13] The dissolution of lignocellulosic materials have also been examined in RTILs.[14–17] These studies indicate that the dissolution of cellulose, the main component of wood, is based on the disruption of the inter- and intramolecular hydrogen-bonding of cellulose and the formation of new hydrogen bonds between the carbohydrate hydroxyl protons and the anions of the IL. Zhang *et al.* also conducted a comprehensive study on cellulose dissolution and derivatization in RTILs.[18–20] Jürgen *et al.* investigated cellulose solubility in a variety of RTILs and have shown the extended solubility of cellulose in phosphate-containing ionic liquids.[21] Existing studies reveal that not only the nature of anion, but also the alkyl chain length of the cation, is also a determinant in controlling the cellulose solubility. Recently, in a review, Ohno *et al.* described the design of ionic liquids for dissolution, depolymerization, and energy conversion of cellulose and their derivatives.[22] Though most of the work in the literature pertaining to biopolymer solubility in RTILs is focused on cellulose, other biomolecules such as proteins (silk fibres and cytochrome), polysaccharides (chitin, chitosan, keratin, dextran, inulin, amylose, pectin, xylan *etc.*) or carbohydrates (glucose, fructose, sucrose and lactose) have also been tested for solubilization.[23–28]

In this work, we studied the dissolution characteristics of polysaccharide agarose in various RTILs. The influence of different side-chain lengths of cation in combination with various anions on the dissolution properties and possible degradation of agarose during the dissolution process was investigated. Agarose dissolved in RTILs was regenerated using methanol. The physicochemical properties of the regenerated agarose have been characterized and compared with that of native agarose. Further, the ability of RTILs to dissolve agarose was used to prepare agarose-based ion-gels. Although the confinement of RTILs in organic polymers such as Nafion, polyvinylidene fluoride (PVdF), polyacrylonitrile (PAN), polymethylmethacrylate (PMMA), polyethylene oxide (PEO), and

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poly(styrene-*b*-methylmethacrylate-*b*-styrene) (PS-PMMA-PS) has been carried out, and successfully tested in some cases for electrochemical applications,[29–35] the confinement of RTILs in biopolymers has been rarely studied.[36–38] Recently, Vidinha *et al.* prepared gelatin-based ion-gels and built an electrochromic window based on Prussian Blue (PB) and poly(3,4-ethylenedioxythiophene) (PEDOT) as electrochromic layers, showing the utility of biopolymer-based ion-gels for electrochemical devices.[36]

We prepared agarose-based ion-gels as smart polymeric conducting materials that combine the chemical versatility of an ionic liquid with the morphological versatility of a biopolymer. Ion-gels have been characterized for gelling, melting and conducting behaviour. The ion-gels thus prepared can be applied in various electrochemical devices, such as soft organic diodes which can produce a unidirectional current response, batteries, fuel cells, electrochromic windows or photovoltaic cells, and can overcome the complexities pertaining to the processing techniques encountered in case of organic polymer ion-gels.

Experimental

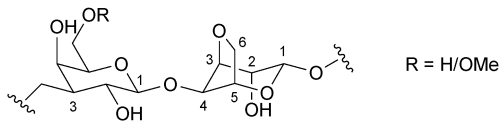
Materials

RTILs: 1-butyl-3-methylimidazolium chloride [C_4mim][Cl], 3-methyl-1-octylimidazolium chloride [C_8mim][Cl], 1-butyl-3-methylimidazolium tetrafluoroborate [C_4mim][BF_4], 3-methyl-1-octylimidazolium tetrafluoroborate [C_8mim][BF_4], *N*-butyl-3-methylpyridinium chloride [C_4mpy][Cl], 1-butyl-3-methylimidazolium methylsulfate [C_4mim][C_1OSO_3], 1-butyl-3-methylimidazolium octylsulfate [C_4mim][C_8OSO_3] and 1-butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6] with stated purities higher than 98% mass fraction, were purchased from Merck. The RTILs were further purified and dried as described in our earlier publication.[39] In brief, the ILs were washed and decolorized in a column comprising of Celite, silica and charcoal using HPLC-grade dichloromethane as solvent. After decolorization, the ILs were dried and degassed under vacuum at 60 °C for 48 h. The process of decolorization and drying was repeated until concordant absorption spectra with no further reduction in the absorption were recorded. Karl–Fisher analysis of the samples indicated that the water content was reduced to less than 0.02 wt% in all the liquids. Agarose was extracted from the red alga *Gracilaria dura* from the Arabian Sea on the west coast of India. The agarose preparation process corresponded to a patent specification (Siddhanta *et al.*, 2005).[40] The agarose (1.5%) had gel strength 1400 g cm^{-2}, gelling temperature 35 °C, sulfate content ≤0.25%, $[\alpha]_{589}^{45}$ −22° and M_w 1.63 × 10^5 g mol^{-1}. Scheme 1 shows the structure of the agarose monomer unit and the constituent ions of the RTILs used in this study.

