

CHAPTER 1 ENVIRONMENT AREA

INFLUENCE OF CHEMICAL STRUCTURE OF ORGANIC COMPOUNDS IN THE ORGANOGEL FORMATION FOR REMOVAL OF ORGANIC SOLVENTS

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Abstract

In this work, the influence between two new organic compounds were compared: a carbamate and a urea to prepare organogels of low molecular weight (LMWGs). The reaction advance for the synthesis of carbamate and urea was followed by thin-layer chromatography. The compounds were tested for organic solvent removal in a model wastewater. The formed gels with the organic solvents were characterized by Fourier transformer infrared spectroscopy (FT-IR), nuclear magnetic resonance of proton (^1H -RMN), high resolution mass spectrometry (HR-MS) and scanning electron microscopy (SEM). The results showed the gel relation (molecules number of gelled solvent by gelator molecule) was lower for the urea (0.98-5.15 wt.%) than the carbamate (1.33-15.17 wt.%). The spectroscopy and microscopy studies showed that the urea gels formed spherical structures with appearance of entanglement fibers, and these were stronger than those made with carbamate, associated to hydrogen bonds.

1. Introduction

The pollution by organic solvents is a major environmental problem because these compounds are widely used in a wide variety of industrial and commercial processes, such as the production of paints, adhesives, cleaners, among others [1]. These solvents can be toxic and persistent in the environment, which can have negative effects on human health and the environment. For example, a way to eliminate the organic solvents of wastewater is adding amphiphilic compounds (low molecular weight organogelators) able to capture and remove them by filtration [1]. The chemical structure of amphiphilic compounds gives them hydrophilic and hydrophobic properties [2 – 4]. They have the ability to trap polar and non-polar solvents and to form supramolecular networks through weak donor-acceptor. That is “non-covalent” intermolecular interactions between “gellant-gellant”, “gellant-solvent”, “solvent-solvent” can be carried out [5 – 11]. These interactions can be done by hydrogen bonding, dipole-dipole, dipole-dipole interactions, van der Waals molecular interactions, molecular stacking π - π , C-H... π molecular interactions, solvophobic effects or molecular surface stress, among others [12].

The organogel form physical networks or supramolecular aggregates, which can be response to physical stimulus such as temperature, light, pH, ultrasound [13 – 16]. It has reported that these structures can used as carriers for drug delivery [16 – 18], tools for water organic contaminants removal [19] and scaffold for tissue regeneration [20]. The used groups to form supramolecular aggregates are peptides [21, 22], amides [15 – 23], ureas [24], carbamates and fatty acids [25].

In this work, two organic compounds were synthesized and characterized. The ability to form supramolecular aggregates and gel from four different solvents was compared.

2. Materials and Methods

2.1. *Materials*

Hexadecyl chloroformate (96 %), hexadecyl isocyanate (97 %), N,N-dimethylethylenediamine (99 %) as high purity chemicals (Sigma-Aldrich, United States). The chemicals were used without previous purification.

2.2. *Methods*

Melting points were determined by using an electrothermal apparatus A29003MB. Fourier transform infrared spectroscopy (FT-IR) was performed in a double beam Perkin-Elmer Model 1605 FT/IR spectrometer with ATR equipment. NMR spectra were recorded in CD Cl₃ or DMSO-d₆ solution on a Varian Mercury spectrometer (300 or 500 MHz for ¹H NMR, 75 or 125 MHz for ¹³C respectively). Chemical shifts were reported in parts per million relatives to Me₄Si as internal standard. Coupling constants J are expressed in Hz. High resolution mass spectroscopy (HR-MS) was analyzed on a micro TOF-Q II with electrospray ionization (ESI) (BrukerDaltonics, Billerica USA). All measurements were carried out by triplicate at room temperature. Purification of the reaction mixtures was carried out by column chromatography using silica gel (Merck 70-230 Mesh) as a solid support or by recrystallization. The progress of the reaction was followed by thin layer chromatography (TLC) on silica gel 60 F254 plates.

