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PAPER

Agarose processing in protic and mixed protic–aprotic ionic liquids: dissolution, regeneration and high conductivity, high strength ionogels†

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We have shown that low viscosity alkyl or hydroxyalkyl ammonium formate (ILs) can dissolve agarose, and higher dissolution can be achieved in the mixed, alkyl or hydroxyalkyl ammonium + imidazolium or pyridinium ILs. The polarity parameters α , β , π^* , $E_T(30)$ and E_T^N of these IL systems were measured to explain their dissolution ability for agarose. Dissolved agarose was either regenerated using methanol as a precipitating solvent or ionogels were formed by cooling the agarose–IL solutions to ambient temperature. Exceptionally high strength ionogels were obtained from the agarose solutions in *N*-(2-hydroxyethyl)-ammonium formate or its mixture with 1-butyl-3-methylimidazolium chloride. Regenerated material and ionogels are characterized for their possible degradation/conformational changes and gel properties (thermal hysteresis, strength, viscoelasticity and conductivity) respectively. A high strength, high conducting ionogel was demonstrated to be able to build an electrochromic window. Such ionogels can also be utilized for other soft matter electronic devices and biomedical applications.

Introduction

Ionic liquids (ILs) (salts with melting points $<100\text{ }^\circ\text{C}$)¹ are normally composed of large asymmetric organic cations and inorganic or organic anions of varying sizes. The desired physical–chemical properties of ILs can be finely tuned by making a judicious choice of cations and anions.^{2–8} Due to the advantageous physical and chemical features, there is a growing use of ILs in various chemical processes.^{1–4} Favourable solubilising characteristics of certain ILs towards the biomass have been found to be particularly useful, and are being extensively explored for the dissolution, functionalization and blending of a variety of biomaterials, which include lignocellulosic materials (wood), cellulose, proteins (silk fibers, cytochrome), polysaccharides (chitin, chitosan, keratin, dextran, inulin, amylose, pectin, xylan, agarose) or carbohydrates (glucose, fructose, sucrose and lactose), *etc.*^{9–31}

A unique combination of the properties of ILs, such as thermal stability, high conductivity/wide electrochemical window and high solvating ability, provides the opportunities of not only *in situ* functionalization of materials but also to make novel hybrid materials, such as an ionogel, wherein IL is immobilized in a way that involves the formation of a three-dimensional network percolating throughout the IL and is responsible for the solid-like behaviour of the resulting material.

Confinement of ILs as gel matrices makes them suitable for an array of applications, which may include stable electrolytes in dye-sensitized solar cells, secondary batteries, electrochromic displays, supercapacitors, electrolytic membranes, fuel cells, electrochemical sensors or biosensors, actuators, *etc.*^{32–45} Ionogels can be obtained by hybridizing ILs with low molecular weight organic gelators, inorganics (*e.g.* carbon nanotubes, silica, *etc.*), polymers or combining organic–inorganic compounds and have been recently reviewed by Bideau *et al.*⁴⁶ The processing of biopolymers with ILs has certain advantages such as dissolved materials can be easily regenerated without degradation using an antisolvent or ionogels can be achieved simply by cooling the solutions at ambient temperatures,²⁹ thus producing sustainable materials that can overcome the complexities pertaining to the processing techniques encountered in the case of organic polymer gels. Reports are available on ionogels obtained from the ILs and biopolymers, like agarose, cellulose, chitosan, starch or the hybrid systems of cellulose with starch or carrageenans, and their applications as useful materials have been demonstrated.^{29,47–55} Although the biopolymer based ionogels have been shown to have many advantages, certain important issues such as preventing leaching of the ILs from gel matrices at longer time scales, improving mechanical strength of ionogels without compromising on conducting nature or even the preparation of high conductivity, high stability ionogels that can be suitable for electrochemical devices still need to be addressed.

Biopolymer agarose, an algal polysaccharide comprising alternating D-galactose and 3,6-anhydro-L-galactose repeating units (Fig. 1), essentially uncharged, is often used as the model system in gelation. Hot water agarose sols form thermo-reversible hydrogels which find numerous applications in various fields such as the food industry, pharmaceutical formulations,

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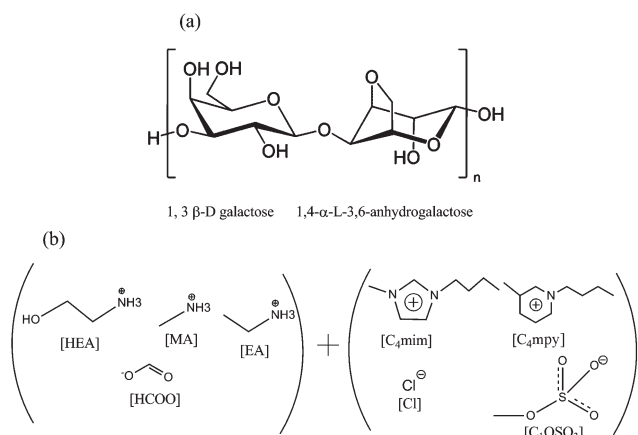


Fig. 1 (a) Idealized repeat unit of agarose, and (b) constituent ions of IL solvent systems.

electrophoresis, tissue engineering or as a matrix for soft matter organic devices.^{56–58} However, the large number of hydroxyl groups makes agarose insoluble in cold water and many common organic solvents, and dissolution of agarose in water at high temperatures creates difficulties in its functionalization and restricts its applications. ILs, particularly with nitrogen based cations (such as containing imidazolium, ammonium, or pyridinium), which have already shown high potential as cellulose solvents,^{9–17} therefore can be alternative media for the processing of agarose. In fact, we have shown the suitability of certain aprotic imidazolium or pyridinium based ILs towards dissolution of agarose and preparation of ionogels therein.²⁹

