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Synthesis and Characterization of Egg Shell (ES) and Egg Shell with Membrane (ESM) Modified by Ionic Liquids

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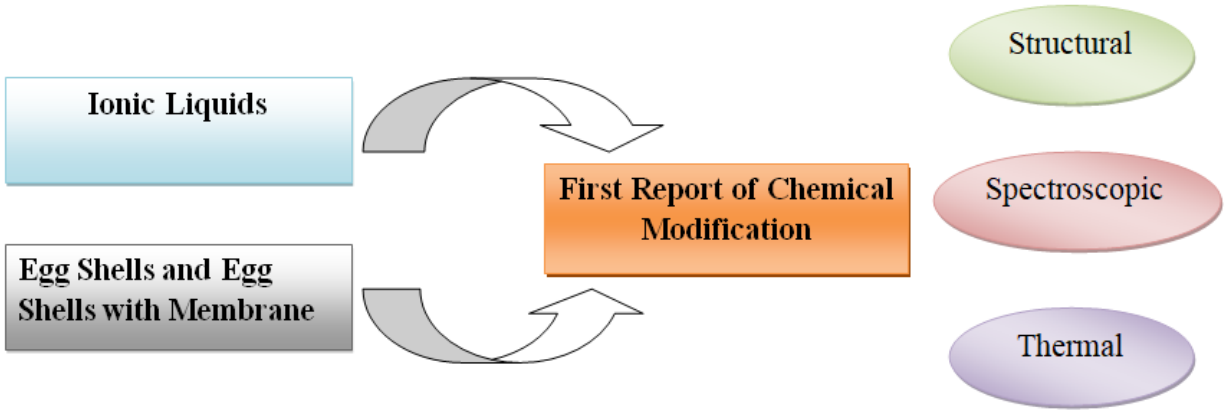
Abstract

Egg shell (ES) is a biological macromolecule mainly containing calcite embedded in proteins and polysaccharides, while shell membrane predominantly contains proteins. Thus ES with membrane (ESM) possesses richer protein contents than ES. In the present work, ES and ESM have been separately modified using mono- and di- cationic imidazolium ionic liquids, $[C_5mim^+][Br^-]$ (IL) and [Bis-$(PhCH_2MIm)^+$][$2Cl^-$] (DIL). Thus four modified products have been obtained namely ES-IL, ES-DIL, ESM-IL and ESM-DIL. In order to determine physico-chemical modifications of the ES due to the interactions with the ionic liquids, the structural, spectroscopic and thermal properties of all products were investigated by means of XRD, FTIR and TG/DTA. The IR spectra display significant changes in the 1400 – 1550 and 2800 – 3100 cm^{-1} regions confirming the insertion of IL and DIL into the ES and ESM layers. Furthermore, the XRD results indicate that this modification process influence the crystal structure of the ES. Thermal analysis suggests that the chemical modification increases the thermal stability of the ES and ESM. It has also been ascertained that presence of proteins in the shell membrane is responsible for increasing thermal stability in the order ES < ESM < ES-IL < ESM-IL < ES-DIL < ESM-DIL.

Keywords: ionic liquids, egg shells, egg shells with membrane, protein, thermal stability.

Journal Pre-proof

Graphical Abstract



Specifications Table

Subject area	Materials Science
Compounds	1-methyl-3-pentylimidazolium bromide, 4,4'-bis-(3-methylimidazolium-1-yl-methyl) biphenyl dichloride
Data category	Structural modification of biological products Egg Shell and Egg Shell Membrane using monocationic $[C_5MIm^+][Br^-]$ (IL) and dicationic $[Bis\text{-}(PhCH_2MIm)^+][2Cl^-]$ (DIL) ionic liquids to synthesize their four modified products.
Data acquisition format	NMR analysis, XRD patterns, IR spectra, Thermal analysis curves, TGA curves
Data type	Analysed and graphical data
Procedure	Known quantities of eggshells and eggshell membranes were taken in two different beakers each having 100 ml of distilled water. Both the beakers were mixed with ionic liquid monocationic $[C_5MIm^+][Br^-]$and methanol. In other two beakers eggshells and eggshell membranes were mixed with dicationic $[Bis\text{-}(PhCH_2MIm)^+][2Cl^-]$ ionic liquids along with methanol. All the solutions were thoroughly stirred at medium speed and room temperature. Modified products thus obtained in each beaker were filtered, washed, dried and finally granulated.
Data accessibility	A detailed spectroscopic analysis of both types of synthesized ionic liquids (IL and DIL) was carried out by ^1H and ^{13}C-NMR spectroscopy. Also, the physical and chemical characterizations of all the six prepared products were made by using XRD patterns, IR spectra and TGA /DTA measurements.

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1. Rationale

The chicken egg is one of the most consumed products in the world [1]. Poultries, food manufacturing units, homes and restaurants produce large amount of chicken egg waste on daily basis. Egg Shell (ES) is a hard outer cover of the egg which protects the albumen fluid of the egg. It is a waste product which is generated in large quantity on daily basis. The inner wall of the ES is covered with a membrane, which is a semi permeable clear film. ES is porous in nature and contains large amount of $CaCO_3$ embedded within polysaccharides and proteins, while eggshell membrane (ESM) mainly contains fibrous proteins [2–3]. The anatomy of ES reveals the presence of layered ceramic materials which are strengthened due to presence of protein, while ESM additionally contain long linear polysaccharides, commonly known as glycosaminoglycans or mucopoly saccharides, along with proteins [4 – 5].