2.3. *Gelation test*

The gelation properties of each compound were tested for four different solvents. The gelation tests were carried out as follows: 1 mL of solvent was put and weighed in capped vial. The compound was added to solvent at intervals of 2 mg until saturation was reached. The mixture was heated with a thermal bath until the solid was dissolved into the solvent, then a clear solution was obtained. This solution was cooled until the observation of gel formation and this temperature was recorded. Finally, the test vial was inverted to check that no flow of the organic solvent out of the gel. The gel was weighed again, and the loss of solvent was calculated. After that the gel was heated and the temperature at which it broke down was taken. The experiments were made by triplicate.

2.4. Scanning Electron Microscopy

A gel sample was deposited over the cooper sample holder and cooled with liquid nitrogen and sputtered with gold. Observations were carried out with in a Scanning Electron Microscope JEOL model JSM 7800F at 1 kV.

3. Results and Discussion

The carbamate **3** was synthesized according of scheme of Figure 1. The N,N-dimethylethylenediamine **2** (0.8 equiv.) was dissolved in dichloromethane (DCM) and put in a round-bottomed flask and stirred vigorously. Then, the hexadecyl chloroformate **1** (1 equiv.) in dichloromethane was added dropwise during 30 min at room temperature. The reaction progress was followed by thin layer chromatography (TLC). After two hours, the mixture reaction was extracted with 5v/v % aqueous hydrochloric acid solution (3 x15 mL) and water (2 x 15 mL). Organic phase was dried (Na_2SO_4), filtered and solvent was evaporated under reduced pressure. Reaction crude product was purified by recrystallization or by silica gel (70-100 mesh) column chromatography. The carbamate was obtained as white solid with a yield of 94 % and melting point of 79-80 °C.

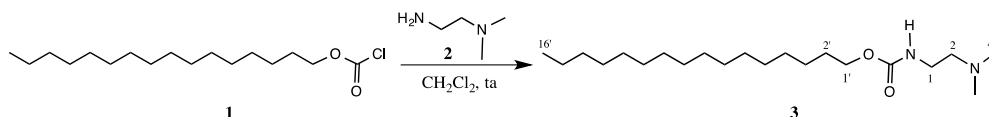


Figure 1. Scheme of reaction for synthesis of carbamate **3**.

The urea **6** was synthesized from hexadecyl isocyanate **4** and phenylenediamine **5**, following the same procedure of carbamate (Figure 2). The urea was obtained as a white solid with a yield of 88 % and melting point of 109-110 °C.

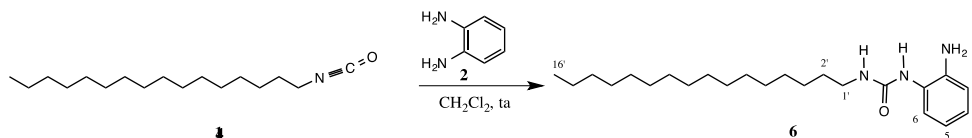


Figure 2. Scheme of reaction for synthesis of urea **6**.

The obtained compounds were analyzed by Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic spectroscopy (NMR) and

high-resolution mass spectroscopy (HR-MS). The spectrum of carbamate **3** shows a wide absorption band around 3311 cm^{-1} attributed to the stretch of N-H group and intense absorption band at 1685 cm^{-1} attributed to carbonyl groups (C=O), (see Figure 3). This is according with the structures of carbamates compounds.