Since the fluidities and attendant conductivity of protic ILs tend to be much higher than those of aprotic ILs, we report here a strategy of using mixed ILs (protic + aprotic) in a way that not only leads to the higher dissolution of agarose, but to significantly increased conductivity and mechanical properties while remaining ionogels. In brief, we investigated the dissolution of agarose in neat alkyl or hydroxyalkyl ammonium formate ILs or their mixtures with imidazolium or pyridinium based ILs. The dissolution behaviour of agarose has been explained by determining the solvent polarity of neat and mixed IL systems. The polarity parameter was assessed from the solvatochromic behavior of Reichardt's dye⁵⁹ and by determining the Kamlet–Taft parameters using fluorescence probe molecules.⁶⁰ Agarose was regenerated from the IL solutions using methanol and the regenerated materials were characterized using high temperature gel permeation chromatography (HT-GPC), FTIR, circular dichroism (CD), and thermogravimetric analysis (TGA) for possible degradation and conformational changes. Ionogels have been characterized for gelling, melting, gel strength, viscoelasticity and conductivity. The suitability of strong ionogels towards building an electrochromic window is demonstrated.

Experimental

Materials

ILs, methyl ammonium formate [MA][HCOO], ethyl ammonium formate [EA][HCOO], and *N*-(2-hydroxyethyl)ammonium

formate [HEA][HCOO], were synthesised according to procedures described in the literature^{61–63} and were characterized using ¹H NMR, ¹³C NMR and mass spectroscopy. 1-Butyl-3-methylimidazolium chloride [C₄mim][Cl], *N*-butyl-3-methylpyridinium chloride [C₄mpy][Cl], and 1-butyl-3-methylimidazolium methylsulfate [C₄mim][C₁OSO₃], with stated purities higher than 98% mass fraction, were purchased from Merck. All the ILs used were dried as described in our earlier publication.⁶⁴ Binary mixtures of ILs were prepared by weight (1 : 1) using an analytical balance with a precision of ±0.0001 g (Denver Instrument APX-200). Reichardt's dye and 4-nitroaniline were procured from SIGMA-ALDRICH, and *N,N*-diethyl-4-nitroaniline was purchased from Oakwood Products, Inc. USA. Agarose extracted from red algae *Gracilaria dura* occurring in the Arabian Sea at the west coast of India was used.⁶⁵ The agarose (1.5%) had gel strength 1400 g cm⁻², gelling temperature 35 °C, sulphate content ≤0.25%, [α]_D²⁰ -22° and *M*_w 1.63 × 10⁵ g mol⁻¹. The repeating unit of agarose and molecular structures of ILs are shown in Fig. 1.

Determination of polarity parameters

For the determination of polarity parameters, aliquots of the solvatochromic probes prepared in absolute methanol were transferred into 1 cm quartz cuvettes, and their solutions were evaporated under vacuum. ILs or mixtures of ILs (1 : 1 w/w) were transferred into the cuvettes. For homogeneity, the solutions were vigorously stirred with a magnetic stirrer. Final probe concentrations were 1.5 × 10⁻⁵ M for Reichardt's dye and 1 × 10⁻⁵ M for *N,N*-diethyl-4-nitroaniline and 4-nitroaniline. UV-Vis absorption spectra of the solutions were recorded for Reichardt's dye, *N,N*-diethyl-4-nitroaniline and 4-nitroaniline using a UV 3600 Shimadzu UV-Vis-NIR spectrophotometer with a thermocell coupled to it. All of the measurements were performed three times and the maximum absorption was determined for each probe from the first derivative of the wavelength scan. The precision of replicated measurements was ±1 nm.

Solubilization, regeneration and preparation of ionogels

Dissolution of agarose in neat ILs and mixed ILs was carried out in 10 ml beakers with continuous stirring in the glove box under an inert atmosphere of N₂. The temperature of the dissolving process was controlled to ±1 °C. Finely powdered agarose was added to either neat ILs or mixed ILs (approx. 5 g, 1 : 1 w/w) in portions of 0.5 wt% every time until the material disappeared. The addition was carried out till the resulting IL 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 70 °C for further characterization. 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, ILs were recovered from the methanol solutions using a rotary evaporator. For ionogel preparation, agarose was dissolved in preheated ILs or mixed ILs to form a 5 wt% solution. After complete dissolution

at around 70 °C, viscous clear solutions were allowed to cool for gelling.

Characterization

The 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 Ultrahydrajel500 and 120 columns in series. Columns were eluted with 0.1 M aqueous NaNO₃ at a flow rate of 0.5 ml min⁻¹. Calibration was performed using a dextran standard ranging from 401 000 to 4400 peak molecular weight. The concentration of agarose solutions in water was 0.02 wt%. FTIR spectra of the native and regenerated materials were recorded at room temperature using a NICOLET 6700 FTIR spectrometer. Thermogravimetric analyses were performed on a TGA/SDTA851 Mettler Toledo under a nitrogen atmosphere from 30 to 450 °C with a heating rate of 10 °C min⁻¹. 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 temperatures of ionogels were determined following the method described by Craigie and Leigh.⁶⁶ Gel strength (g cm⁻²) was measured using a Nikkansui type gel tester (Kiya Seisakusho Ltd, Tokyo, Japan). Measurements were performed on a 5% agarose ionogel using a solid cylindrical plunger 1.127 cm in diameter. Viscoelastic measurements were performed on an Anton Paar Physica MCR 301 rheometer, USA, using the parallel plate PP50/P-PTD200 geometry (50 mm diameter; 0.1 mm gap). The frequency dependences of dynamic storage (G') and loss (G'') moduli were examined in the linear viscoelastic regime (pre-determined at each temperature). The temperature dependences of G' and G'' were measured with a strain amplitude of 5% and a frequency of 0.1 rad s⁻¹, and a heating rate of 0.5 °C min⁻¹. The temperature was controlled by a Viscotherm VT2 circulating water bath. Conductivity measurements were carried out with a digital conductivity meter (SYSTRONICS, Conductivity TDS Meter 308) in a manner similar to that described by Li *et al.*⁶⁷ The cell constant was determined with aqueous KCl solutions of varying concentrations. Since measurements are at single frequency effects of electrode polarization are not taken into account. Small discrepancies could also be caused by a little bit of moisture contamination. Because of no available data in the open literature we could not compare the temperature dependence of conductivity of the investigated ILs. 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. For the preparation of an electrochromic window, polymerization of a poly(3,4-ethylenedioxythiophene) (PEDOT) monomer unit was done on a glass-indium tin oxide (ITO) plate in an aqueous