Solubilization, regeneration and preparation of ion-gels

Dissolution of agarose in different RTILs was carried out in 10 ml beakers with continuous stirring with a magnetic stirrer in a glove box under an atmosphere of N_2. The temperature of the dissolving process was controlled to ±1 °C. Finely powdered agarose was added to RTILs (approx. 5 g) in portions of

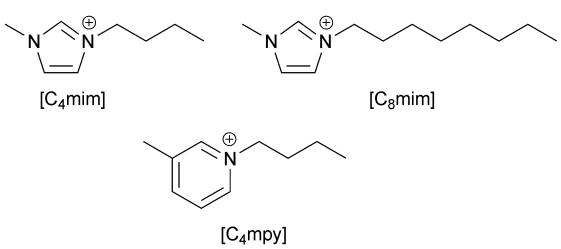
Idealized repeat unit of agarose:



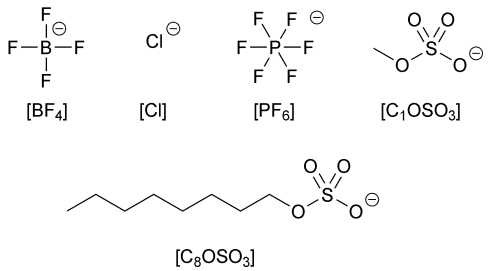
1,3-β-D-galactose 1,4-α-L-3,6-anhydrogalactose

Constituent ions of the RTILs used in this study:

Cations:



Anions:



Scheme 1

0.5 wt% every time until the material disappeared. Addition was carried out until the resulting ionic liquid solutions were clear. Dissolution experiments were conducted at 70 °C and were monitored visually. The agarose was regenerated from the solutions by adding methanol and dried in an oven at 60 °C for further characterization. The completion of regeneration was monitored visually. Complete regeneration was ensured by addition of an excess amount of methanol to the solutions left after regeneration. No further precipitation indicated complete regeneration. The yield of the regenerated material was always >95 wt%. After regeneration of agarose, RTILs were recovered from the methanolic solutions using a rotary evaporator. For ion-gel preparation, agarose was dissolved in preheated RTILs to form a 3 wt% solution. After complete dissolution at around 70 °C, viscous clear solutions were allowed to cool for gelling.

Characterization

Molecular weight of native and regenerated agarose was determined through high-temperature gel permeation chromatography (HT-GPC) using a Waters 2695 Separation Module equipped with a 2414 RI detector and having Ultrahydrajel 500 and 120 columns in series. Columns were eluted with 0.1 M aqueous $NaNO_3$ at a flow rate of 0.5 ml/min. Calibration was performed using Dextran standard ranging from 401000 to 4400 peak molecular weight. The concentration of agarose solutions in water was 0.02% w/w. FT-IR spectra of the native

Table 1 Solubility of agarose in RTILs at 70 °C, and gelling temperature (T_{gel}), melting temperature (T_m), molecular weight (M_n and M_w), polydispersity (P) and crystallinity indices (CI) of regenerated agarose (2 wt%)