Due to porous and membrane like properties, both ES and ESM attracted considerable attention to effectively utilize these waste materials as potential adsorbents for the removal of some hazardous chemicals. The past decade has witnessed publication of several research papers and review articles on the utilization of ES and several toxic dyes and metal ions have been proficiently removed from waters and wastewaters by using this material [6 – 10]. Numerous previous studies have also indicated that the thermal, morphological and textural properties of ES strongly depend upon its elemental composition and its high adsorption ability is due the available pores [11 – 16].

In recent years, modifications of existing materials have been extensively carried out to develop a variety of new products with better chemical and physical properties [17, 18]. For example, surface modification using ionic liquids is an eco-friendly process to generate an adsorbent with better scavenging properties [19 – 21]. Reports are available where imidazolium based ionic liquids have been used as modifier for different adsorbents and the developed materials are found to possess improved pore sizes, thermal stability and adsorption capability [22 – 23]. In recent years, the imidazole ionic liquids with different functional groups have been chemically modified and used as supported ionic liquids phases (SILPs). These materials have successfully employed as de-acidifies to crude oils [24] and mercury adsorption from a gas stream [25]. To the best of our knowledge, the modification of biological products as ES and ESM using ionic liquids have not been carried out so far and neither the evidences are available in the literature regarding their preparation nor about their structural, spectroscopic and thermal properties. Hence, the aims of this work is a novel attempt to structurally modify ES and ESM using monocationic $[C_5MIm^+][Br^-]$ (IL) or dicationic [Bis-$(PhCH_2MIm)^+][2Cl^-]$ (DIL) ionic liquids and to synthesize their four modified products, henceforth

called ES-IL, ES-DIL, ESM-IL and ESM-DIL. This paper includes synthesis procedures of of all the six above mentioned materials and studies on their structural, spectroscopic and thermal properties.

2. Procedure

ES were collected from a restaurant of University campus of Sidi Bel Abbes in western Algeria. After cleaning all the waste ES with running gentle stream of water, samples were rinsed several times with deionized water. To get egg shells without the membranes (ES), the membranes were manually stripped from the inner walls of the washed ES, and the products were again washed and dried in an oven. The remaining ES were directly dried in the oven and called egg shell with membrane (ESM). The dried eggshells, with or without membranes, were ground separately in an agate mortar and the obtained fine powders particles were sieved to 200 μm. Finally, the calcinations process was performed at 600°C for 60 min (with a heating rate of 10°C/min) and the products were kept in vacuum desiccator until use.

High purity chemicals 1-methylimidazole, [4,4'- bis (chloromethyl)-1,1'- biphenyl] and pentyl bromide (97%) were purchased from M/s Fluka and used as received. Deionized H_2O was obtained with a Millipore ion-exchange resin deionizer. Solvents used in synthesis, purification and NMR characterization (N,N-dimethylformamide and diethyl ether) were also procured from M/s Fluka. $CDCl_3$ and deuterated dimethyl sulfoxide (DMSO-d_6) were obtained from M/s Aldrich.

2.1. Preparation of monocationic IL and dicationic DIL

Both ionic liquids, IL and DIL, were synthesized (Scheme 1) from the 1-methylimidazole precursor according to reported procedures [26, 27]. The first ionic liquid, IL with IUPAC name 1-methyl-3-pentylimidazolium bromide, was prepared under microwave exposure by the chemical reaction of 1-methylimidazole and pentyl bromide for 5 min at 110°C. The reaction mixture was evaporated at reduced pressure and the product thus obtained was washed repeatedly with diethyl ether (5×20 mL) to remove any excess pentyl bromide. Then the product was dried under vacuum for 8 h to obtain a product with high purity. A viscous slightly yellowish liquid with 93% yield was obtained.

The second ionic liquid, DIL with IUPAC name 4,4'-bis-(3-methylimidazolium-1-yl-methyl) biphenyl dichloride [Bis-$(PhCH_2MIm)^+$][$2Cl^-$], was also prepared under microwave irradiation. 3.28 g (3.18 ml, 40 mmol) of 1-methylimidazole was mixed with 5.02 g (20 mmol) of the [4,4'-bis (chloromethyl) -1,1'- biphenyl] in N,N- dimethylformamide (3 ml) at 100 °C for 3 min. The resulting crude precipitate was collected by filtration and washed three times upon addition of diethyl ether (100 ml) to remove any unreacted reactants, and then it was dried under high vacuum for 8 h, to obtain a white hygroscopic solid of high yield (≈ 97%).

Furthermore, in order to obtain high purity, both IL and DIL were dried under vacuum (10^{-3} bar) with phosphorus pentoxide for 72 h to remove any possible water contamination before their use. The water content was kept below 280 ppm. This measure was carried out by coulometric Karl Fischer titration, performed by a Metrohm 831.

2.2. Chemical modification of ES and ESM

In a beaker, 100 ml of distilled water was added into a mixture of IL (0.5752g) and ES (2.5133g), while in another beaker DIL (0.2957 g) was mixed with ES (1.4029 g) by taking the same volume of distilled water. In each beaker 20 mL methanol was added and the solutions were stirred at medium speed and room temperature. After 24 hours of thorough mixing, the ES in both beakers were found to be modified by IL and DIL, respectively. Thus ES-IL and ES-DIL precipitates were separated by filtration, washed several times with distilled water, dried in a convection oven at 60°C during 24 h and finally crushed in a mortar. The obtained materials were kept in a vacuum desiccator until use. The same protocols were followed to prepare both ESM-IL and ESM-DIL.