solution of 0.1 M KCl. An agarose-[HEA][HCOO] + [C₄mim]-Cl solution was spread over the PEDOT/glass-ITO plate and allowed to gelate. The experiments were performed on a biopotentiostat AFCBP-1 Pennsylvania, USA 16127 using a three-electrode cell wherein the glass-ITO/PEDOT/ionogel was used as a working electrode, Ag/Ag-Cl as a reference electrode and platinum as a counter electrode with a 100 mV s⁻¹ scan rate in the range of -0.2 V to 1.3 V, 10 sweeps and 5 cycles.

Results and discussion

Dissolution and regeneration

Dissolution results of agarose in the ILs [HEA][HCOO], [MA][HCOO], [EA][HCOO] and their mixtures with [C₄mim][Cl] or [C₄mpy][Cl] or [C₄mim][C₁OSO₃] at 70 °C are listed in Table 1. It is observed that agarose has very good solubility in [MA][HCOO] and [EA][HCOO], whereas the solubility in [HEA][HCOO] is lesser than that in water. When compared to neat ILs, an increase in the solubility of agarose was observed in general in the mixed IL systems. Exceptionally higher solubility was observed in the systems [MA][HCOO] or [EA][HCOO] + [C₄mpy][Cl] or [C₄mim][C₁OSO₃]. The solubility of agarose in ILs depends on both the nature of the cation and the anion. IL systems containing [C₁OSO₃]⁻ anions dissolved higher amounts of agarose, whereas the ammonium ILs having hydroxyl groups in the cation are not very effective in solubilising agarose. Similar to cellulose, the high efficiency of ILs containing [HCOO]⁻, [Cl]⁻ or [C₁OSO₃]⁻ towards agarose solubilisation is due to strong interactions of these ions with the hydroxyl groups of agarose which eventually leads to disruption of the hydrogen bonding network of this polymer.

Specific physicochemical properties such as polarity of a solvent strongly influence the dissolution of materials. The most widely used scales for polarity are $E_T(30)$ and E_T^N , which are determined by the charge-transfer absorption band of Reichardt's dye in a solvent.⁵⁹ Therefore, we determined the $E_T(30)$ and E_T^N values of ILs and mixed ILs at agarose dissolution temperature (Table 2). As indicated by large $E_T(30)$ values, the ILs used are of reasonably good polarity and the mixing of protic-aprotic ILs does not alter the $E_T(30)$ values very significantly. More specifically, one can assess the solvent polarity by determining the Kamlet-Taft parameters, which provides a quantitative measure of solvent polarizability (π^* parameter), hydrogen bond donor (HBD) capacity (α parameter), hydrogen bond acceptor (HBA) capacity (β parameter).⁶⁰ Kamlet-Taft parameters of neat and mixed ILs are reported in Table 2. As can be seen from Table 2, the α parameter slightly decreases when the ILs [C₄mim][Cl] or [C₄mpy][Cl] are added to the alkyl or hydroxyalkyl ammonium ILs, while it hardly changes upon addition of [C₄mim]-[C₁OSO₃]. Recent studies have revealed that ILs with higher β values are more capable of dissolving biomaterials, such as cellulose.^{16,68,69} The higher dissolution of agarose in alkyl ammonium ILs can be attributed to their very high β values. Also, the β values were considerably raised when the ammonium ILs were mixed with imidazolium (particularly, [C₄mim]-[C₁OSO₃]) or pyridinium ILs, and possibly the reason for higher dissolution of agarose. β values of IL/mixed IL systems vs. agarose solubility are plotted in Fig. 2, and it is seen that a near

Table 1 Solubility (*s*) of agarose in ILs/mixed ILs (1 : 1 w/w) at 70 °C, molecular weight (M_n and M_w), polydispersity (*P*), degree of polymerization (D_p), and decomposition temperature (T_d) of regenerated agarose