Water/RTILs	Solubility (wt%)	T_{gel} (°C)	T_m (°C)	M_n	M_w	P	CI
H_2O	8.0	36	84	83950	163000	1.87	12.0
[C_4mim][Cl]	16.0	32	78	77850	152000	1.95	8.8
[C_4mim][BF_4]	Insoluble	—	—	—	—	—	—
[C_4mim][PF_6]	Insoluble	—	—	—	—	—	—
[C_4mim][C_1OSO_3]	5.0	34	76	81100	162400	2.00	11.5
[C_4mim][C_8OSO_3]	Insoluble	—	—	—	—	—	—
[C_8mim][Cl]	4.5	32	74	70250	142300	2.03	10.7
[C_8mim][BF_4]	Insoluble	—	—	—	—	—	—
[C_4mPy][Cl]	13.0	28	70	39500	98200	2.49	10.1

and regenerated materials were recorded at room temperature using NICOLET 6700 FT-IR spectrometer. Thermogravimetric analyses were performed on a TGA/SDTA851 Mettler Toledo under nitrogen atmosphere from 30 to 450 °C with a heating rate of 10 °C min^{-1}. X-ray measurements were performed using a Philips X'pert MPD system with CuKα radiation (λ = 1.54056 Å). Surface morphology was examined through SEM using a LEO 1430 VP Carl Zeiss scanning electron microscope. For recording the micrograph, samples of equal thickness were gold-coated. Circular dichroism (CD) spectra of agarose solutions (0.05 wt%) in a wavelength range of 180 to 240 nm were recorded on a Jasco J-815 CD spectrometer. Experiments were carried out in a 1 cm path length cuvette at 25 °C, and were expressed as the average of five scans. The response time and the bandwidth were 2 s and 0.2 nm respectively. Samples for recording the spectra were taken in a quartz cuvette which was immediately sealed after sampling to avoid evaporation. The desired temperature was achieved with an inbuilt peltier device. The melting and gelling temperature of hydrogels/ion-gels was determined following the method described by Craigie & Leigh.[41] Conductivity measurements were carried out with a digital conductivity meter (SYSTRONICS, Conductivity TDS Meter 308) in a manner similar to that described by Wenjing *et al.*[42] The cell constant was determined with aqueous KCl solutions of varying concentrations. Since measurements are at single frequency, hence the effects of electrode polarization are not taken into account. Small discrepancies could also be caused by a little bit of moisture contamination. Because of the non-availability of data in open literature, we could not compare temperature dependence of conductivity of the investigated RTILs. During measurements the sample and the electrode were sealed in a glass cell and placed in a constant-temperature water bath. The repeatability and estimated uncertainty of the measurements are ±1% and ±3% respectively. The glass transition temperatures (T_g) for the ILs were determined using differential scanning calorimetry measurements using a Mettler Toledo DSC822 thermal analyzer. Measurements were performed between −120 and 20 °C at a heating rate of 5 °C min^{-1}.

Results and discussion

Dissolution and regeneration

We conducted solubility experiments of agarose in the following RTILs: [C_4mim][Cl], [C_8mim][Cl], [C_4mim][BF_4], [C_8mim][BF_4], [C_4mpy][Cl], [C_4mim][C_1OSO_3], [C_4mim][C_8OSO_3] and [C_4mim][PF_6]. Solubility results at 70 °C are listed in Table 1. From Table 1, it can be seen that the agarose is soluble in [C_4mim][Cl], [C_8mim][Cl], [C_4mpy][Cl], [C_4mim][C_1OSO_3] whereas [C_4mim][BF_4], [C_8mim][BF_4] and, [C_4mim][C_8OSO_3] could not dissolve it. The solubility of agarose in RTILs depends on the nature of both cation and anion. For same alkyl chain length, RTILs containing chloride anion show better solubility for agarose as compared to the methylsulfate anion. RTILs comprising the non-coordinating tetrafluoroborate or hexafluorophosphate anions, or the amphiphilic octylsulfate anion, did not dissolve agarose. Similar to cellulose, high efficiency of RTILs containing chloride anion, such as [C_4mim][Cl] and [C_4mpy][Cl], for agarose solubilisation is due to strong interaction of chloride ions with the hydroxyl groups because of the very high hydrogen-bonding basicity of these ionic liquids. The interactions between chloride ions with the hydroxyl groups leads to disruption of the hydrogen-bonding network of the polymer and results in a higher solubility. RTILs having a longer alkyl chain at the cation are less efficient in dissolving agarose, whereas the cations 1-butyl-3-methylimidazolium and *N*-butyl-3-methylpyridinium have comparable solvating ability. Unlike cellulose, where the alkyl chain length of the cation has very limited effect on solubility,[21] we observed a remarkable decrease of solubility of agarose with increase in alkyl chain length of the cation (*e.g.* 16 and 4.5 wt% agarose could be dissolved in [C_4mim][Cl] and [C_8mim][Cl] respectively). The solubility of other biopolymers, like chitin (10 wt% at 110 °C), chitosan (10 wt% at 110 °C), starch (10 wt% at 80 °C) or amylopectin (5 wt% at 70 °C) in [C_4mim][Cl] is lower than agarose.[26–28] The solubility of mono- or disaccharides (glucose, fructose or sucrose) in the same IL is also lower (5 wt% at 70 °C) than agarose. Similar to agarose, other biomolecules are not very soluble in those ILs with large non-coordinating anions such as [BF_4] and [PF_6].