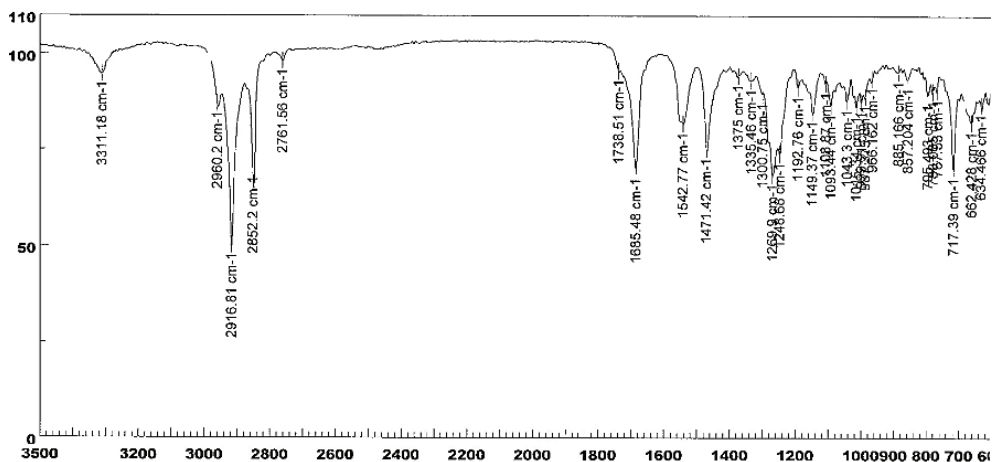


Figure 3. Infrared spectrum of carbamate 3.

Figure 4 presents the $^1\text{H-NMR}$ spectrum of carbamate **3**, and shows intense lines attributed to the deuterated solvent because the solvent was gelled by the organic compound. The characteristic signals of methylene protons bonded to oxygen $\text{CH}_2\text{-O}$ are detected at 4.03 ppm, while the methylene from $\text{CH}_2\text{-N}$ is shifted at 3.65 ppm.

The attributed signal to N,N-dimethylethylenediamine appears at 3.28 ppm due to H interaction from nitrogen; $(\text{NCH}_3)_2$ was observed as an intense line at 2.92 ppm. In the same way, the aliphatic chain shows three additional signals at 1.59 ppm attributed to H interaction from oxygen, 1.29 ppm attributed to the signal of $(\text{CH}_2)_{13}$, and 0.88 ppm corresponding to terminal methyl of chain.

The results of HR-MS of carbamate **3** showed an experimental m/z of 357.3486 (Figure 5) meanwhile the theoretical corresponds to 357.3481 as $(\text{M}+1)$, confirming the formation of organic compound.

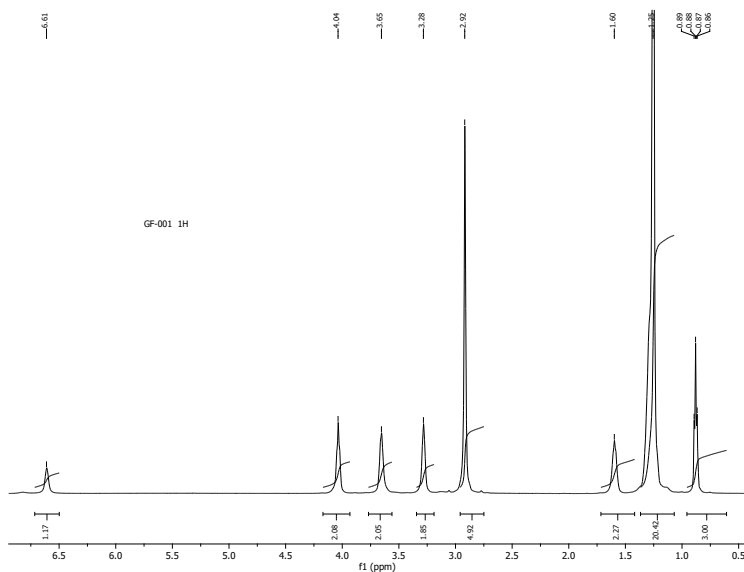


Figure 4. ¹H NMR spectrum of carbamate **3**.

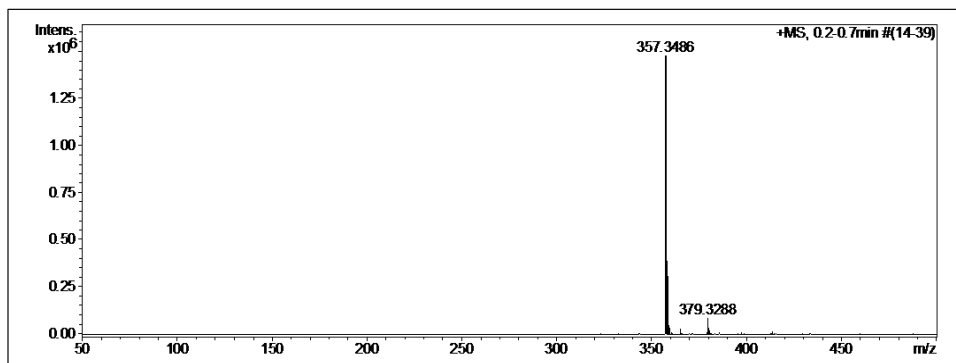


Figure 5. HR-MS spectrum of carbamate **3**.