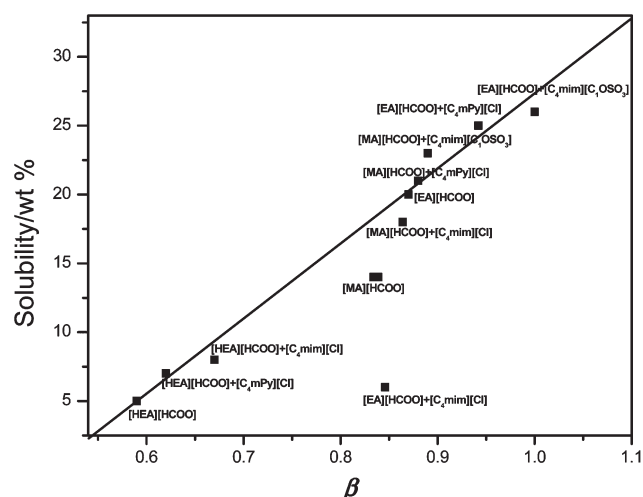
Entry	Solvent system	x_1	<i>s</i> (wt %)	M_n	M_w	<i>P</i>	D_p	T_d (°C)
0	Water	—	8	83 950	163 000	2.60	537	303
1	[HEA][HCOO]	1	5	81 531	160 326	2.31	527	300
2	[MA][HCOO]	1	14	61 879	130 259	3.16	432	301
3	[EA][HCOO]	1	20	44 933	127 908	2.74	420	330
4	[HEA][HCOO] + [C ₄ mim][Cl]	0.62	8	73 907	160 470	2.82	527	287
5	[MA][HCOO] + [C ₄ mim][Cl]	0.69	18	72 681	148 760	2.71	489	303
6	[EA][HCOO] + [C ₄ mim][Cl]	0.66	7	69 398	159 217	2.91	523	265
7	[HEA][HCOO] + [C ₄ mpy][Cl]	0.63	7	66 020	138 124	2.89	454	288
8	[MA][HCOO] + [C ₄ mpy][Cl]	0.70	21	47 147	140 822	2.98	463	295
9	[EA][HCOO] + [C ₄ mpy][Cl]	0.67	25	46 192	115 630	2.75	380	303
10	[HEA][HCOO] + [C ₄ mim][C ₁ OSO ₃]	0.70	14	82 387	161 787	1.97	532	313
11	[MA][HCOO] + [C ₄ mim][C ₁ OSO ₃]	0.76	23	43 490	98 073	2.63	322	304
12	[EA][HCOO] + [C ₄ mim][C ₁ OSO ₃]	0.73	26	68 451	156 960	2.29	450	290

Table 2 $E_T(30)$, E_T^N , Kamlet–Taft parameters of ILs or mixed ILs (1 : 1 w/w) at 70 °C

Entry	Solvent system	$E_T(30)$ (kcal mol ⁻¹)	E_T^N	α	β	π^*
1	[HEA][HCOO]	59.6	0.882	1.11	0.59	0.97
2	[MA][HCOO]	59.3	0.873	1.02	0.83	1.05
3	[EA][HCOO]	56.4	0.787	1.10	0.87	0.77
4	[HEA][HCOO] + [C ₄ mim][Cl]	55.7	0.765	0.77	0.67	1.10
5	[MA][HCOO] + [C ₄ mim][Cl]	57.0	0.802	0.87	0.86	1.07
6	[EA][HCOO] + [C ₄ mim][Cl]	58.9	0.861	1.04	0.85	1.01
7	[HEA][HCOO] + [C ₄ mpy][Cl]	56.0	0.772	0.75	0.62	1.14
8	[MA][HCOO] + [C ₄ mpy][Cl]	54.2	0.718	1.02	0.88	0.71
9	[EA][HCOO] + [C ₄ mpy][Cl]	55.5	0.758	0.91	0.94	0.92
10	[HEA][HCOO] + [C ₄ mim][C ₁ OSO ₃]	57.8	0.827	0.97	0.84	1.01
11	[MA][HCOO] + [C ₄ mim][C ₁ OSO ₃]	57.0	0.802	1.02	0.89	0.90
12	[EA][HCOO] + [C ₄ mim][C ₁ OSO ₃]	57.2	0.809	1.13	1.00	0.79

linear correlation exists in most cases. Deviation from this correlation for the system [EA][HCOO] + [C₄mim][Cl] is perhaps due to the formation of ionogel at the working temperature and hence no more agarose could be dissolved.

Agarose was regenerated from their IL/mixed IL solutions by adding methanol at room temperature. Mixtures were stirred for about 1 h to ensure complete precipitation. 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. Molecular weight, polydispersity index and degree of polymerization of the material are noted in Table 1. Results show that agarose regenerated from most of the ILs and mixed ILs had comparable molecular weights to that of native agarose. The agarose regenerated from the solvent systems [EA][HCOO] + [C₄mPy][Cl] and [MA][HCOO] + [C₄mim][C₁OSO₃] had comparatively lower molecular weight and degree of polymerization indicating a certain amount of degradation in the material. FTIR spectra of the native and regenerated agarose are compared in Fig. 3. The

**Fig. 2** Linear correlation between solubility of agarose and β parameter of ILs/mixed ILs at 70 °C.

spectra show that regenerated agarose largely maintains the native structure. Characteristic IR bands at 773, 894, and 932 cm⁻¹ because of 3,6-anhydro-*b*-galactose skeletal bending in agarose⁷⁰ remain unaltered in the regenerated material except those regenerated from the solvent systems containing pyridinium based ILs wherein these bands appear slightly diminished. The IR bands at 1158 and 1071 cm⁻¹ corresponding to C–O–C– and glycosidic linkage^{70,71} are also altered in the regenerated material. No peak corresponding to IL moieties indicates that ILs or mixed ILs are fairly non-coordinating media for the processing of agarose. Since FTIR bands indicated the alterations in local linkage geometries, we recorded the circular dichroism (CD) spectra of agarose regenerated from various solvent systems 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.⁷² In solution, the low intensity of the band is the consequence of highly extended chain geometries. Analysis of CD spectra (Fig. 4a–c) reveals distinct conformational preferences in the chains of regenerated agarose. The material regenerated from solutions of pure alkyl or hydroxyalkyl