Agarose was regenerated from RTILs by adding the solutions to methanol at room temperature. Mixtures were stirred for about 1 h to ensure complete precipitation. Regenerated material was again checked for its gelling and melting behaviour in water. Both gelling and melting temperature of hydrogels prepared from regenerated agarose lowered slightly (Table 1). The lowest gelling temperature was observed for the hydrogel prepared using agarose regenerated from [C_4mpy][Cl], indicating some degradation of material. In order to examine the possible degradation of the material, we determined the molecular weight from gel permeation chromatography and recorded

FTIR spectra of the regenerated agarose. The molecular weight and polydispersity index of the material is noted in Table 1. Results show that agarose regenerated from [C_4mim][C_1OSO_3], [C_8mim][Cl] and [C_4mim][Cl] had comparable molecular weights to that of native agarose, whereas the material regenerated from [C_4mpy][Cl] had lower molecular weight. FTIR spectra of the native and regenerated agarose are compared in Fig. 1. The spectra show that regenerated agarose largely maintains its native structure. Characteristic IR bands at 773, 894 and 932 cm^{-1} (due to the 3,6-anydro-*b*-galactose skeletal bending in agarose[40]) remain unaltered in the material regenerated from water, [C_4mim][C_1OSO_3] and [C_8mim][Cl], but appear slightly diminished when regenerated from [C_4mim][Cl] and [C_4mpy][Cl]. The IR bands at 1158 and 1071 cm^{-1} (corresponding to C–O–C and glycosidic linkage[43,44]) are also altered in the regenerated material. No peak corresponding to the imidazolium or pyridinium moiety indicates that these RTILs are a fairly non-coordinating media for dissolution of agarose. Since FTIR bands indicated the alterations in local linkage geometries, we recorded the circular dichroism (CD) spectra of agarose regenerated from various RTILs for the examination of expected conformational changes. The CD spectrum of polysaccharides is an indicator of their overall secondary structure, and in the case of agarose, a characteristic CD spectrum with a positive band centred at ~185 nm is observed. In solution, the low intensity of the band is the consequence of highly extended chain geometries. Analysis of CD spectra (Fig. 2) reveals distinct conformational preferences in the chains of regenerated agarose. The material regenerated from solutions of [C_4mim][C_1OSO_3] reproduces the features of native agarose with only a slight loss in intensity, and indicate very limited conformational change in the regenerated material. The CD band of the agarose regenerated from [C_8mim][Cl] and [C_4mim][Cl] appears to be red-shifted, with a loss in intensity. Significant loss in intensity in case of agarose regenerated from [C_4mim][Cl] suggests the disruption of the ordered structure. In case of agarose regenerated from [C_4mpy][Cl], a very large decrease in the CD band intensity is observed, and the band is highly red-shifted, which is indicative of both change in conformation and disruption of ordered structure.

