Journal of Molecular Liquids 157 (2010) 83–87

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Short Communication

# Ionic liquid-assisted gelation of an organic solvent

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ARTICLE INFO

*Article history:*
Received 27 October 2009
Received in revised form 3 June 2010
Accepted 26 August 2010
Available online 31 August 2010

*Keywords:*
Ionic liquids
Organogel
Conductivity

ABSTRACT

Tetrafluoroborate-containing ionic liquids allow for a room temperature gelation of dimethylsulfoxide, which contains an organogelator at below the minimum gelation concentration. The gel formation has no effect on the mobility of ions, as the conductivity values of ionic liquid-DMSO gels are virtually identical to those of ionic liquid-DMSO solutions.

## 1. Introduction

Gelation of organic solvents using small molecules, *i.e.*, low molecular weight organogelators, holds great promise for various areas of science and engineering [1]. Gels, as soft materials, with unique thermo reversible electronic and/or mechanical properties that are capable of modulating input–output responses are appealing as sensors, membranes and molecular devices [1]. Generally, from the structural point of view, organogels can be viewed as three-dimensional supramolecular assemblies of the organogelator molecules that "trap" solvent molecules within their network [1].

Ionic liquids, compounds that are composed entirely of ions and possess phase transition temperatures at or around room temperature, have attracted considerable attention in recent years due to their wide range of applications [2]. Primarily, ionic liquids have been used as solvents for organic reactions and separation processes. Recently ionic liquids have also been exploited as advanced materials and energetic salts [3]. Gelation of ionic liquids is an interesting and potentially useful area of research that might have implications in the areas of materials and energy [4]. Specifically, gelled ionic liquids have been successfully used in dye-sensitized solar cell systems and gas separations [5].

A great number of organic compounds have limited solubility in ionic liquids. In addition, high viscosity of ionic liquids affects a variety of other physical properties such as conductivity, for example. These issues significantly limit the utility of these solvents. In this light, studies on the ionic liquid–molecular solvent mixtures are of interest [6].

During our studies on ionic liquid gelation of molecular organic solvents, we noticed that mixtures of $[C_4{-}mim]BF_4$ **1** and dimethylsulfoxide (DMSO) could be gelled by a known organogelator **A** [7] (Fig. 1) below **A**'s minimum gelation concentration. Since high concentrations of organogelators are known to impair physical properties of the gels, such as the ionic conductivity, for example, minimizing the gelator's concentration, while still producing a gel is highly advantageous. Here, we wish to report on a new ability [8] of certain ionic liquids to induce the gelation of a molecular solvent containing small amounts of **A**.

## 2. Materials and methods

### 2.1. General

All chemicals and solvents were from commercial sources (Sigma-Aldrich or Acros), they were of highest grade possible, and were used as received All ionic liquids were prepared according to literature procedures following the general sequence shown in Scheme 1 [9]. Tetrabutylammonium tetrafluoroborate and sodium tetrafluoroborate were from Aldrich, and were used as received.

### 2.2. Synthesis of ionic liquids

All tetrafluoroborate ionic liquids were treated with charcoal and repetitive dissolutions into $CH_2Cl_2$ followed by filtration and removal of $CH_2Cl_2$ to get rid of colored and inorganic impurities. Finally, the ionic liquids were dried *in vacuo* to remove the residual $CH_2Cl_2$. NMR spectra were recorded on a Varian-300 and chemical shifts are reported in parts per million relative to internal tetramethylsilane.

**$[C_4{-}mim]BF_4$, 1**: [9b] $^1$H NMR (300 MHz, DMSO$-d_6$) $\delta = 9.07$ (1H, s), 7.73 (1H, t, $J = 1.8$ Hz), 7.67 (1H, t, $J = 1.8$ Hz), 4.13 (2H, t, $J = 7.2$ Hz), 3.83 (s, 3H), 1.74 (2H, pent, $J = 7.7$ Hz), 1.22 (2H, six, $J = 7.7$ Hz), 0.88 (3H, t, $J = 7.2$ Hz).

