



## Investigation of the effect of silica sources on ionogels prepared from imidazolium based ionic liquid via sol-gel method

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### Abstract

Ionic liquids have many interesting properties such as low vapor pressure, wide liquid range, non-volatility, ionic conductivity, and high thermal stability. Even though these properties make ionic liquids a good alternative in various technological devices; problems such as leakage and portability limits the use of ionic liquids. In recent years, ionogels have gained significant value by overcoming the liquid form problems and by preserving the basic properties of ionic liquids. In this study, imidazolium based ionic liquid was changed to ionogel by using a silica source such as tetraethylorthosilicate (TEOS), tetramethylortosilicate (TMOS) and methyltrimethoxysilane (MTMS), and formic acid was used as both solvent and catalyst. The effects of different silica sources, molar ratios of components, gelling and aging time on ionogel formation were investigated by experimental studies. Synthesized ionogels were characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy and Ultraviolet-Visible (UV-Vis) Spectroscopy analyzes. The stable ionogels were obtained with 1: 8 silica: formic acid molar ratio, 96 hours of gelation time and 8 days of aging time. It has been determined that the synthesized ionogels have smooth and transparent structure.

*Keywords:* ionic liquids; ionogels; formic acid; MTMS; TEOS; TMOS.

### 1. Introduction

Ionic liquids have been intensely used in studies on material science. Ionic liquids are an organic salt group found as liquid at low temperature (<100 °C) [1]. Due to their ionic conductivity, superior chemical properties, thermal stability, non-volatility, and wide liquid range, they have been used mainly in electrometallurgy, high temperature batteries and organic synthesis. Therefore, the use of ionic liquids in synthesis, energy fields and green chemistry has become widespread [2]. One of the most interesting aspects is that the polarity, density and viscosity of ionic liquids can be changed with different combinations of cationic and anionic components. As a result of the increasing interest on the subject, ionic liquids have been focused as an alternative to conventional organic solvents [3]. In addition to utilizing from the advantageous properties of ionic liquids, their liquid state leads to problems such as leakages and preventing miniaturization, which limits their usage in various devices. Therefore, no matter what the application is, many problems can occur when it is tried to benefit from the advantageous of ionic liquids in the solid-state materials [2]. In this respect, giving solid form to ionic liquids has gained importance in recent years.

Sol-gel method is known to be the most suitable method to immobilize a liquid in a solid matrix and defined as transition from liquid form (solution) to solid form (gel) [2,4]. In the method, the hydrolysis and condensation reactions occurs in the presence of a catalyst. The solution is left to gelation and then aging to obtain stronger structure [5].

The ionogels are defined as a very important class of composites, combining both liquid and solid properties, while preserving the main properties of ionic liquids [6]. Also, they are entitled as “a new hybrid materials” [7]. Ionogels mainly consist of an ionic liquid and a continuous solid phase [5].

The inclusion of ionic liquids in the pores has a direct effect on the ionic liquid properties [5]. Ionogels exhibit important mechanical, conductivity, thermal and rheological properties as well as the properties which make them composite group [6].

In the literature, it has been stated that sol-gel-synthesized silica structures are quite good as a matrix with the good mechanical and chemical stability, porous structure, and negligible shrinkage

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properties [8]. The gelation time of ionogels is a variable parameter according to the components of the process and temperature [9].

In this study, ionogels were prepared by hybridizing

## 2. Materials and methods

### 2.1. Materials

The chemicals used in the study are tetramethylortosilicate (TMOS-Sigma-Aldrich, 98%), tetraethylortosilicate (TEOS-Sigma-Aldrich,  $\geq 99\%$ ), trimethoxymethylsilane (MTMS-Sigma-Aldrich, 95%), formic acid (Sigma-Aldrich,  $\geq 95\%$ ).

### 2.2. Synthesis of ionogels

Imidazolium based ionic liquid (MAL[NTf<sub>2</sub>]) was synthesized by our team in Queen's University Belfast Ionic Liquid Laboratories in Belfast, Northern Ireland. Ionogels were synthesized by non-hydrolytic sol-gel process. TMOS, TEOS and MTMS were used as source of silica. The acid-catalyzed conditions required to form Si-O structure were achieved using formic acid. Synthesis was carried out at room conditions.