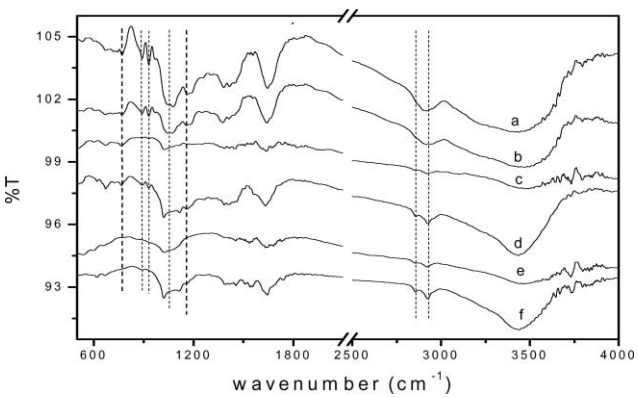


Fig. 1 FTIR spectra of agarose regenerated from various solutions: (a) native agarose; (b) water; (c) [C_4mim][C_1OSO_3]; (d) [C_8mim][Cl]; (e) [C_4mim][Cl]; (f) [C_4mpy][Cl]. Spectra are shifted vertically for clarity.

Thermal stability of the regenerated material was checked by performing thermo-gravimetric analysis (TGA). TGA profiles are shown in Fig. 3. The decomposition of both the native and regenerated material is characterized by a narrow temperature range from 275 to 300 °C. Agarose regenerated from RTILs when compared to the native material show nearly same onset temperature except that from [C_8mim][Cl], which shows a slightly lower onset temperature. No significant weight loss was observed in TGA curves of the agarose regenerated from [C_4mim][Cl], [C_4mpy][Cl] and [C_4mim][C_1OSO_3] before the decomposition temperature. The very low weight loss suggests that the agarose regenerated from these RTILs retained less moisture. Since TGA measurements are at relatively high heating rates (10 °C min^{-1}), data can be considered semi-qualitatively.

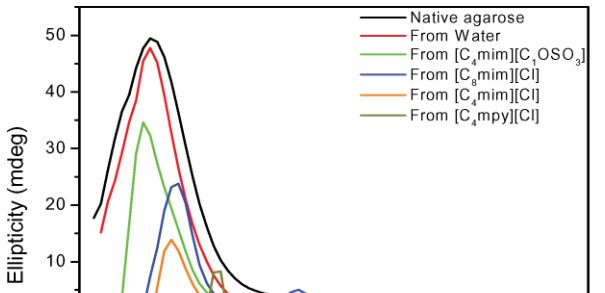


Fig. 2 CD spectra of native and regenerated agarose in aqueous solutions (0.05 wt%) recorded at 25 °C.

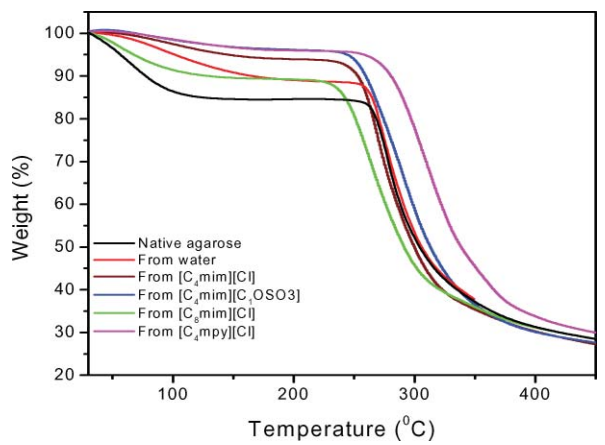


Fig. 3 Thermal decomposition profiles of native and regenerated agarose. Samples were heated under nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

X-ray diffraction spectra were collected for original and regenerated agarose. The diffractograms shown in Fig. 4 show a small broad peak around $2\theta = 20°$ for the native as well as for regenerated agarose. The crystallinity indices determined from the ratio of area of crystalline peak to the total peak area is very low for the native agarose, and did not change much for the regenerated material (Table 1). The absence of sharp or narrow peaks and the low crystallinity indicate that the regenerated material, like native agarose, is amorphous in nature. We examined the surface morphology of the native and regenerated material by recording SEM micrographs at similar