3. Instrumentation

The structure and purity of both synthesized ionic liquids, IL and DIL, were confirmed by NMR analysis. ^{1}H-NMR (500 MHz) and ^{13}C-NMR (125.75 MHz) spectra were recorded by means of a Bruker DRX 400 MHz spectrometer. Spectra were recorded in (DMSO-$\mathbf{d_6}$) and ($CDCl_3$), using the DMSO residual peak as the ^{1}H internal reference (δ = 2.5 and 3.3), and the central peak of DMSO-$\mathbf{d_6}$ at δ = 39.5 as the ^{13}C reference. Chemical shifts (δ) are given in ppm and referred to the internal solvent signal, namely TMS and $CFCl_3$, respectively.

The structures of IL, DIL, ES-IL and ES-DIL, ESM-IL and ESM-DIL were characterized by Fourier transform infrared spectroscopy (FT-IR) performed by a Perkin-Elmer Spectrum BX spectrophotometer with a resolution of 4 cm^{-1} in the range 4000 – 650cm^{-1}.X-ray diffraction (XRD) patterns were collected on a Philips X-Pert diffractometer using Ni filtered Cu Kα radiation (λ =1.54056 Å) in the 2θ range 2-80º with a step size of 0.02º at room temperature. All measurements of thermo-gravimetry (TGA) and differential thermal analysis (DTA) were performed by means of an apparatus model SetaramSetSys Evolution 1200, with a fixed temperature rate of 5°C/min, in an argon flux of 60 ml/min. An initial mass of ~30 mg was used for each sample measurement.

3.1. NMR characterization

The structures of IL and DIL are confirmed by using ^{1}H, ^{13}C-NMR spectroscopy and ascertain the absence of any impurities, e.g. residuals of the reactants or by-products. The synthesizing process and NMR spectroscopic data are given in Table 1.

3.2. XRD characterization

Figure 1 shows the XRD pattern of ES and ESM before and after the modification by IL and DIL ionic liquids. Firstly, the peaks are identified by comparing them with the Joint Committee on Powder Diffraction Standards (JCPDS) files and others similar works [28 – 32]. All patterns before and after modifications show many fine and quite intense peaks. At the first look, the compared XRD pattern of ES, ESM eggshells are quite similar, except for a little difference related to the intensity of the peaks that could be related to the presence of the membrane associated with shell.

3.3. Infrared analysis

In order to obtain a clear idea on the structural changes, first FTIR analysis of IL and DIL alone was performed, and their spectra are shown in Figure 2 and spectrum of DIL was found richer in modes as compared to IL.Similarly spectra of ES and ESM alone were measured at room temperature in the IR absorbance range 500 to 4000 cm^{-1}andpresented in Figures 3. Spectra recorded after modification of ES and ESM by IL and DILare exhibited in Figure. 4.

3.4. Thermal analysis

In order to study the effect of thermal behaviours of ES and ESM modified by IL and DIL, TGA and DTA measurements were carried out. The obtained resulting thermograms and heat flux curves are presented in Figures 5 to 7. Upon heating, the TGA curves of IL and DIL show that their decomposition start at 240 °C and in the temperature range 350–480 °C complete decomposition occurs, depending on their structures.

4. Data, Value and Validation

4.1. XRD characterization

Figure 1 indicates that in both ES and ESM, strong peaks appearing at 2θ = 29.40° and 37.38°, are the characteristic peaks of the calcite ($CaCO_3$) phase, while those appearing at 2θ =32.18°, 39.32°, 43.14°, 47.10°, 48.46°, 53.84°, 57.38°, 64.30° and 67.36° correspond to calcium oxide (CaO) [30]. These results confirm the presence of calcite and calcium oxide as the main constituents in the ES powder [33, 34]. The peaks visible at 2θ = 17.94, 26.46°, 34.18 and 50.90° are the characteristic peaks of calcium hydroxide $Ca(OH)_2$ [29 – 31]. These peaks are more intense in ESM due to the presence of OH group, suggesting that the ESM has moisture adsorption capability. Indeed, the appearance of $Ca(OH)_2$ may be due to the exposure of CaO to atmospheric air [32]. Niju et al. [29] obtained similar peaks for calcined ES and Rivera et al. [35] obtained similar peaks for calcium oxide derived from ES.

By comparing the XRD results of ES and ESM with the respective IL/DIL modified products, the appearance of a new peak at 71.70° and the disappearance of a peak at 37.41° can be observed in the case of IL/DIL modified ES. On the other hand, the disappearance of two peaks at 37.41° and 67.42° and the appearance of a new peak at 32.16° are observed for IL/DIL modified ESM.

Upon close inspection, it is noted that diffraction peaks of ES and ESM still exist in ES modified with IL/DIL and ESM. However, it must be noted that the increase of the intensity of the peaks located at 2θ =29.40°, 34.18°, 47.10° indicates a partial dissolution of CaO in water and the formation $Ca(OH)_2$ as final product [29 – 32].