In the same way, the urea compound was analyzed by the same techniques. The Figure 6 shows FT-IR spectrum for the urea **6**, where a broad absorption band at 3280 cm^{-1} is observed, corresponding to NH and NH_2 groups and two intense bands at 1636 and 1556 cm^{-1} attributed to carbonyl groups (C=O).

The urea **6** also gelled the deuterated solvents. For this reason, the ¹H MNR spectrum shows a quadruplet at 3.17 ppm by the protons of methylene group bonds to nitrogen (Figure 7). Other signals were also observed as: a quadruplet at

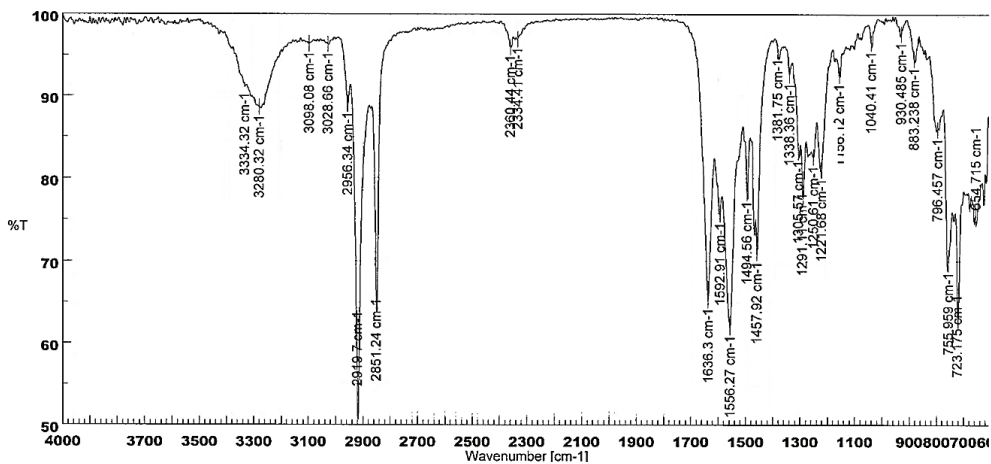
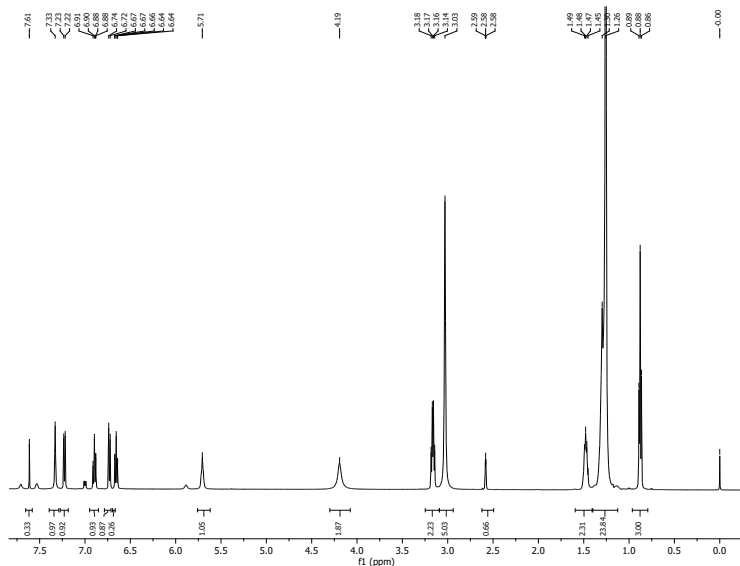


Figure 6. Infrared spectrum of urea 6.

Figure 7. ^1H NMR spectrum of urea 6.