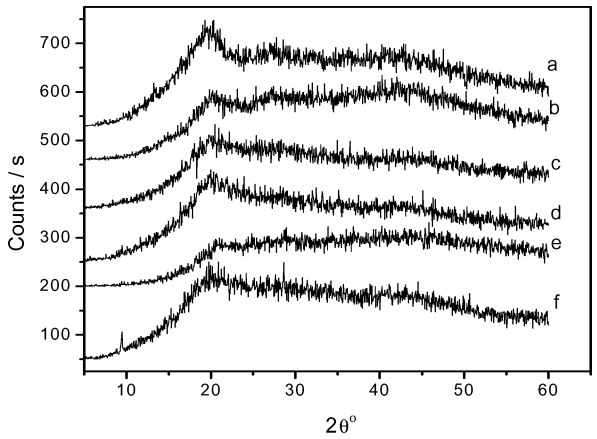


Fig. 4 PXRD spectra of agarose regenerated from various solutions: (a) native agarose; (b) water; (c) [C_4mim][C_1OSO_3]; (d) [C_8mim][Cl]; (e) [C_4mim][Cl]; (f) [C_4mpy][Cl]. Spectra are shifted vertically for clarity.

magnification. Fig. 5 shows that surface morphology of the material regenerated from different RTILs resembled that of native agarose, except that regenerated from [C_4mpy][Cl], which shows a certain degree of modification in surface roughness.

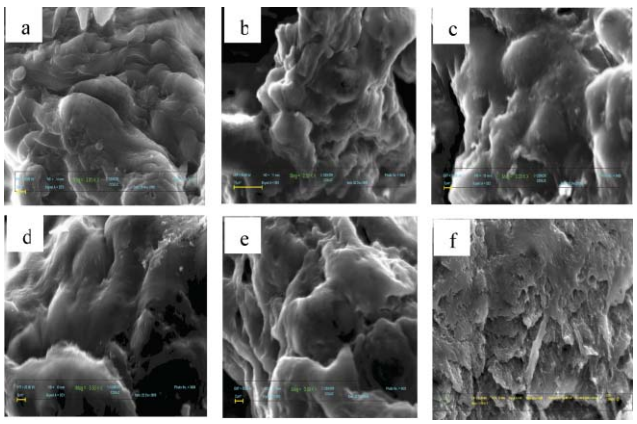


Fig. 5 SEM micrographs of agarose regenerated from various solutions: (a) native agarose; (b) water; (c) [C_4mim][C_1OSO_3]; (d) [C_8mim][Cl]; (e) [C_4mim][Cl]; (f) [C_4mpy][Cl].

Ion-gels

Upon cooling, the viscous solutions of agarose in RTILs (except that of [C_4mpy][Cl]) formed thermoreversible conducting ion-gels (Fig. 6). For a reasonable comparison, we prepared 3 wt% ion-gels in different ionic liquids. Dried and powdered agarose was dissolved in preheated RTILs and allowed to cool to room temperature. Different solutions gelled at different temperatures. Gelling and melting temperatures of various ion-gels were monitored through visual inspection of the liquid and gel state. Agarose solutions of [C_4mim][Cl] and [C_8mim][Cl] gelled at temperatures about 5 °C higher and 5 °C lower, respectively, than the corresponding hydrogel, whereas the solutions of [C_4mim][C_1OSO_3] gelled at lower temperatures. The physicochemical observations of different ion-gels are recorded in Table 2. As can be seen from Table 2, unlike agarose hydrogels, ionic-gels lacked thermal hysteresis, and have only a narrow range of gelling and melting temperature. The formation of

Table 2 Gelling temperature (T_{gel}), melting temperature (T_m) and ionic conductivity of RTILs and ion-gels at gel temperature

RTILs	T_{gel} (°C)	T_m (°C)	κ_{RTILs} (mS cm^{-1})	$\kappa_{Ion\text{-}gel}$ (mS cm^{-1})
[C_4mim][Cl]	40	53	0.250	0.290
[C_4mim][C_1OSO_3]	17	25	0.802	0.854
[C_8mim][Cl]	30	35	0.034	0.049
[C_4mPy][Cl]	Viscous liquid	—	Solid	—