4.2. IR characterization

In the Figure 2, spectral zone 500 - 600 cm^{-1}, the IR bands observed at 558, 625, 655, 758, and 848 cm^{-1} in the IL spectrum are assigned to the C–C vibrations of the pentyl chain [36], while, the bands at 567, 626, 669, 706, 749, 772, 803 and 826 cm^{-1}correspond to the C–C deformation vibrations of the phenyl ring and methylene groups of the DIL. The C–H bending vibrations and C–N stretching modes present in ($N–CH_2$) and ($N–CH_3$) are observed at 1169 in the IL spectrum, and at 1166 in the DIL spectrum. On the other hand, bands appearing at 1335, 1380 cm^{-1} in the IL spectrum and at 1319, 1339, 1361 cm^{-1} in the DIL spectrum are attributed both to the vibration (C–C) and to the stretching vibration (C–N) [37, 38].

Figure 2 also explains that the vibration bands with wavenumbers in the range of 1400–1700 cm^{-1} represent mainly the C=C, and C=N bond stretching within the imidazole ring and phenyl ring modes [39]. The bands at around 1466, 1571, 1633 and 1673 cm^{-1} in IL spectrum can be assigned to the C=C and C=N stretching vibrations of the imidazolium cation of IL. Also, the bands at 1407, 1503 1574, 1627 and 1660 cm^{-1} in the DIL spectrum can be assigned to the same mode of C=C and C=N stretching vibrations of the imidazolium cation and the C=C vibration of the aromatic phenyl ring. The IR bands observed at 2858, 2932 and 2956 cm^{-1} in the IL spectrum are assigned to C–H stretching in the aliphatic pentyl chain [40, 41]. The bands at the highest frequency, 3065 and 3139 cm^{-1} for IL are assigned to the symmetric stretching modes of C2–H and C4/5 positions of the imidazole ring [42]. The methylene group and the aromatic C–H modes of the phenyl ring are observed in the region 2863, 2930 cm^{-1} in the DIL spectrum, respectively. Moreover, the high wavenumber modes at 3033, 3082 and 3140 cm^{-1} can be assigned to stretching vibrations of imidazole ring in the DIL spectrum [43].

With the help of Figure 3 a similar behaviour in both spectra can be observed. The absorption bands occurring at 714, 873, 1047/1060 and 1410/1418 cm^{-1} can be attributed to the vibrations of the carbonate CO_3^{-2} anions [31, 34]. Moreover, the weak IR peaks at2359 and 2514 cm^{-1} indicate the presence of organic matter in the ES spectrum; these modes are more intense in the case of the ESM spectrum. The bands located at 3420, 3725 and 3835 cm^{-1} in the ESM spectrum and at 3391, 3731 and 3863 cm^{-1} in ES have been attributed to H-bonded water due to humidity [44], while the sharp peak at 3640 cm^{-1} is due to the stretching vibration of hydroxyl groups attached to calcium oxide. These observations are in good agreement with the XRD characterization that shows the presence of $Ca(OH)_2$ in both ES and ESM.

Figure 4 presents graphs showing IR spectra of ES and ESM after modification by IL and DIL. These spectra exhibited similar bands in the region 400–1300 and 3300–4000 cm^{-1} related to the structure of ES and ESM. IR spectra of modified ES and ESM indicate the occurrence of the IL and DIL functionalities. The small peaks in the region 1400– 1550 cm^{-1} with a varying intensity were characteristic of the asymmetric bending vibrations of the methylene $–CH_2–$ in the case of DIL and methyl CH_3 groups of the pentyl chains in the case of IL [40 – 42]. In addition, the C=C vibrational frequencies are the significant characteristic bands in the vibrational spectra of ES and ESM modified by IL and DIL. These new peaks appearing at 1593 cm^{-1} can be attributed to the stretching of the C=C vibrations of phenyl and imidazolium rings. A pentyl chain in IL and phenyl groups gives significantly stronger peaks in the ranges of 2800–3100 cm^{-1}. A very weak peaks near between 2900 and 3200 cm^{-1} can be observed in the spectra of the imidazolium modified ES and ESM. These new observed peaks confirmed the insertion of IL and DIL into the ES. The presence of the characteristic bands of IL and DIL in the IR spectra of the ES and ESM highlight the efficiency of the proposed process.

4.3. Thermal analysis

Interestingly, at room temperature the monocationic IL is liquid, while the DIL is solid and the melting temperature of DIL [Bis-$(PhCH_2MIm)^+$] [$2Cl^-$] is higher than the boiling temperature of the IL [C_5mim^+][Br^-][35].The fact that the DIL starts decomposing before the IL can be explained by its higher size and molecular structure[45, 46], knowing that [Bis-$(PhCH_2MIm)^+$] has a bulkier cation, as compared to [C_5mim^+], a saturated alkyl chains [39, 43].It is also significant that the anionic part (chloride or bromide) does not have any significant influence on the degradation temperature of IL and DIL. With the help of Figure 5 it can be observed that the thermal stability of the DIL is lower than that of the IL and the TGA curve of DIL exhibits a multistep degradation.

The TGA curves of ES, ESM and their IL/DIL modified products are reported in the temperature range 25 – 900 °C (Figure 6). For all the substances two stages of weight losses are observed. For ES, a total 18.75% weight loss was observed starting from 366°C up to 438°C, while in the case of ESM the loss started from 389 °C, was completed at 445°C and only a 4% loss was recorded. This initial step of weight loss is originated from the decomposition of the organic matter, i.e. proteins, in ESM as compared to ES. This is in agreement with studies carried out by Mittal et al., which suggested that the carbonates, sulphates and phosphates of calcium, magnesium and organic matter are the major constituents of the ES, while ESM contains organic protein materials in addition [6]. Figure 6 also confirms that the chemical modification by ionic liquids IL and DIL increases the thermal stability of the ES. The second step of weight loss between 550 and 875°C, is attributed to the decomposition of calcium carbonate. In this stem weight loss started at 646 °C and completed at 737

°C for ES and from 670 °C to 767 °C for ESM. Kaewtatip et al. [47], reported that weight losses of ES and ESM of this step are attributed to the release of CO_2 to give CaO.