1.26 ppm due to aliphatic chain and a triplet at 6.66 ppm ($J=9$ Hz, H_2), a doublet at 6.72 ppm ($J=9$ Hz, H_3), a triplet at 6.8 ppm ($J=9$ Hz, H_4) and a doublet at 7.23 ppm attributed to H_6 , confirming the presence of urea compound.

The HR-MS spectrum of urea 6 showed an m/z experimental of 389.3142, while the theoretical was 398.3147 as sodium salt. However, an m/z experimental

of dimer (m/z 751.6576), trimer (m/z 1148.9628) and tetramer (m/z 1525.2926) were also obtained, attributed to the high ability of self-assembly of urea (Figure 8).

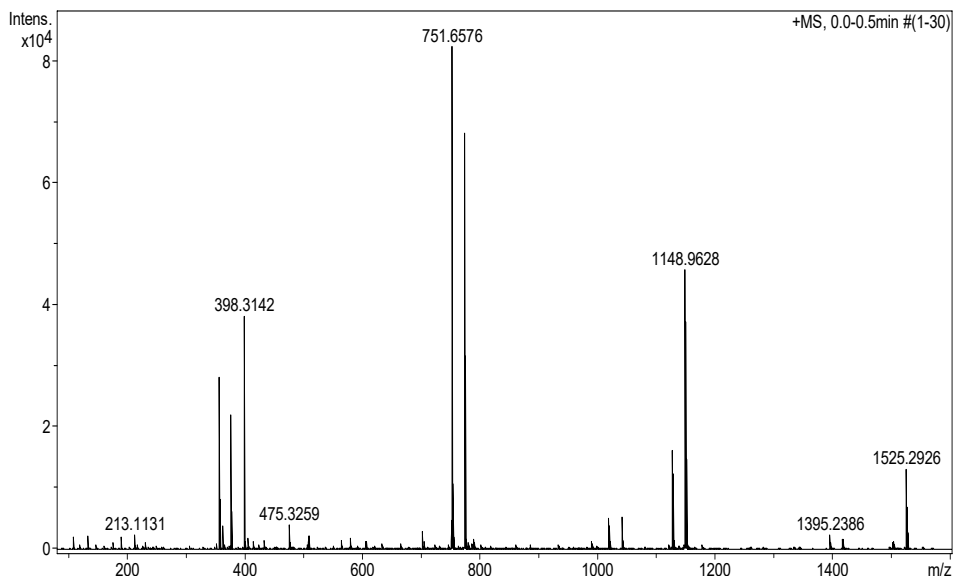


Figure 8. HR-MS spectrum of urea 6.

In this work, two organic compounds were synthesized: a urea and a carbamate. Both compounds have a hydrophilic part and a hydrophobic part [2 – 4], which allow that they can form supramolecular networks and interact in a non-covalent way, when they are in contact with solvents. For this reason, their ability to self-assemble was tested under four organic solvents and the determination of critical gelation concentration, defined as the minimum concentration required to obtain the molecular self-assembly to gel a solvent. The used solvents to carbamate were hexane, toluene, 1,4-dioxane and 2-propanol while the used solvent to urea were: carbon tetrachloride, xylene, toluene and 1,4-dioxane. The experiments consist of the addition of the organic compound at intervals of 2 mg in a volume of solvent previously weight. The mixture at each interval was heated until the solution turns transparent. After that, the mixture was cooled until the gel formation and the temperature was recorded. All the experiments were made by triplicate.

The photos of formed organogels with xylene, toluene and 1,4-dioxane with the carbamate is shown in Figure 9. The gels feature a semi-transparent appearance and colorless. This was observed to all solvents.



Figure 9. Carbamate gels obtained with: A) xylene; B) toluene; C) 1,4-dioxane.

The photos of obtained gels with urea in presence of xylene, toluene, 1,4-dioxane and carbon tetrachloride are presented in Figure 10. The results showed that the gels made with xylene and toluene had a transparent appearance, while the gels formed with dioxane and carbon tetrachloride were opaque and white in color.