The silica source, formic acid and ionic liquid were mixed in different molar ratios (1 : 8 : 0.35) to prepare the ionogels. The components were allowed to stir at 30 °C for 10 minutes. After the process was complete, the reaction mixture was allowed to gel

## 3. Results and discussion

The synthesis of ionogels was conducted by non-hydrolytic sol-gel process. The hydrolytic method uses alcohol and water for the sol-gel reaction, whereas a non-hydrolytic process uses a gel-catalyzing agent such as formic acid. Formic acid acts both as a solvent and as a catalyst for hydrolysis and condensation. Moreover, this method prevents the unwanted water in ionic liquids [10].

imidazolium-based ionic liquid with different silica sources such as TEOS, TMOS and MTMS and formic acid. Prepared ionogels were characterized by using SEM, FTIR, Raman, UV-Vis analysis.

under room conditions. The covers were then opened and the structure allowed to aging at room temperature. The aging process was followed by continuous control of the total mass of the components and the reaction vessel. When the total mass remained constant, the aging process was completed and ionogels were obtained.

### 2.3. Characterization techniques

Surface morphology of the synthesized ionogels were determined by SEM analysis and Zeiss Supra 40 VP was used to obtain SEM images.

FTIR spectra of ionogel samples were taken using Perkin Elmer Spectrum 100 in the 4000-400 cm<sup>-1</sup> region.

Raman spectra of ionogels were recorded with Bruker Senterra Dispersive Raman Microscope Spectrometer.

Transmittance of the ionogels were measured in the 200-800 nm region using a Shimadzu UV-250.

In order to investigate and compare the effect of silica sources and molar ratios on the structure of ionogels, experimental studies were performed by TMOS (1), TEOS (1) and TMOS/MTMS (0.5/0.5), TEOS/MTMS (0.5/0.5). Compositions of ionogels prepared using different molar ratios of silica source, formic acid and ionic liquid are given in Table 1 and Table 2.

Table1.Molar ratios and images of ionogels components synthesized by TMOS and TMOS/MTMS.



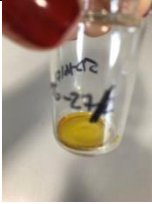

	<b>Ionic liquid</b>	<b>Formic acid</b>	<b>TMOS</b>	<b>MTMS</b>	
<b>SD-MALFIL-IG-40</b>	0.35	8	1	-	
<b>SD-MALFIL-IG-41</b>	0.35	8	0.5	0.5	

Table2.Molar ratios and images of ionogels components synthesized by TEOS and TEOS/MTMS.

	<b>Ionic liquid</b>	<b>Formic acid</b>	<b>TEOS</b>	<b>MTMS</b>	
<b>SD-MALFIL-IG-27</b>	0.35	8	1	-	
<b>SD-MALFIL-IG-42</b>	0.35	8	0.5	0.5	

The studies conducted to determine the gelling time showed that the most stable structures for ionogel at different molar ratios of the components were obtained for 96 hours gelling time. Aging times for the ionogels were determined as 8 days. Ionogels were found to have 96 hours gelling time and 8 days of aging time for TMOS: formic acid: ionic liquid molar ratio at 1: 8: 0.35 (code no: 40) and TEOS: formic acid: ionic liquid molar ratio at 1: 8: 0.35 (code no: 27). The best results were obtained using silica: formic acid molar ratio at 1: 8 as the optimum ratio of the components in the synthesis of ionogels. In the literature, it has been stated that the addition of MTMS provides gels to become more stable, prevents fractures and provides water stability [11]. According to

Table 1 and Table 2, when the MTMS was added to the composition as the silica source, stable ionogels could not be obtained. In addition, the effects of TMOS and TEOS on the structure of ionogels, the studies were conducted separately with TMOS and TEOS. According to the obtained ionogel forms, it was observed that TEOS provided more stable structures than TMOS (Figure 1). The reason for this may be that TEOS can provide more stable structures with its longer bonding. In the literature, it has been stated that the silica skeleton obtained by the polymerization of the formic acid-catalyzed silica source is formed by covalently bonded ionogels with single-step sol-gel synthesis which includes the in-situ immobilization of the ionic liquid [12].

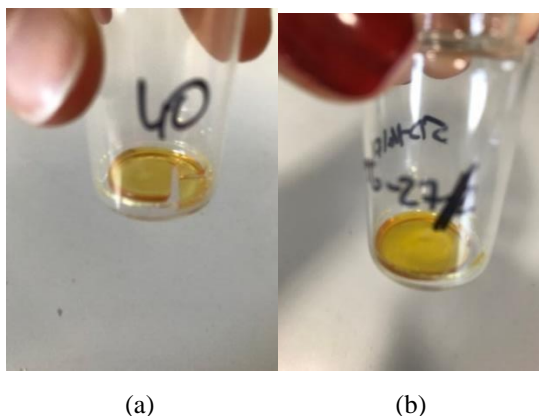


Figure 1. Molar ratios of ionogel components (a) TMOS : formic acid : ionic liquid = 1 : 8 : 0.35, (b) TEOS : formic acid : ionic liquid = 1 : 8 : 0.35.