In the similar manner TGA curves ES and ESM were recoded before and after modification by IL and DIL and presented in Figure 6. The difference in values of weight losses observed in the first step of the decomposition of both ES and ESM with IL and DIL is due to the introduction of IL and DIL inside the layered ES and ESM (Figure 6). The higher weight loss in the case of ESM-DIL is due to the presence of larger amount of DIL into the layered structures of ESM.

The DTA curves of ES, ESM and their modified products are recorded in the same temperature range and presented in Figure 7. For each sample, two endothermic peaks are visible, the first endothermic peaks at 422°C for ES and at 428 °C ESM corresponding to decomposition of their organic matter, while, the peaks at 437°C for ES-IL and 446°C ESM-IL and at 452°C for ES-DIL and 455°C for ESM-DIL are associated to the thermal decomposition of organic spaces of the ES and ESM and decomposition of IL and DIL. The second stage is associated with the thermal decarbonation of calcium carbonate in all samples. This clearly indicates the DTA analysis is consistent with the TGA results.

Thus from these thermo-grams and depending on modified egg shell by IL or DIL ionic liquid type, it can be safely interpreted that the thermal stability of these materials follow the order ES<ESM<ES-IL< ESM-IL<ES-DIL<ESM-DIL. On the basis of obtained results it can be safely interpreted that both IL and DIL produce effective, eco-friendly and more thermally stable modified products of ES and ESM, which can be used for a variety of applications for example water treatment.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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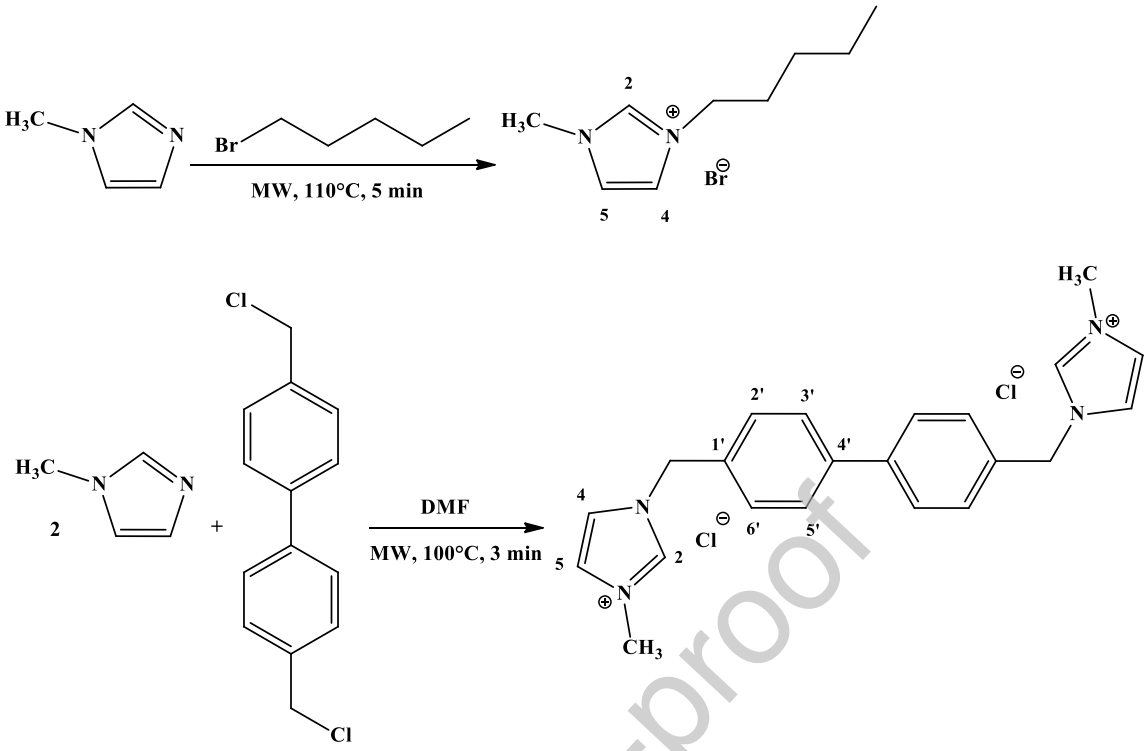
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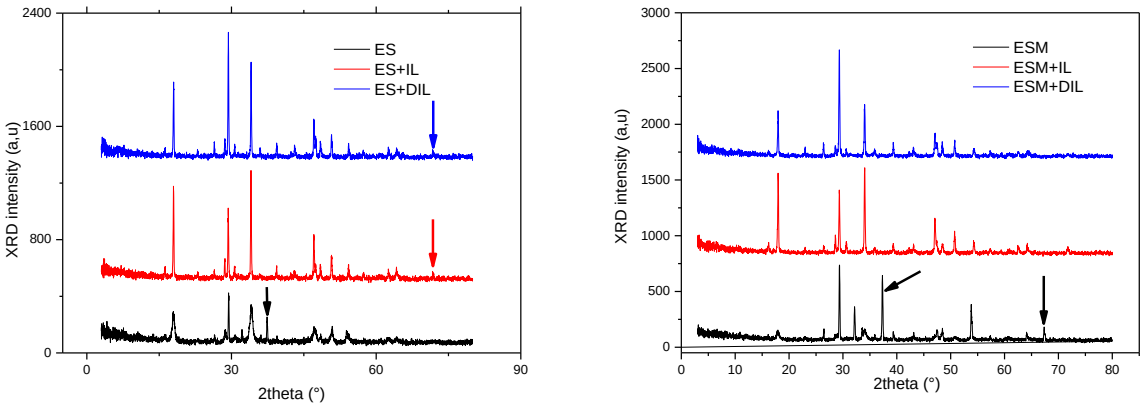
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Scheme 1. General procedure for the synthesis of IL and DIL, (MW: Microwave).