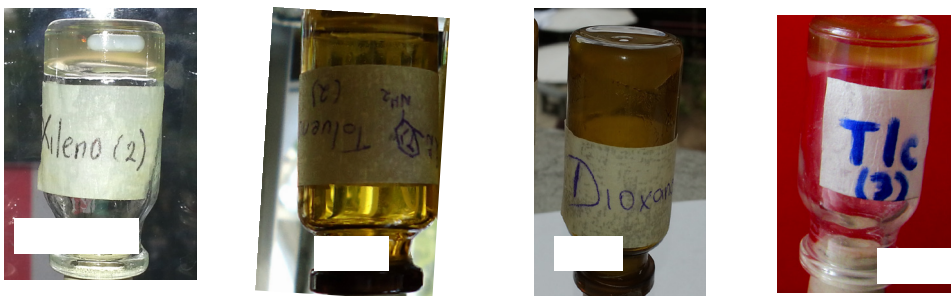


Figure 10. Urea gels obtained with: A) xylene; B) toluene; C) 1,4-dioxane; D) carbon tetrachloride.

The results of supramolecular networks formation of carbamate with each solvent are summarized in Table 1, while the results for the urea are presented in Table 2.

Table 1. Conditions for the gel formation of carbamate with different solvents

Solvent	Solvent quantity (g)	Error	Carbamate quantity (g)	Error	Gel formation temperature (°C)	Gel breaking temperature (°C)	wt.%
Hexane	0.3262	0.0066	0.0767	0.0021	2	20	15.0
Xylene	0.3231	0.0101	0.0578	0.002	43	26	15.2
Toluene	0.9558	0.0175	0.0446	0.0019	10	20	4.46
1,4-dioxane	0.7542	0.006	0.0571	0.0011	2	20	7.04
2-propanol	0.5768	0.0186	0.0574	0.0014	0	9	9.05

Table 2. Conditions for the gel formation of urea with different solvents

Solvent	Solvent quantity (g)	Error	Urea quantity (g)	Error	Gel formation temperature (°C)	Gel breaking temperature (°C)	wt.%
Carbon tetrachloride	0.9944	0.0048	0.0178	0.0001	1	25	1.76
Xylene	1.0942	0.0492	0.0064	0.0001	12	12	0.58
Toluene	0.9883	0.0931	0.0615	0.0445	10	55	5.86
1,4-dioxane	0.9837	0.0545	0.0534	0.0002	5	35	5.15

Despite the formation of supramolecular networks for all solvents, their ability is limited because the higher quantities of carbamate to form gels compared with urea. It is likely the urea had great capacity of self-assemble and forming non-covalent networks. These results are coincident with the appearance and colors obtained in the organogels. For example, it was observed that the gel formed with urea in xylene was the one that used the least amount of organic compound (0.58 wt.%) and it had a transparent appearance, while the gels formed with toluene and 1,4-dioxane, the used concentration was 5.86 wt.% and 5.15 wt.%, respectively, and their appearance was semi-transparent and colorless. The urea in carbon tetrachloride formed a gel with a concentration of 1.76 wt.% of organic compound.

On the other hand, the best formed gel with carbamate was obtained with toluene, using a concentration of 4.46 wt.% of organic compound with a homogenous appearance of gel. The obtained concentrations in the organogel formation are coincident that those obtained in other works reported by bibliography [14, 26]. Due to the presented ability of carbamates and ureas to form organogels with organic solvents, it is possible that they can be applied as organic solvent trappers in the wastewater treatment. It is also possible that once the gel traps the solvent it can be reobtained by a filtering process, regenerated and reused several times the compound, which could be considered as an economical and sustainable treatment for water treatment.

The formation and breaking temperatures of gels were also measured. The results showed that carbamate gels with all solvent feature low temperatures of gel formation ($0 < T/°C < 10$) as compared with those gel formation from urea ($1 < T/°C < 12$). Concerning the breaking temperatures, urea has higher values ($12 < T/°C < 55$) than the carbamate, where the higher reached temperature was of 26 °C.

It has reported that the gel formation depends on number and interaction type between “gelator-gelator-solvent”. These interactions can be identified as hydrogen bonding, van der Waals forces, π - π interactions and acceptor-donor. Since the urea has two N-H bonding in its structure, while the carbamate only has one, the urea had the best ability to form organogels due to these supramolecular interactions. In addition, the adjacent polar groups as amine and/or hydroxyl (donor acids) increase the ability of functional groups to form organogels and trapping organic solvents. It has also reported that the gelling capacity of molecules with low molecular weight improves if in their structure have an aromatic part [7].