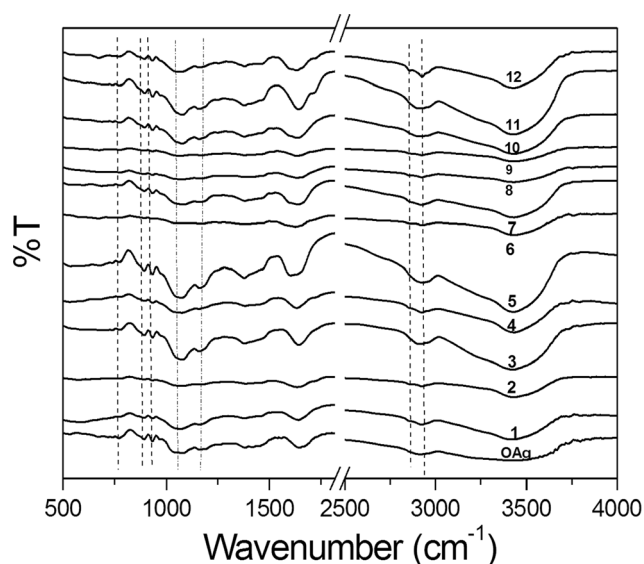


Fig. 3 FTIR spectrum of native agarose and regenerated agarose. Spectra are shifted vertically for clarity and numbered according to the entries in Table 1.

ammonium ILs reproduces the features of native agarose with only a slight loss in intensity and indicates very less conformational change in the regenerated material. The CD band of the agarose regenerated from mixed ILs appears to be slightly red shifted with a certain degree of loss in intensity, suggesting some conformation change and disruption of the ordered structure. Regenerated material was also checked for thermal stability by performing thermo-gravimetric analysis (TGA). TGA profiles are shown in Fig. 5. The decomposition of both the native and regenerated material is characterized by a narrow temperature range from 275 to 300 °C. Agarose regenerated from most of the IL systems shows nearly the same onset decomposition temperature as that of the native material. The material regenerated from the mixed IL systems containing pyridinium ILs shows slightly lower onset decomposition temperature indicating some degradation which is also confirmed from other techniques. The slight initial weight loss in samples 7, 9, 10, 11, and 12 (Fig. 5) may be due to the presence of moisture as a consequence of modified texture of the agarose regenerated from different ILs.

Ionogels

Upon cooling, the agarose dissolved viscous solutions of ILs/mixed ILs resulted in the formation of thermoreversible conducting ionogels (Fig. 6). For a reasonable comparison we prepared 5 wt% ionogels in different ILs/mixed ILs. Dried and powdered agarose was dissolved in preheated solvent systems and allowed to cool till gelled. Gelling and melting temperatures of various ionogels were monitored through visual inspection of the gel and liquid state and are noted in Table 3. At 30 °C (where gel strength is measured), agarose solutions comprising [HEA]-[HCOO], [HEA][HCOO] + [C₄mim][Cl], [MA][HCOO] + [C₄mim][Cl], [EA][HCOO] + [C₄mim][Cl], [EA][HCOO] + [C₄mpy][Cl] or [HEA][HCOO] + [C₄mim][C₁OSO₃] were gelled to different strengths, while the other solutions remained as viscous liquid. Gel strength measured using a Nikkansui type

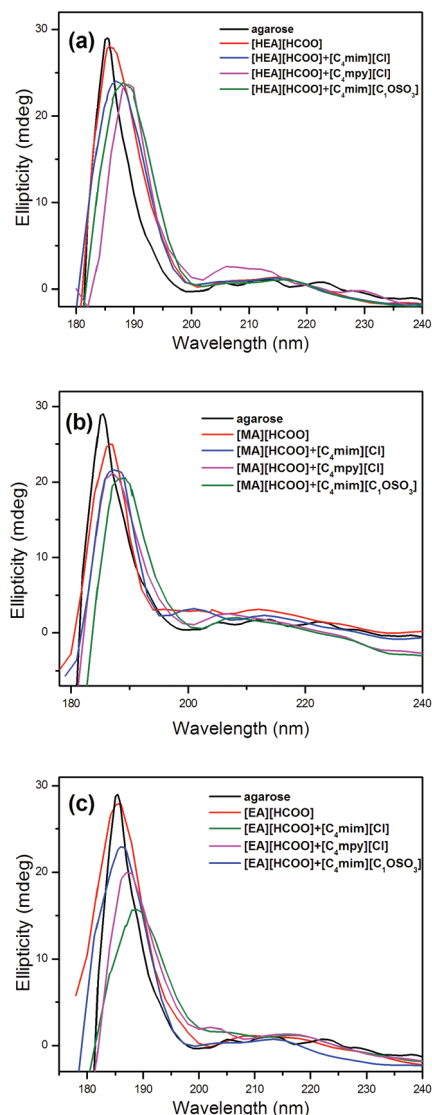


Fig. 4 Comparison of CD spectra of native and regenerated agarose from (a) [HEA][HCOO]/mixed ILs, (b) [MA][HCOO]/mixed ILs, and (c) [EA][HCOO]/mixed ILs in aqueous solutions (0.05 wt%) recorded at 25 °C.

gel tester at 30 °C is also given in Table 3. Unlike agarose hydrogels, most of the ionogels lacked thermal hysteresis, and there is only a narrow range of gelling and melting temperature. The formation of ionogels is expected to occur in a slightly different fashion than the formation of water based agarose gels.⁷³ Since agarose is essentially a neutral biopolymer, hydrogen bonding between ILs and the hydroxyl groups of agarose molecules must be playing an important role in gelling. Large ions will interact with agarose strands and prevent the formation of double helical structures, and finally lead to a comparatively weaker gel. The neat [MA][HCOO] or [EA][HCOO] formed weak ionogels and addition of [C₄mpy][Cl] or [C₄mim]-[C₁OSO₃] to these ILs, through enhanced agarose dissolution, did not impart strength to the ionogels. However, the addition of [C₄mim][Cl] strengthened the ionogel to a good extent. [HEA]-[HCOO] formed ionogels with very high gel strength and addition of [C₄mim][Cl] or [C₄mpy][Cl] (which otherwise forms

a weak ionogel) also resulted in formation of ionogels with a sufficiently good gel strength. This is probably due to the plasticizing effect of the hydroxyl group of the cation of the IL. The IL/mixed IL matrix is immobilized in the gel matrix through

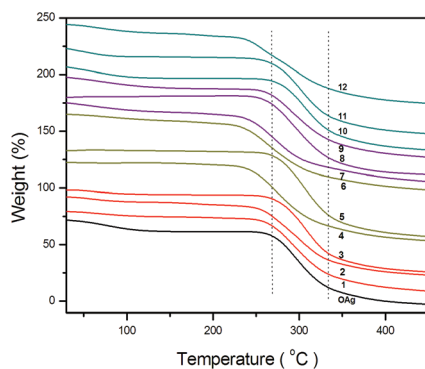


Fig. 5 Thermal decomposition profiles of native and regenerated agarose (numbered according to the entries in Table 1). Samples were heated under a nitrogen atmosphere at a heating rate of 10 °C min^{-1} .