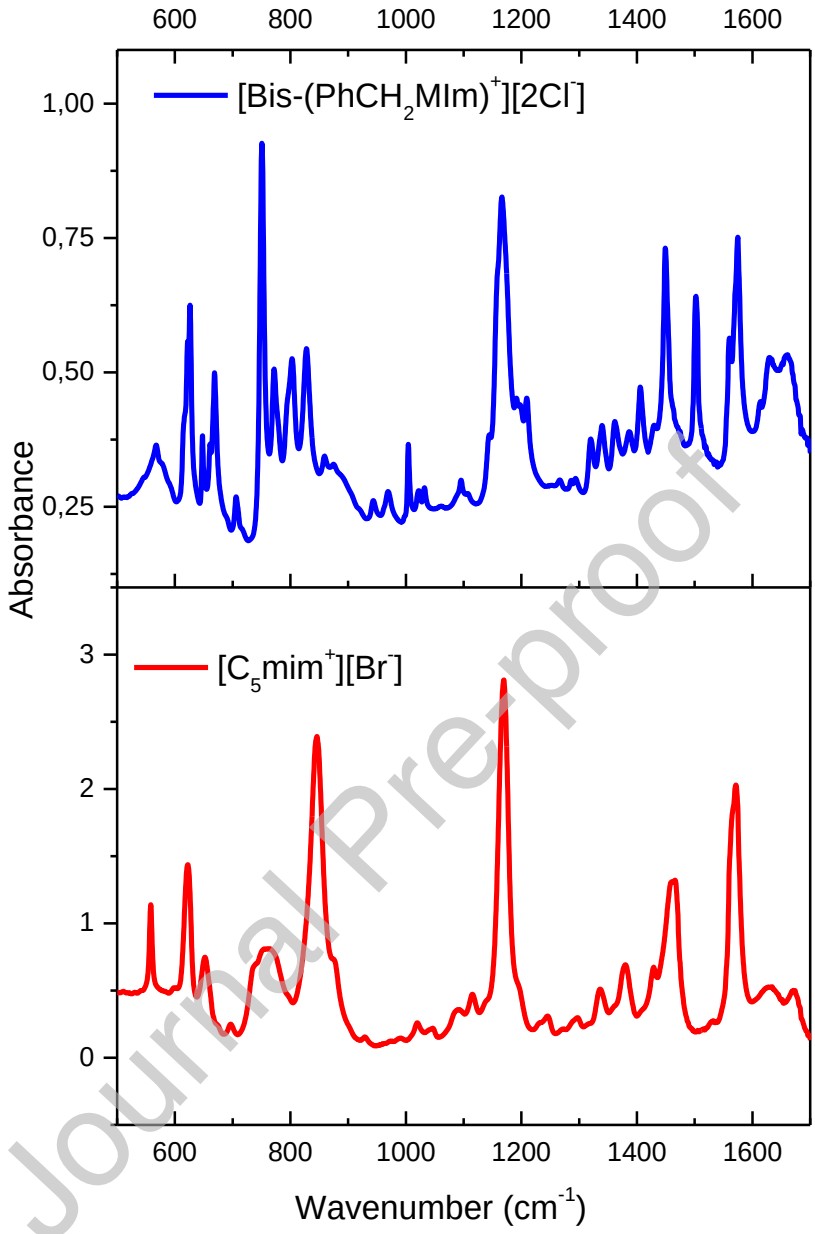
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Figure 1. XRD patterns of egg shell (ES) and egg shell with membrane (ESM) before and after modification by monocationic ionic liquid (IL) and dicationic ionic liquid (DIL)