### 3.1. SEM analysis

SEM analysis were performed to characterize the morphology of ionogels. The images obtained by the analysis provided information on the porosity of ionogels, the state of the pores and the homogeneity and uniformity of the surface. Synthesized ionogels have smooth and homogen

surfaces. In the literature, it is stated that ionic liquids consist of very close packed silica structures. [13]. These packed silica structures provide porous microstructures are called as skeletons of ionogels [14]. Figure 2 presents the SEM images of synthesized ionogels.

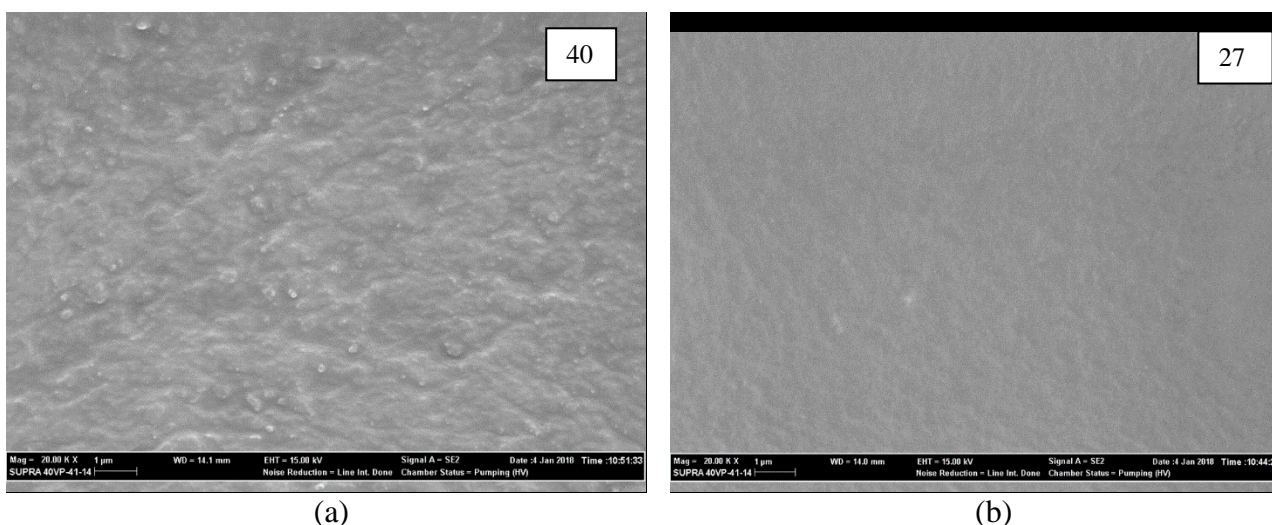


Figure 2. SEM images of the synthesized ionogels (Molar ratios of components (a) TMOS : formic acid : ionic liquid = 1 : 8 : 0.35, (b) TEOS : formic acid : ionic liquid = 1 : 8 : 0.35).

### 3.2. FTIR analysis

FTIR analyzes were performed to determine the functional groups of synthesized ionogels. FTIR spectra of ionogels indicate that ionic liquid is the main component of ionogels due to the dominant vibration bands of ionic liquid [15].

Since the C - H vibrations of the imidazolium ring and its alkyl chains are appear between 2900-3200  $\text{cm}^{-1}$ , imidazolium chain at around 3147  $\text{cm}^{-1}$  belongs

to C - H stretch vibrations [10]. Peaks observed at around 2962  $\text{cm}^{-1}$  indicate C - H stretches of the aliphatic chain [10]. It is estimated that  $\sim 1565 \text{ cm}^{-1}$  peaks belong to amine groups and  $\sim 1530 \text{ cm}^{-1}$  peaks show N - H vibrations [16]. Vibrations in the range of 1400-1200  $\text{cm}^{-1}$  are estimated to belong to O=S=O [17]. 430-452  $\text{cm}^{-1}$  range belongs to Si-O vibration in Si-O-Si modes [18 - 20]. Figure 3 shows the FTIR spectra of ionogels.