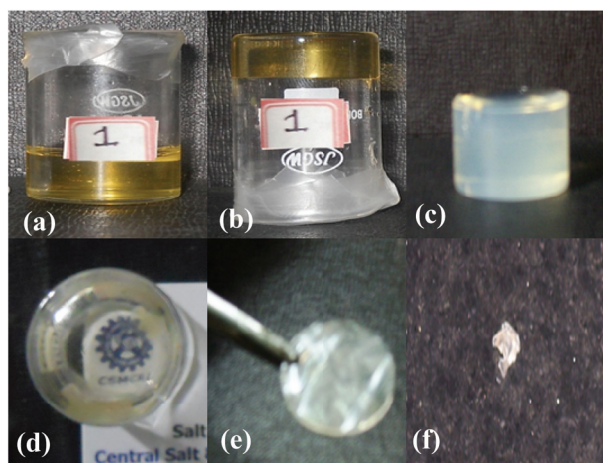


Fig. 6 Representative (a) agarose-IL sol, (b) agarose ionogel, (c) ionogel cuboid, (d) transparent ionogel film, (e) stable ionogel thin film, and (f) shrunk hydrogel (note: the photograph of shrunk hydrogel is reproduced from our earlier paper, ref. 29).

strong hydrogen bonding between protons of the hydroxyl group of the cation and oxygens of agarose as well as due to the hydrogen bonding between agarose protons and IL anions.

Dynamic shear measurements were performed on various ionogels at 30 °C (temperature at which gel strengths are reported using a Nikkansui type gel tester). The results of frequency dependences of dynamic storage (G') and loss moduli (G'') are demonstrated in Fig. 7. As can be seen from Fig. 7, G' is larger than G'' and is nearly frequency independent showing a solid-like behavior of the agarose-IL systems. A thermoresponsive gel transition of ionogels was observed from the temperature dependences of G' and G'' measured at a frequency of 0.1 rad s^{-1} . A transition for both G' and G'' as a function of temperature is indicative of gel temperature (a representative system is shown in Fig. 8 and the results of other systems are provided as ESI, Fig. S1–S3†). Beyond the crossover of G' and G'' the agarose-IL solutions are optically transparent ionogels. The gel temperatures obtained from temperature dependent rheology measurements are consistent with the results obtained from the visual inspection of gelling temperature provided in Table 3. We also conducted the dynamic strain sweep experiments on various ionogels over a wide range of strains (0.1 to 100%) at a frequency of 100 rad s^{-1} . The observed G' and G'' trends of various ionogels under large strains are shown in Fig. 9. For most of the ionogels a linear viscoelastic regime is maintained indicating no deformation of the gel microstructure even at 100% strain. In the case of ionogels formed in the IL systems [HEA][HCOO] + [C₄mim][Cl], [MA][HCOO] + [C₄mim][Cl] or [EA][HCOO] + [C₄mim][Cl], G' continues to decrease with the increase in strain showing a continuous change in gel microstructure wherein the molecular connections in the gel network are disrupted under the large strains.

Since a low matrix (agarose) is enough to prepare ionogels of sufficiently good gel strength, such ionogels will have advantages in terms of retaining the conducting properties of native ILs. Therefore, we examined the conductivity behaviour of various ionogels and compared it with the conductivity of native ILs. Conductivity was found to depend mainly on the nature of constituent ions of ILs and varied between ~ 3 to $\sim 36\text{ mS cm}^{-1}$ at 25 °C (Table 3). The conductivity of ammonium based ILs is quite higher when compared to the imidazolium or pyridinium ILs²⁹ and follows the order [MA][HCOO] > [EA][HCOO] > [HEA][HCOO]. The temperature dependence of conductivity of

Table 3 Gelling temperature (T_{gel}), melting temperature (T_{m}), gel strength, and ionic conductivity of ionogels (κ_{ionogel}) and IL systems (κ)

Entry	Solvent system	x_1	$T_{\text{gel}}\text{ (°C)}$	$T_{\text{m}}\text{ (°C)}$	Gel strength (g cm^{-2}) at 30 °C	$\kappa\text{ (mS cm}^{-1}\text{)}$ at 25 °C	$\kappa_{\text{ionogel}}\text{ (mS cm}^{-1}\text{)}$ at 25 °C
1	[HEA][HCOO]	1	36	56	>1850	3.274	3.458
2	[MA][HCOO]	1	21	23	Liquid	35.98	31.91
3	[EA][HCOO]	1	24	26	Liquid	19.20	16.83
4	[HEA][HCOO] + [C ₄ mim][Cl]	0.62	51	59	590	3.326	3.326
5	[MA][HCOO] + [C ₄ mim][Cl]	0.69	35	34	330	12.73	11.97
6	[EA][HCOO] + [C ₄ mim][Cl]	0.66	45	45	540	7.902	7.158
7	[HEA][HCOO] + [C ₄ mpy][Cl]	0.63	37	42	490	2.611	2.541
8	[MA][HCOO] + [C ₄ mpy][Cl]	0.70	22	37	Weak gel	10.84	9.353
9	[EA][HCOO] + [C ₄ mpy][Cl]	0.67	34	46	140	6.078	5.682
10	[HEA][HCOO] + [C ₄ mim][C ₁ OSO ₃]	0.70	28	44	<100	3.424	4.215
11	[MA][HCOO] + [C ₄ mim][C ₁ OSO ₃]	0.76	18	19	Liquid	16.45	13.79
12	[EA][HCOO] + [C ₄ mim][C ₁ OSO ₃]	0.73	22	25	<100	11.93	11.13