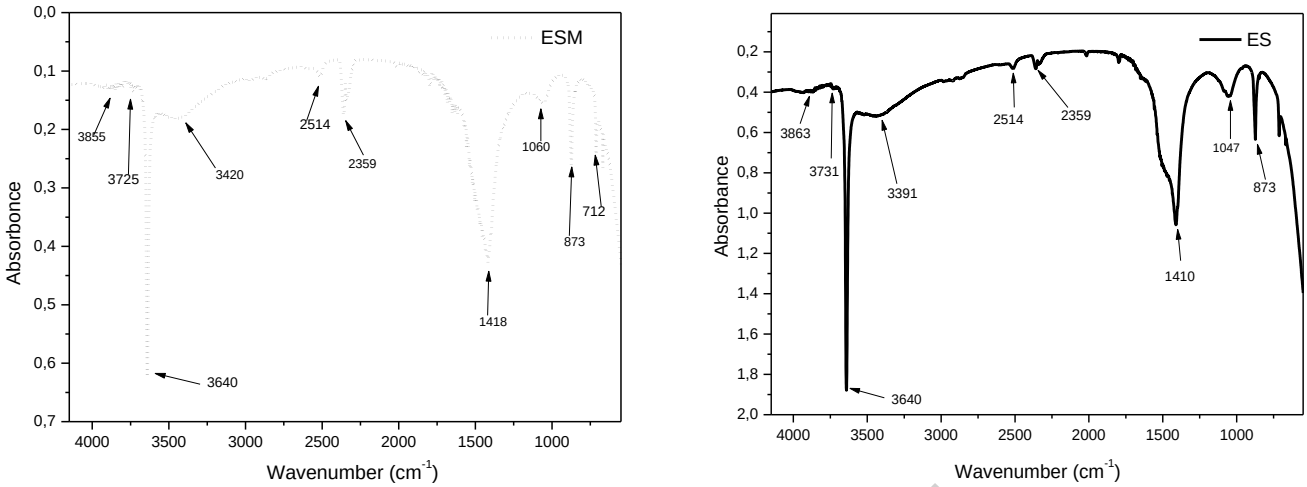
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Figure 2. IR spectra of monocationic ionic liquid (IL) and dicationic ionic liquid (DIL)



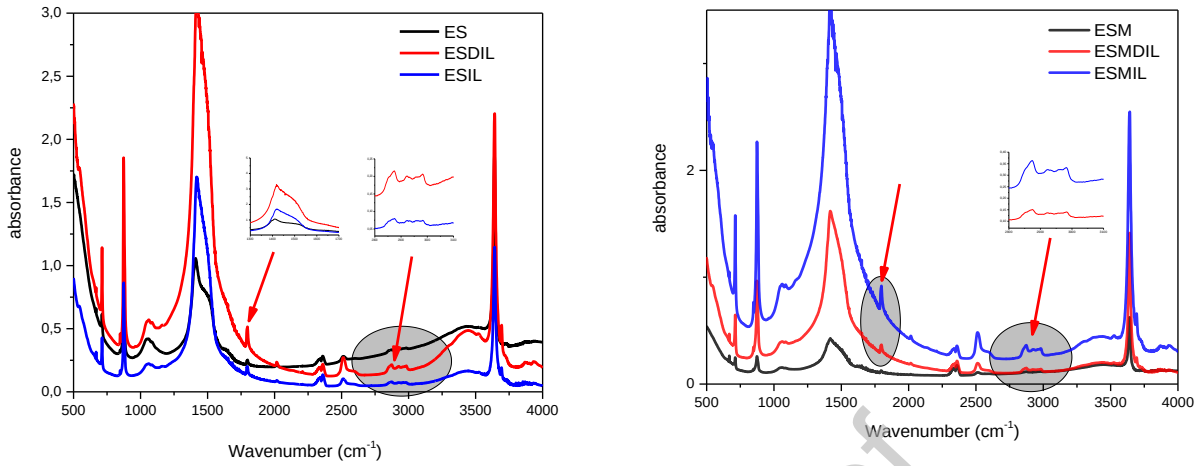
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Figure 3. IR spectra of egg shell (ES) and egg shell with membrane (ESM)



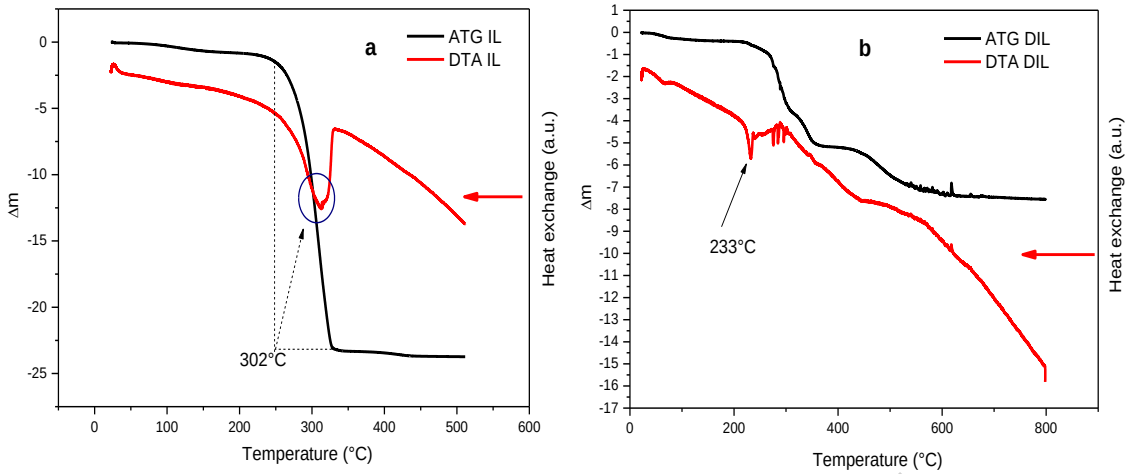
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Figure 4: **IR spectra of egg shell (ES) and egg shell with membrane (ESM) after modification by monocationic ionic liquid (IL) and dicationic ionic liquid (DIL)**