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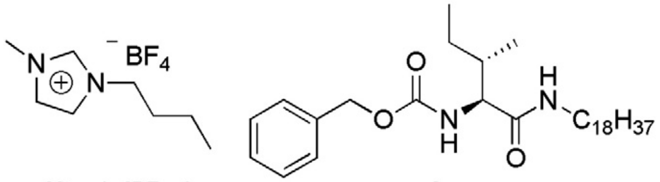
doi:10.1016/j.molliq.2010.08.011



[C$_4$-mim]BF$_4$, **1**  **A**

**Fig. 1.** Structures of ionic liquid **1** and organogelator **A**.

**[Bn−mim]BF$_4$, 2**: [10] $^1$H NMR (300 MHz, DMSO−d$_6$) δ = 9.18 (1H, s), 7.77 (1H, t, $J$ = 1.8 Hz), 7.70 (1H, t, $J$ = 1.8 Hz), 5.40 (2H, s), 3.84 (3H, s).

**[HO(CH$_2$)$_2$−mim]BF$_4$, 3**: [11] $^1$H NMR (300 MHz, DMSO−d$_6$) δ = 9.04 (1H, s), 7.69 (1H, t, $J$ = 1.8 Hz), 7.65 (1H, t, $J$ = 1.8 Hz), 5.14 (1H, s), 4.19 (2H, t, $J$ = 4.8 Hz), 3.84 (3H, s), 3.70 (2H, m).

**[C$_{12}$−mim]BF$_4$, 1**: [9b] $^1$H NMR (300 MHz, DMSO−d$_6$) δ = 9.06 (1H, s), 7.73 (1H, t, $J$ = 1.8 Hz), 7.67 (1H, t, $J$ = 1.8 Hz), 4.13 (2H, t, $J$ = 7.5 Hz), 3.83 (3H, s), 1.75 (2H, m), 1.22 (18H, m), 0.84 (3H, t, $J$ = 6.6 Hz).

**[C$_4$−py]BF$_4$, 5**: [12] $^1$H NMR (300 MHz, DMSO−d$_6$) δ = 9.06 (2H, d, $J$ = 5.6 Hz), 8.59 (1H, d, $J$ = 7.9 Hz), 8.14 (2H, t, $J$ = 6.9 Hz), 4.59 (2H, t, $J$ = 7.7 Hz), 1.88 (2H, pent, $J$ = 7.7 Hz), 1.27 (2H, six, $J$ = 7.7 Hz), 0.89 (3H, t, $J$ = 7.2 Hz).

**[Bn−py]BF$_4$, 6**: [12] $^1$H NMR (300 MHz, CDCl$_3$) δ = 9.64 (2H, d, $J$ = 5.6 Hz), 8.43 (1H, t, $J$ = 7.9 Hz), 8.01 (2H, t, $J$ = 6.7 Hz), 7.68 (2H, m), 7.31 (3H, m), 6.30 (2H, 1 s).

**[HO(CH$_2$)$_2$−py]BF$_4$, 7**: [13] $^1$H NMR (300 MHz, DMSO−d$_6$) δ = 8.99 (2H, d, $J$ = 5.4 Hz), 8.60 (1H, tt, $J$ = 7.5, 0.9 Hz), 8.15 (2H, t, $J$ = 6.6 Hz), 5.20 (1H, s), 4.64 (2H, t, $J$ = 5.1 Hz), 3.84 (2H, t, $J$ = 5.1 Hz).

**[C$_{12}$−py]BF$_4$, 8**: [14] $^1$H NMR (300 MHz, CDCl$_3$) δ = 8.54 (2H, d, $J$ = 5.8 Hz), 8.48 (1H, t, $J$ = 8.0 Hz), 8.05 (2H, t, $J$ = 7.2 Hz), 4.64 (2H, t, $J$ = 7.4 Hz), 2.00 (2H, m), 1.24 (18H, m), 0.87 (3H, t, $J$ = 6.6 Hz).

### *2.3. Conductivity measurements*

The specific conductance values were obtained by the direct current four-electrode method using a custom-made glass cell (Fig. 2) and Ag-electrodes at 25.00 ± 0.01 °C. The measurements were performed using: Hewlett Packard 34401A multimeter ($E_{std}$), Keithley 182 sensitive digital voltmeter ($E_{cell}$), AMEL instructions general purpose potentiostat model 2049 (constant current source) and Leed&Northrup 1000 Ohm D–C resistance standard ($R_{std}$). The conductance cell was calibrated using KCl solutions, according to literature procedures [15].