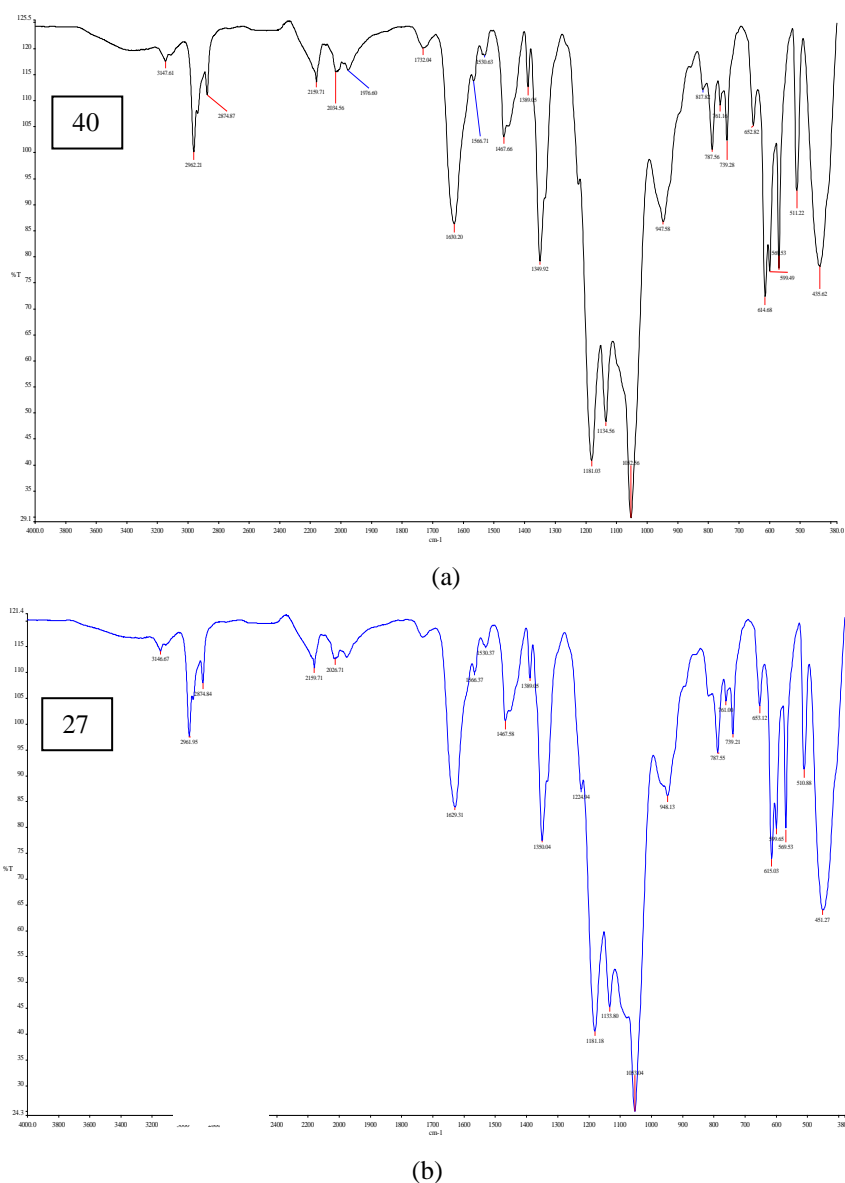


Figure 3. FTIR spectra of ionogels (molar ratios of components) (a) TMOS : formic acid : ionic liquid = 1 : 8 : 0.35, (b) TEOS : formic acid : ionic liquid = 1 : 8 : 0.35).