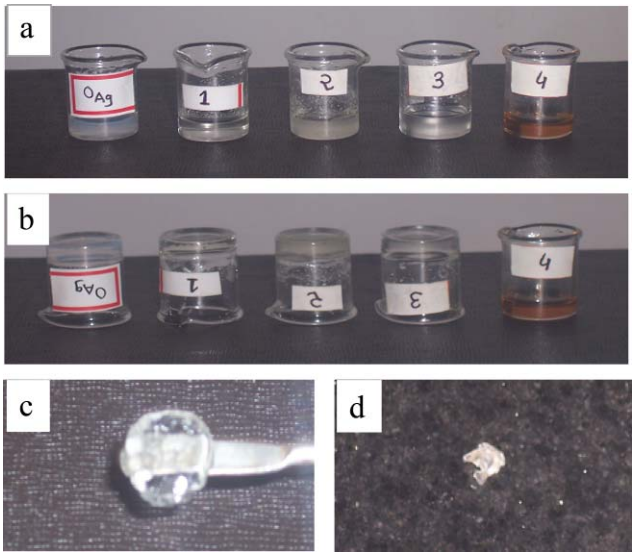


Fig. 6 (a) Agarose sols (3 wt%): (o_{Ag}) water; (1) [C_4mim][C_1OSO_3]; (2) [C_8mim][Cl]; (3) [C_4mim][Cl]; (4) [C_4mpy][Cl]; (b) ion-gels (no gel formation in [C_4mpy][Cl]); (c) stable ion-gel and (d) shrunk hydro-gel.

ion-gels is expected to occur in slightly different fashion compared to that of water-based agarose gels. Since agarose is essentially a neutral biopolymer, hydrogen-bonding between RTILs and the hydroxyl groups of the agarose molecules must play an important role in gelling. The presence of large ions will interact with agarose strands and prevent the formation of double helical structures, and finally lead to a weaker gel. For comparison of biopolymer-based ionic gels, we found only one (very recent) report, wherein Vidinha *et al.* prepared ion-gels using gelatin and ionic liquids.[36] In such gels both the matrix and solvents are charged, and gel formation is governed primarily by electrostatic interactions. They were able to prepare gelatin-based ion-gels in many imidazolium-based ionic liquids, but the ratio of RTIL and gelatin was too high (ranging from 6 : 1 to 1 : 3). A higher matrix–solvent ratio leads to gels with low conductivity (which is normally two orders of magnitudes less than those of pure RTILs). Here, agarose-based ion-gels have the advantage that a very small amount of agarose is sufficient to prepare ion-gels, and hence the conducting properties of the native RTILs can be retained in the gels. We examined the conductivity behaviour of various ion-gels and compared them with the conductivity of the native RTILs. Fig. 7 shows the comparison of temperature dependence of conductivity of ion-gels and pure RTILs. For both neat RTILs and ion-gels the temperature dependence of conductivity follows a similar track and increases monotonously with increasing temperature. The

Table 3 VFT equation parameters of ionic conductivity data

RTILs/RTILs + agarose (3 wt%)	$\ln\kappa_0$ (mS cm^{-1})	B (K)	T_0 (K)	T_g (K)
[C_4mim][C_1OSO_3]	6.46 ± 0.04	711.4 ± 5.5	183.0 ± 2.0	187
[C_4mim][C_1OSO_3] + agarose	6.63 ± 0.02	764.7 ± 2.4	176.2 ± 3.0	—
[C_4mim][Cl]	9.55 ± 0.03	1408.1 ± 4.0	184.5 ± 2.0	197
[C_4mim][Cl] + agarose	10.23 ± 0.12	1578.6 ± 16.0	175.5 ± 3.0	—
[C_8mim][Cl]	9.55 ± 0.12	1784.9 ± 17.9	165.0 ± 2.0	190
[C_8mim][Cl] + agarose	9.98 ± 0.26	1928.7 ± 42.6	155.0 ± 3.0	—