### *2.4. Gel preparation for the conductivity measurements*

The gel electrolytes were formed by mixing organogelator **A**, DMSO, and ionic liquid in a vial followed by heating with a heat gun until a homogeneous solution was obtained. The mixture was transferred into the cell by syringe while hot followed by the insertion of the electrodes. The measurement was performed after the gel was formed.

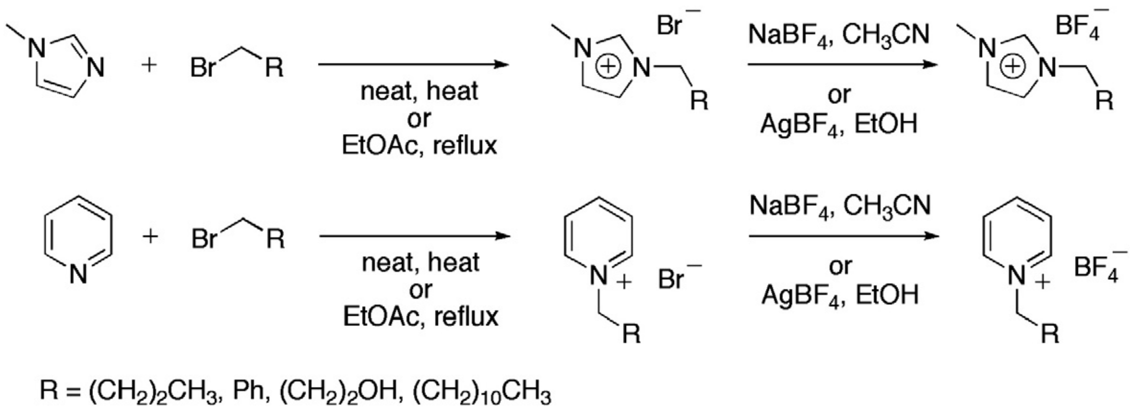
### *2.5. $T_{gel}$ measurements*

$T_{gel}$ were determined using test-tube-tilting method: [16] a vial containing the gel was inversely (or horizontally, *i.e.*, on its side) immersed into a water-bath and the temperature was raised at 1 °C/min. The $T_{gel}$ was recorded as the temperature when the gelled mass started to flow downward.

## 3. Results and discussion

**A** was reported to gelate a variety of molecular solvents [7]. 10 mg/ml is a minimum gelator concentration for **A** to gel DMSO [7]. In order to test the ability of [C$_4$−mim]BF$_4$ to assist in the gelation of DMSO, we prepared a 2 mg/ml solution of **A** in DMSO and, as expected, no gelation of DMSO was observed. However, upon addition of [C$_4$−mim]BF$_4$ (20% v/v) an instantaneous formation of a stable transparent gel occurred at room temperature. The gel formation was thermoreversible. We then examined whether **1**, which contained 2 mg/ml of **A**, could be gelled by the addition of various amounts of DMSO. However, no gelation was observed when DMSO was added to the solution of **A** in **1**. In this case the dissolution of the ionic liquid into DMSO took place, leading to the precipitation of **A**. The gel formation of the obtained heterogenoues mixture was only observed upon subjecting it to a heating/cooling procedure, *i.e.*, the vial was heated with the heat gun until a homogeneous mixture was obtained and then allowed to cool to room temperature. The gel formation was observed visually by the inverse tube method.

In order to gain an insight into the role of **1** in the gelation process, we probed **1**-DMSO-**A** interactions using NMR spectroscopy, using DMSO−d$_6$ in place of DMSO. Chemical shifts of ionic liquids are known to be environment and concentration dependent [17]. Therefore, if the ionic liquid is trapped within the gel, one would expect the chemical shifts to be distinct from those observed in the solution. Our experiments revealed that all chemical shifts of **1** (both $^1$H and $^{19}$F nuclei resonances) were identical in the gel state and in the DMSO solution, *i.e.*, in the presence and absence of **A**, respectively. These experiments indicated that the ionic liquid is neither a part of the gel network nor does it undergoes any aggregation processes upon gelation. Due to low gelator concentration, it was not possible to estimate the behavior of **A** in neither solution nor the gel states. Collectively, the observations presented above indicated that the ionic