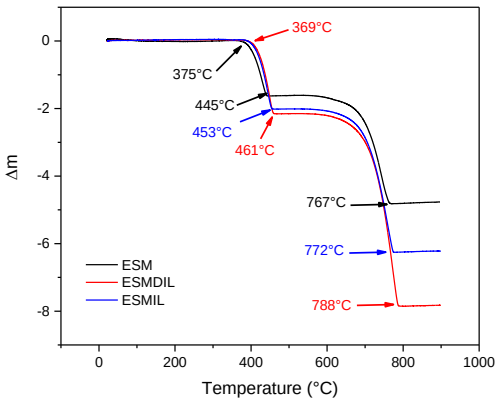
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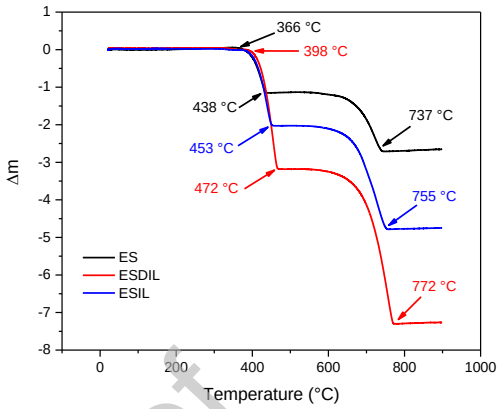
Figure 5. Thermal analysis curves of monocationic ionic liquid (IL) and dicationic ionic liquid (DIL)



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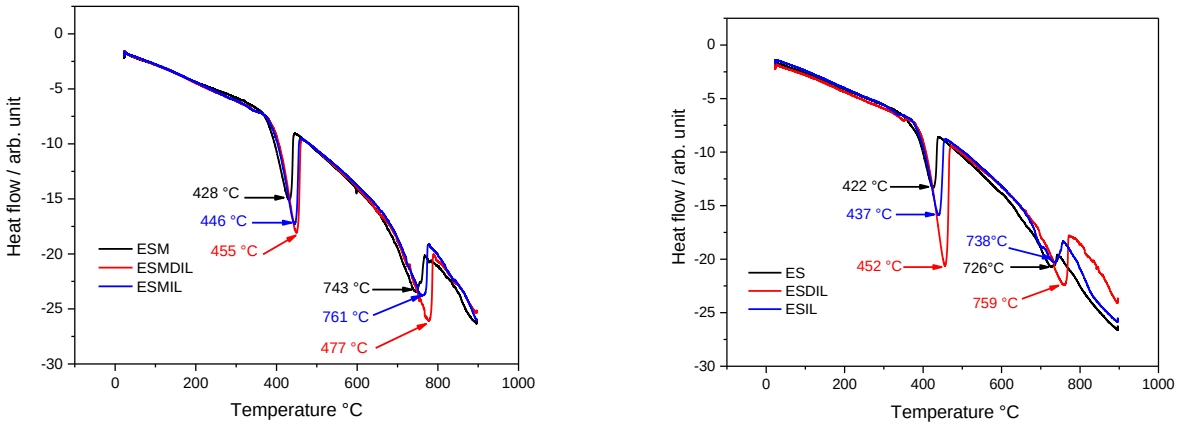
Figure 6: TGA curves of egg shell (ES) and egg shell with membrane (ESM) before and after modification by monocationic ionic liquid (IL) and dicationic ionic liquid (DIL)





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Figure 7: **DTA curves of egg shell (ES) and egg shell with membrane (ESM) before and after modification by monocationic ionic liquid (IL) and dicationic ionic liquid (DIL)**



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Table – 1. NMR Spectroscopic Data of Monocationic **and** Dicationic Ionic Liquids

Type of Ionic Liquid	Details of ^{1}**H-NMR** and ^{13}**C-NMR** Spectrum
Monocationic **[C_5mim$^+$][Br^-]**	**^{1}H-NMR ($CDCl_3$) δ_H (ppm)** 10.08 (1H, s, N^+CHN), 7.42 (1H, s, N^+CH), 7.26 (1H, s, NCH=), 4.28-4.24 (2H, t, J=2.6 Hz, N^+CH_2), 4.02 (3H, s, NCH_3), 1.86-183 (2H, m, J=6.4 Hz, NCH_2CH_2), 1.37-1.31 (4H, m, J=2.8 Hz, $NCH_2CH_2CH_2CH_2$), 0.81 (3H, t, J=6.8 Hz, $N^+(CH_2)_4CH_3$)
	^{13}C-NMR ($CDCl_3$) δ_C (ppm) : 13.23(NCH_3), 19.30($N^+(CH_2)_4CH_3$), 29.42(NCH_2), 32.02($NCH_2CH_2CH_2CH_2$), 36.50($NCH_2CH_2CH_2$), 49.17($NCH_2CH_2CH_2$), 122.10, 123.28(C-4 and C-5), 137.90(C-2).
Dicationic Ionic Liquid **[Bis-($PhCH_2MIm)^+$] [$2Cl^-$]**	**^{1}H NMR (500 MHz, DMSO-d_6):** 3.88 (s, 6H, 2 × CH_3), 5.51 (s, 4H, 2 × N-CH_2-Ar), 7.56 (d, 4H, 2 ×HC-C(CH_2)-CH), 7.76 (d, 4H, 2 × HC-C(C)-CH), 7.89 (s, 2H, H_3C-NCH), 7.95 (s, 2H, -NCH), 9.45 (s, 2H, 2 ×NCHN).
	^{13}C NMR (DMSO-d_6): 36.6(NCH_3), 52.1(NCH_2), 122.8, 124.6(C-2', C-3', C-5'and C-6'), 127.8, 129.3(C-1' and C-4'), 134.7, 137.3(C-4 and C-5), 140.1(C-2).

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