The gels of both organic compounds were analyzed by FT-IR. The spectra of carbamate and urea gels with toluene are presented in Figure 11, as an example. The results show that the intensity of the stretching in the vibrational bands of

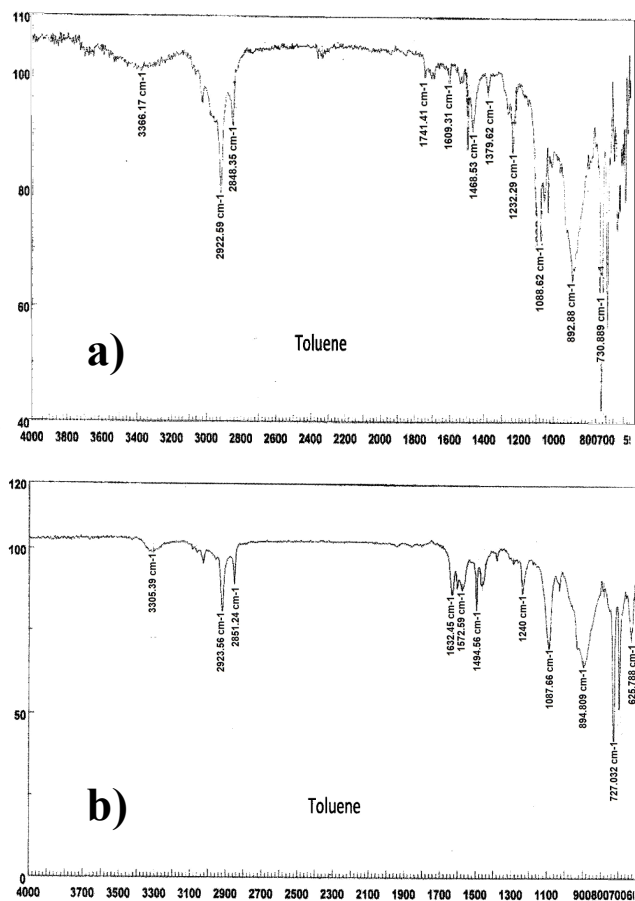


Figure 11. FT-IR gel spectra of a) carbamate with toluene and b) urea with toluene.

the NH_2 , OH, CH and $\text{HNC}=\text{ONH}$ bonds are reduced in the formed gels for both compounds. Additionally, the spectra showed very intense bands close to 890 cm^{-1} , because the bending vibrations (or deformation) of H-C-H causing intermolecular interactions by London dispersion.

According to FT-IR results a theoretical scheme of carbamate self-assemble to form the gel is presented in Figure 12, because it is possible assume that the organic compound starts to form non-covalent interactions between functional groups, creating supramolecular networks “gelator-gelator” and “solvent-gelator” in two and three dimensions. These interactions involve intermolecular forces as hydrogen-donor bond interactions (solvent acidity) or hydrogen-acceptor bond interactions (solvent basicity). These results can be coincident with the protein aggregation model developed by Boden [27] and the Hamilton model [28]. Both mechanisms explain that the gel formation follows three stages. In the first one, the primary structure is formed by a molecular recognition phenomenon that induces molecular aggregation or self-assembly, followed by the formation of a secondary structure through the anisotropic aggregate growth that define its morphology (micelles, vesicles, fibers corkscrews, disks, lamellae or tubules). Finally, a tertiary structure is created by the intersection of macro-nodes, generating aggregates that allow the gel stability. In this stage, the gel formation, the precipitation or crystallization of system is observed [29].