**Scheme 1.** Synthesis of ionic liquids.

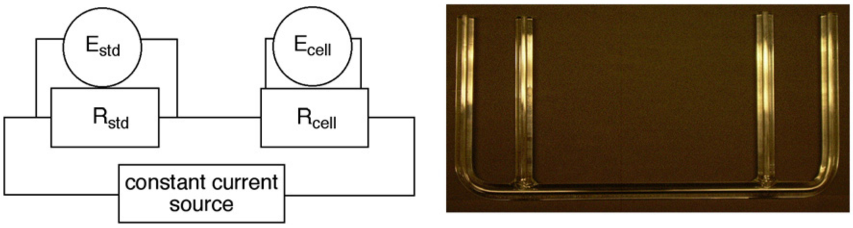


**Fig. 2.** Set-up (left) and the photograph of the cell (right) for the conductivity measurements.

liquid had a crucial, yet complementary role in the overall gelation process, while **A** was primarily responsible for the gel formation.

To further explore the gelating ability of $[C_4\text{—mim}]BF_4$, we prepared a set of **1**/DMSO mixtures (Fig. 3) with various concentrations of **1**, which contained a fixed amount (2 mg/ml) of **A**. A gradual increase, *i.e.*, from 5 to 10 to 15% (v/v) of **1**, led to a visual increase of the mixture's viscosity, and a formation of the stable transparent gel was observed once the amount of **1** reached 20% (Fig. 3). Increasing the amount of the ionic liquid up to 70% resulted in a transition from transparent to non-transparent, off-white gels. Mixtures containing >75% of **1** were viscous heterogeneous solutions. The gel–sol transition temperature ($T_{gel}$) of the gels appeared to be dependent on the ionic liquid content (Fig. 3). $T_{gel}$ gradually changed as the concentration of the ionic liquid increased to 40% v/v. Subsequent increase of the ionic liquid content had only a marginal impact on the $T_{gel}$ values and at 70% of **1**, the temperature decreased to *ca.* 50 °C.

It is noteworthy that gelation of ionic liquids by low molecular weight organogelators requires extensive heating to dissolve the organogelator into ionic liquids [4,5]. In all the cases shown in Fig. 3, the gelation occurred at room temperature upon the addition of the ionic liquid.

Small amounts of water in some ionic liquids are known to alter their physical properties [18]. In view of a hygroscopic nature of tetrafluoroborate ionic liquids as well as that of DMSO, small amounts of water might be expected to affect the gelation. Since the formation of the gels is done on a bench-top, it is likely that various amounts of water (at least at *ppm* levels) will always be present, even if the ionic liquids are extensively dried. In order to evaluate the effect of water on the ability of **1** to assist in the gelation of DMSO, we prepared a gel that contained **A** (2.0 mg/ml), DMSO (80% v/v) and **1** (20% v/v). Incremental addition of water up to 1% (v/v), followed by heating/cooling cycles, after each portion of water was added produced the gel. This indicated that the gel formation was unaffected by these amounts of water. Addition of water (up to 10% v/v) to the solution of **A** (2.0 mg/ml) in DMSO caused a precipitation of **A**. Hence, the observed induced room temperature gelation of DMSO by the ionic liquid **1** is not caused by the presence of small amounts of water, but rather is attributed to the specific interactions of **1**, **A** and DMSO.

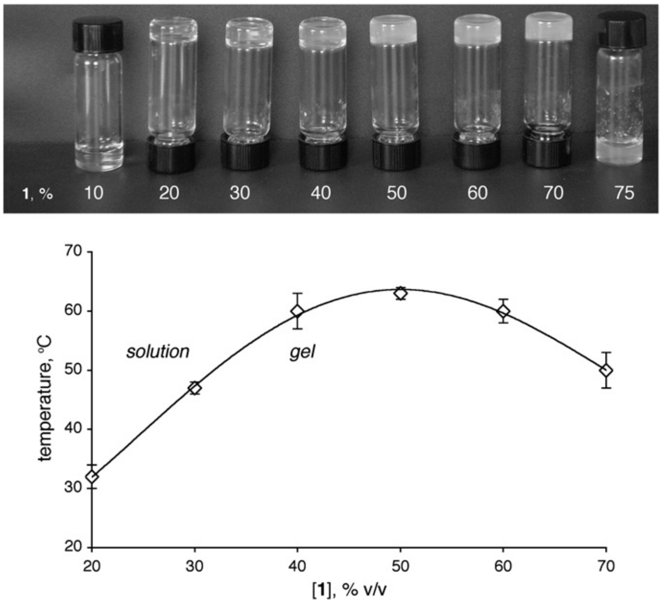


**Fig. 3.** Solutions and gels of **1** various concentrations of **1** in the **A**/DMSO mixture (top) and the corresponding $T_{gel}$ (bottom) as a function of [**1**], % (v/v); $T_{gel}$ values are the average of two or three measurements ± SD. Line is just for guiding an eye.