### 3.3. Raman spectroscopy

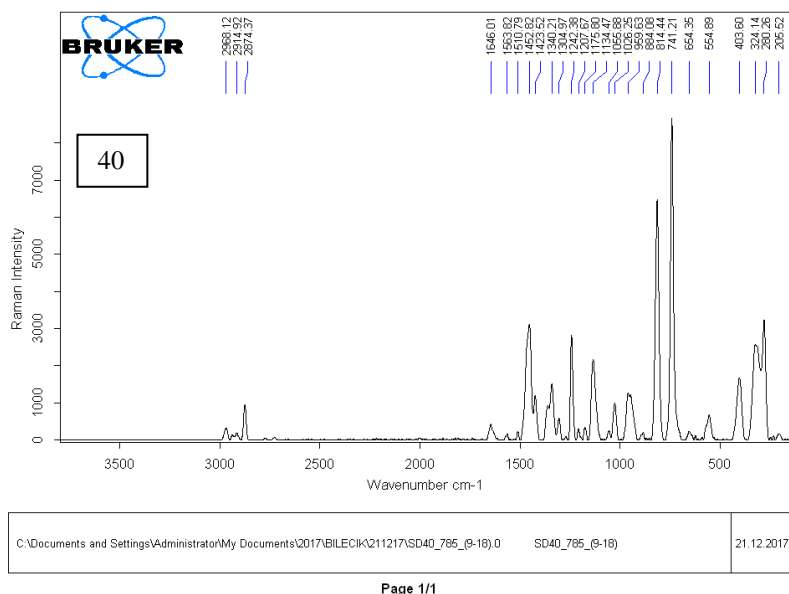
The functional group analysis of ionogels was analyzed using Raman spectroscopy. Raman spectra of ionogels were observed to be very similar to each other. Raman analysis shows C-H vibrations in the range of 3000 - 2800  $\text{cm}^{-1}$ , which supports FTIR

analysis. O=S=O vibrations are estimated to be between 1400-1200  $\text{cm}^{-1}$  [17]. The peaks observed at  $\sim 400 \text{ cm}^{-1}$  indicate Si-O vibrations. Figure 4 shows the Raman spectra of ionogels.

### 3.4. UV-Vis analysis

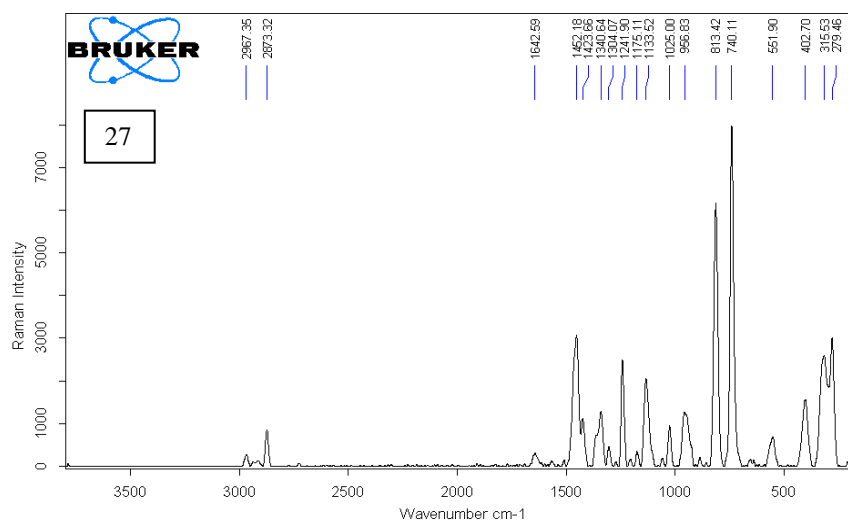
UV-Vis analysis were performed to determine the light transmittance of synthesized ionogels. UV-Vis spectra showing the absorbance values of ionogels against wavelength in the wavelength range of 200-

800 nm were examined. 74 % and 71% maximum % transmittance values were obtained for 40 and 27 coded ionogels, respectively for the ionogels with approximately 1-2 mm thickness.



Page 1/1

(a)



(b)

Figure 4. Raman spectra of ionogels (Molar ratios of components) (a) TMOS : formic acid : ionic liquid = 1 : 8 : 0.35, (b) TEOS : formic acid : ionic liquid = 1 : 8 : 0.35.

#### 4. Conclusion

In this study, ionic liquid was gelled in order to make the liquid form compatible for the applications where the liquid form has disadvantages and to give it a solid form. For this reason, ionogel formation parameters were examined in detail. The parameters such as silica source type, ionic liquid/silica ratio, silica/formic acid ratio, gelation time and aging time were studied in the synthesis of ionogels. The characterization of these ionogel forms was performed by SEM, FTIR, Raman and UV-Vis analysis. According to the results of SEM analysis, it was determined that the ionogels have homogeneous

and smooth surfaces. FTIR and Raman analysis showed the formation of Si-O structures belonging to the ionogels. The light transmittance of ionogels were evaluated with UV-Vis analysis and it was determined that this feature could be used for different application areas. When the MTMS was added to the composition as the silica source, stable ionogels could not be obtained. In addition, the effects of TMOS and TEOS on the structure of ionogels, it was observed that TEOS provided more stable structures than TMOS.

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