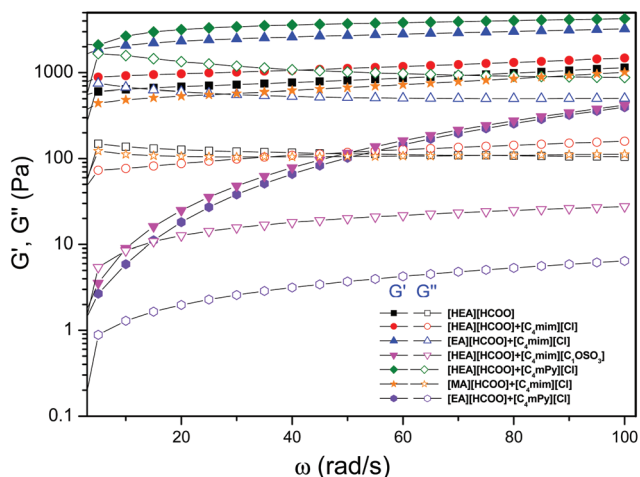


Fig. 7 Frequency dependence of dynamic storage (solid symbols) and loss moduli (open symbols) (G' and G'') of different ionogels at a strain $\gamma = 5\%$ and 30°C temperature.

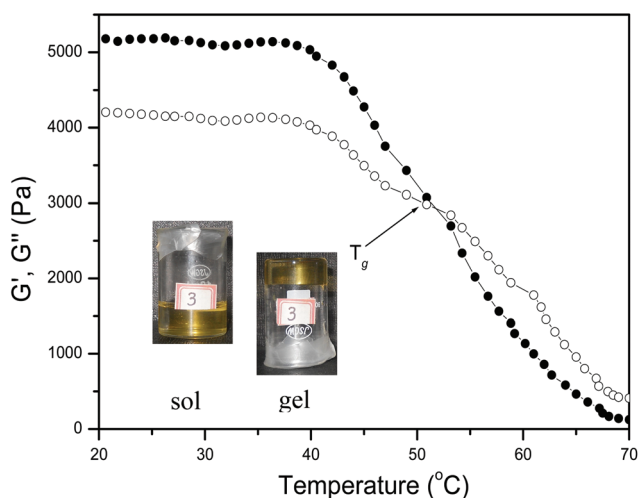


Fig. 8 Temperature dependence variation of dynamic storage (solid symbol) and loss moduli (open symbol) (G' and G'') of a representative ionogel ($[\text{HEA}][\text{HCOO}] + [\text{C}_4\text{mim}][\text{Cl}]$) at frequency $\omega = 0.1 \text{ rad s}^{-1}$ and a strain amplitude of $\gamma = 5\%$.

ILs/mixed ILs and ionogels is shown in Fig. 10(a–c). For both ILs and ionogels conductivity increases monotonously with the increase in temperature and follows a similar track. As expected, because of the reduced mobility of ions in the gel state, the conductivity of ionogels is found to be slightly lower than the pure ILs over the investigated temperature range. Like gelatin based ionogels,⁵⁴ agarose based ionogels when connected to a power supply lit up the LED exhibiting mixed electronic and ionic conduction. For the demonstration of suitability of ionogels in electronic devices we used a reasonably good strength and ionic conductivity ionogel prepared in the mixed IL system $[\text{HEA}][\text{HCOO}] + [\text{C}_4\text{mim}][\text{Cl}]$ and poly(3,4-ethylenedioxythiophene) (PEDOT) to build an electrochromic window (Fig. 11). The electrochromic window built with the ionogel was found to have capacity for charge transport and electrical conduction, and changed the colour of PEDOT on the glass-ITO plate from bleached state to slight blue to brownish with the variation in voltage.

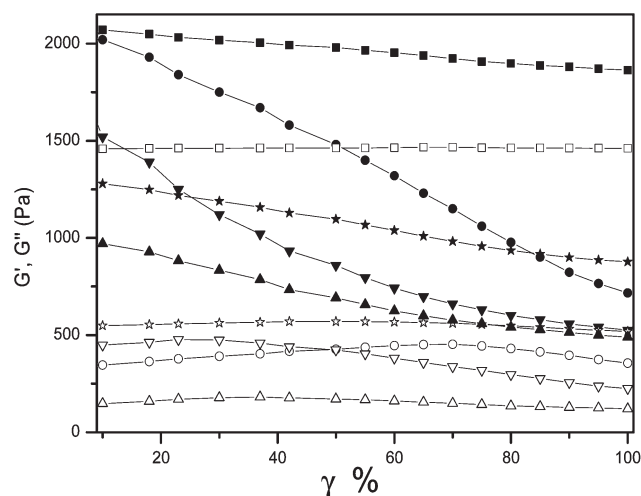


Fig. 9 Strain dependence of dynamic storage (solid symbol) and loss moduli (open symbol) (G' and G'') of ionogels prepared in $[\text{HEA}][\text{HCOO}]$ (■), $[\text{HEA}][\text{HCOO}] + [\text{C}_4\text{mim}][\text{Cl}]$ (★), $[\text{HEA}][\text{HCOO}] + [\text{C}_4\text{mpy}][\text{Cl}]$ (●), $[\text{MA}][\text{HCOO}] + [\text{C}_4\text{mim}][\text{Cl}]$ (▼), $[\text{EA}][\text{HCOO}] + [\text{C}_4\text{mim}][\text{Cl}]$ (▲).