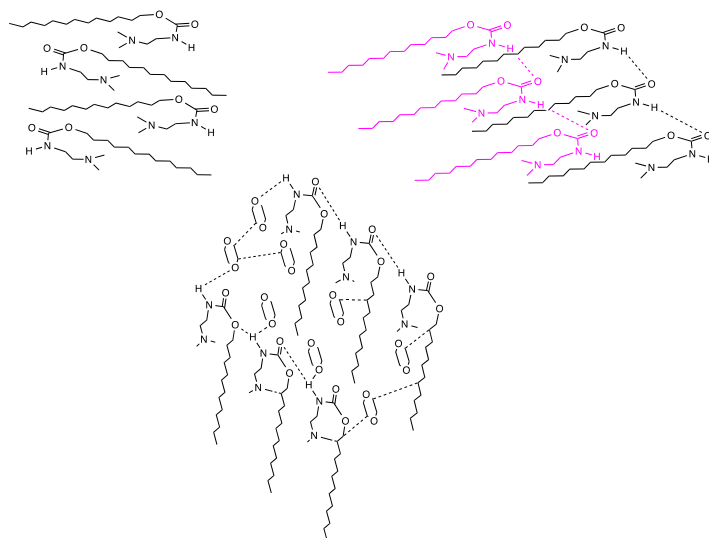


Figure 12. Scheme of non-covalent interactions in the gel formation.

Gel morphology was analyzed by scanning electron microscopy. The Figure 13 shows the micrographs of carbamate organogels produced with the different solvents where spheroidized clusters of fiber are observed. Now the structures less defined to carbamate gels were made with hexane and xylene (Figure 13a and 13b), while the gels prepared with 1,4-dioxane and 2-propanol, structures more defined were observed with diameters close to $20\ \mu\text{m}$.

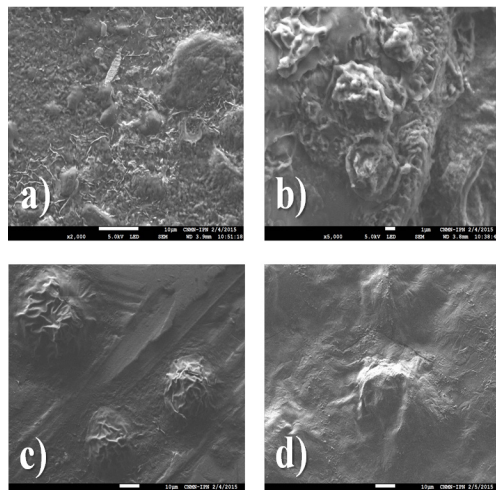


Figure 13. Carbamate organogels with a) hexane, b) xylene, c) 1,4-dioxane, d) 2-propanol.

The electron micrographs of urea gels with the solvents are present in Figure 14. Fiber clusters with spheroidized morphology are observed with mean diameter of $0.8\ \mu\text{m}$.

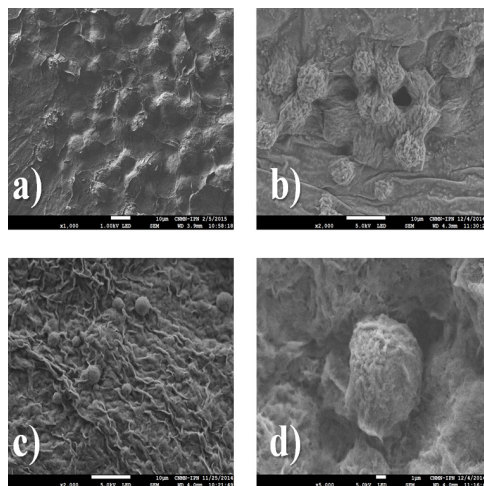


Figure 14. Urea organogels with a) carbon tetrachloride, b) xylene, c) toluene, d) 1,4-dioxane.

4. Conclusions

In this work two organic compounds were synthesized: a carbamate and a urea. The carbamate 3 was obtained as an amorphous white solid with a yield of 94 %, melting point 89-90 °C, m/z 357.3486; while urea 6 was obtained as a white solid, yield 88 %, melting point 109-110 °C and m/z 398.3142.

The organic compounds were able to produce reversible gels with all tested organic solvents. The amount of used urea in the gel formation was lower than used for carbamate. This result is attributed to the interactions by hydrogen bonding between amino groups of urea in the self-assemble process of organogels. Finally, these organogels have great potential to be use in the removal of organic solvents from contaminated water.

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