Intrigued by this novel property of $[C_4\text{—mim}]BF_4$ **1** to induce the room temperature gelation of DMSO in the presence of small amounts of **A**, we screened other common ionic liquids, such as $[C_4\text{—mim}]X$, where $X = NO_3$, $PF_6$, Br, and $NTf_2$. It appeared that none of these ionic liquids was able to produce a gel upon addition to the DMSO solution of **A** neither at room temperature nor upon exposing the mixture to the heating/cooling gel-forming procedure. Hence, it appeared that $BF_4$-anion was crucial for the observed phenomenon. In order to probe the scope of ionic liquid-assisted gelation, we screened other molecular solvents. Interestingly, the ionic liquid-induced gelation of organic solvents was specific to DMSO as no gel formation was observed when **1** was added to the solutions of **A** in methanol, ethanol, iso-propanol, acetonitrile, tetrahydrofuran, dimethylformamide, and acetone. Collectively, these data indicated that a very specific and fine balance exists within this system, *i.e.*, **1**-**A**-DMSO, which is responsible for the gelation process.

Next, we tested the effect of the cation on the gelation of DMSO in a series of tetrafluoroborate ionic liquids/solids (Figs. 1 and 4). It appeared that only imidazolium- and pyridinium-containing ionic liquids had the ability to assist in the gelation of DMSO (Table 1). Several structural features appeared to be important for the gelation. The substituent on the nitrogen had a profound effect on the gelation of **A**/DMSO solution.

Specifically, short alkyl chain-containing ionic liquids are more efficient in the gelation process. For example, butyl-containing ionic liquids **1** and **5** are superior to those ionic liquids or solids with dodecyl-containing ionic liquids **4** and **8**. Although **4** did not induce an immediate formation of the gel upon addition to **A**/DMSO solution, a notable increase of the viscosity was noted after a week for solutions containing >30% of **4**. Ionic solid **8** (up to 50% content) failed to gel the **A**/DMSO mixture. Ionic liquids containing a benzyl group, **2** and **6**, were proven efficient gel inducers.

Hydroxy-containing ionic liquids, **3** and **7**, required a slightly smaller amount of **A** which may be attributed to an additional hydrogen-bonding moiety that might be involved in the interactions with **A**. The aromatic cation, either an imidazolium or a pyridinium, is essential for the gelation as neither $[C_{4444}N]BF_4$, **9**, nor $NaBF_4$, **10**, (up to 60% w/v) induced the gelation of a **A**/DMSO mixture even after 14 days.

Further, we examined the ionic conductivity of the ionic liquid-DMSO gel (Table 1). In the gel state, *i.e.*, ionic liquid/**A**/DMSO system, the mobility of ions in the ionic liquids was not impaired by the gel formation, since the conductivity of the solution states, *i.e.*, ionic liquid/DMSO, and the gel states were virtually identical. These data are in accord with the NMR experiments described above, which also