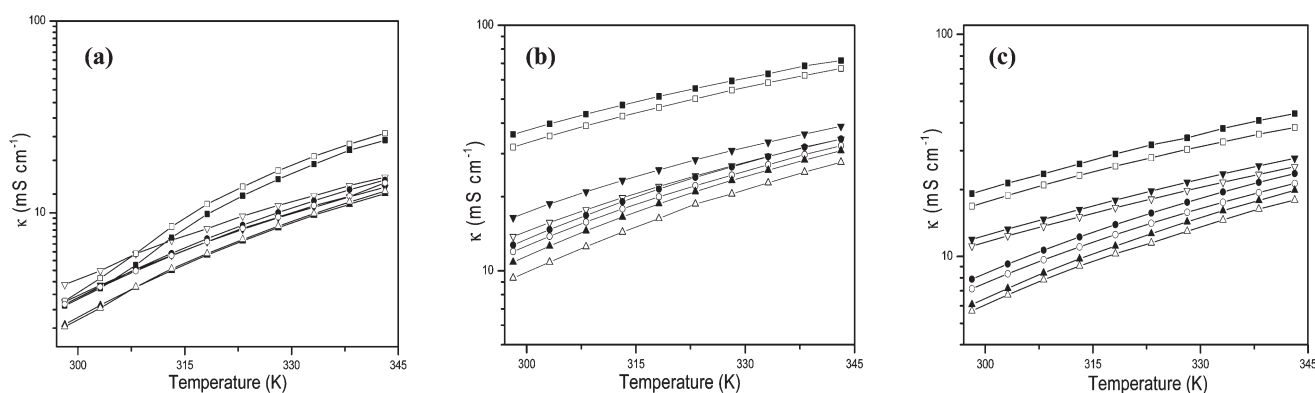


Fig. 10 Temperature dependence of ionic conductivity in neat and mixed ILs: (a) $[\text{HEA}][\text{HCOO}]$ (■), $[\text{HEA}][\text{HCOO}] + [\text{C}_4\text{mim}][\text{Cl}]$ (●), $[\text{HEA}][\text{HCOO}] + [\text{C}_4\text{mpy}][\text{Cl}]$ (▲), $[\text{HEA}][\text{HCOO}] + [\text{C}_4\text{mim}][\text{C}_1\text{OSO}_3]$ (▼); (b) $[\text{MA}][\text{HCOO}]$ (■), $[\text{MA}][\text{HCOO}] + [\text{C}_4\text{mim}][\text{Cl}]$ (●), $[\text{MA}][\text{HCOO}] + [\text{C}_4\text{mpy}][\text{Cl}]$ (▲), $[\text{MA}][\text{HCOO}] + [\text{C}_4\text{mim}][\text{C}_1\text{OSO}_3]$ (▼); and (c) $[\text{EA}][\text{HCOO}]$ (■), $[\text{EA}][\text{HCOO}] + [\text{C}_4\text{mim}][\text{Cl}]$ (●), $[\text{EA}][\text{HCOO}] + [\text{C}_4\text{mpy}][\text{Cl}]$ (▲), $[\text{HEA}][\text{HCOO}] + [\text{C}_4\text{mim}][\text{C}_1\text{OSO}_3]$ (▼). Hollow symbols correspond to agarose-IL sol-gels (5 wt%).

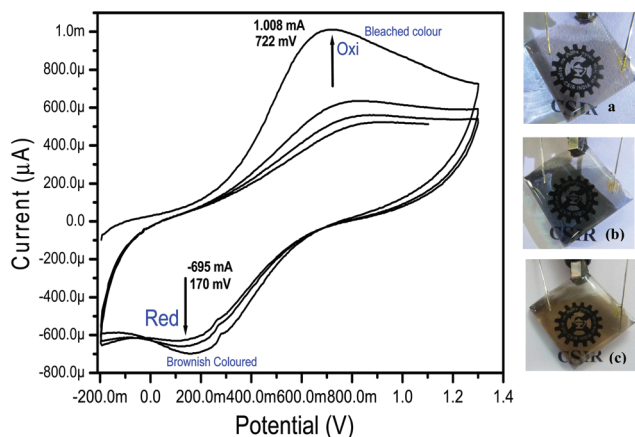


Fig. 11 Cyclic voltammograms obtained for PEDOT/ITO-glass/ionogel devices for 10 cycles at a 100 mV S^{-1} scan rate between -0.2 V to 1.3 V and an electrochromic smart window of PEDOT/glass-ITO/ionogels (a) bleached state; (b and c) colored state.

Conclusions

Very high dissolution of agarose can be achieved in low viscosity ammonium based ILs and their mixtures with imidazolium or pyridinium based ILs. The higher dissolution of agarose can be attributed to the high hydrogen bond acceptor capacity of the investigated solvent systems and is found to be nearly linearly correlated. Dissolved agarose can be easily regenerated using methanol as the antisolvent without much degradation in terms of molecular weight or conformation. Ionogels of reasonably good strength and conductivity can be obtained by cooling the agarose-IL solutions to ambient temperatures. Viscoelastic measurements indicated that the microstructure for most of the ionogels, particularly based on hydroxyalkyl ammonium formate ILs or their mixtures, remained unaltered even under large strains. Such an ionogel was found to be highly suitable for building an electrochromic window. These studies will be helpful in utilizing synergetic effects of ILs as novel non-coordinating media for higher dissolution and *in situ* functionalization of biomaterials. High conductivity, high strength ionogels may be of potential use in soft matter electronic devices and biomedical applications. The use of ILs in the processing of biomaterials would have advantages in terms of safe handling because of their non-flammable and non-volatile nature and can have environmental benefits in terms of recyclability.

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