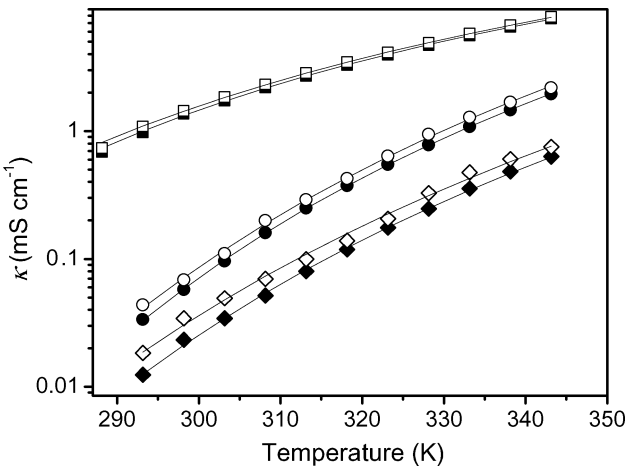


Fig. 7 Temperature dependence of ionic conductivity in neat RTILs: (■) [C_4mim][C_1OSO_3]; (●) [C_4mim][Cl]; (◆) [C_8mim][Cl]. Hollow symbols correspond to agarose–RTIL sol–gels (3 wt%). The corresponding VFT data is plotted as solid lines.

conductivity data is reasonably well fitted by the Vogel–Fulcher–Tammann (VFT) equation,[45]

$$\ln\kappa = \kappa_0 \exp[-B/(T - T_0)] \quad (1)$$

where κ_0 and B are fit parameters and T_0 is the so-called VFT temperature. The fitted curves together with the experimental data are shown in Fig. 7. The best-fit parameters for specific conductivity are given in Table 3. The VFT temperature, T_0 (which in general is considered as the glass transition temperature, T_g, for glass-forming compounds), has been measured using DSC. T_0 and T_g are compared in Table 3. Consistent with the literature,[46] the VFT temperatures are below the glass transition temperatures (T_g) determined using differential scanning calorimetry.

Conductivity depends mainly on the nature of the constituent ions of the RTILs. The conductivity of [C_4mim][C_1OSO_3] is very high compared to [C_8mim][Cl] and [C_4mim][Cl]. The temperature dependence of the conductivity is also very sensitive in the case of [C_4mim][C_1OSO_3], and shoots up from 0.74 to 7.59 mS cm^{-1} when the temperature is raised from 15 to 70 °C. Increasing temperature introduces thermal motion and may lead to a cooperative mechanism of ion conduction between cation and anion at higher temperatures. The low viscosity of [C_4mim][C_1OSO_3] is also responsible for its higher conductivity. The conductivity difference between [C_8mim][Cl] and [C_4mim][Cl] is larger at high temperatures. Over the investigated temperature range, the conductivity of the ion-gel is even higher (4–6%) than the pure RTILs. This higher conductivity in agarose sols and gels of RTILs is perhaps due to the inherent moisture and traces of metal ions in agarose. Like gelatin-based ion-gels,[36] agarose-based ion-gels, when connected to a power supply, lit up an LED, thus exhibiting mixed electronic and ionic conduction. Additional measurements will be necessary to utilize these ion-gels in electrochemical devices.

Conclusions

The dissolution characteristics of the biopolymer agarose have been studied in different RTILs. Hydrophobic RTILs did not dissolve agarose, whereas shorter side-chain length hydrophilic ionic liquids with chloride anion showed good dissolving ability. Dissolved agarose was regenerated using methanol and found to retain its native properties. Agarose regenerated from a solution of [C_4mpy][Cl] was slightly degraded. Agarose dissolved in RTILs (except [C_4mpy][Cl]) formed soft ion-gels, without compromising the conductivity of the neat RTILs. Ion-gels prepared in [C_4mim][C_1OSO_3] were found to be highly conducting. The studies will be helpful in utilizing RTILs as a novel non-coordinating media for functionalization of agarose and preparation of highly conducting biopolymer-based ion-gels for different electrochemical applications. The studies will also widen the use of confined ionic liquids for various bio-applications. Future work will focus on issues concerning mechanical stability of ion-gels.

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