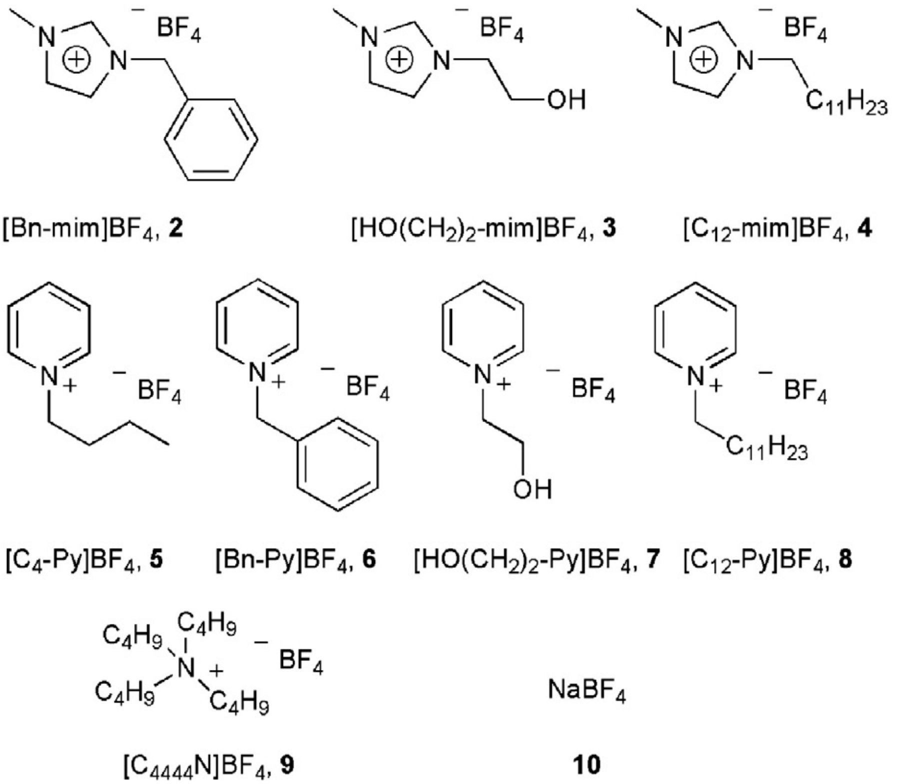


**Fig. 4.** Structures of ionic liquids and solids.

showed that the ionic liquid is not a part of the gel network. In the case of the **1**/DMSO/**A** gel, we also measured the conductivity as a function of time and found that no significant changes during the sol to gel transition were taking place.

We also found that the presence of small molecules in DMSO solutions, including Zn-tetraphenylporphyrin, krypto-BODIPY [19] and Congo red dyes (mM concentrations), had no impact on the ability of the ionic liquids to induce the gel formation. This observation should potentially create opportunities for designing novel soft materials with tunable properties [20].

In order to check whether the structure of the organogelator had any effect on the ionic liquid-induced gelation, we have tested another “super” organogelator, *i.e., trans*(1*R*,2*R*)-*N*,*N*′-1,4-cyclohexane diyl bis dodecanamide [21]. No gelation was noted with any of the tetrafluoroborate-containing ionic liquids **1**–**8** (Figs. 1 and 4). This indicates that a very fine balance exists between the structure of the organogelator and the ionic liquid, which leads to the gelation of DMSO.

**Table 1**
Properties of ionic liquid/**A**/DMSO gels and solutions.

| Ionic liquid (% v/v)[a] | [**A**], mg/ml[b] | *k*, mS cm$^{-1}$[c] | |
|---|---|---|---|
| | | Gel | Solution[d] |
| **1** (20) | 1.7 | 14.6 | 15.2 |
| **2** (23) | 1.7 | 12.9 | 12.9 |
| **3** (9) | 1.3 | 10.2 | 10.4 |
| **4** (−) [e] | – | – | – |
| **5** (23) | 1.7 | 15.3 | 15.6 |
| **6** (20) | 1.4 | 13.2 | 13.3 |
| **7** (13) | 1.3 | 12.4 | 12.3 |
| **8** (−)[e] | – | – | – |

See text for details.
[a] Minimum ionic liquid concentration.
[b] Minimum **A** concentration at the minimum ionic liquid content.
[c] Electrolytic conductivity.
[d] No gelator **A** is present.
[e] No gelation occurred.

## 4. Conclusions

In summary, we have identified a new ability of ionic liquids to assist a common organogelator in gelling the organic solvent. In the presence of below the minimum gelation concentration of the organogelator, tetrafluroborate ionic liquids induced a room temperature gelation of DMSO.

## Acknowledgement

This work was supported by the donors of the American Chemical Society Petroleum Research Fund (47965-G7). N.W.S. would like to thank ACS Division of Medicinal Chemistry for the predoctoral fellowship. J.M.K. acknowledges TCU-SERC. S.V.D. is a recipient of the TCU-JFSR award. The authors are grateful to Professor Onofrio Annunziata and Mr. Jamie Cuanzon for their helpful discussions and for making the conductivity cell, respectively.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.molliq.2010.08.011.

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