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Metal-containing Ionic Liquids as Catalyst in PET Glycolysis

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Abstract: *Metal-containing ionic liquids with general formula [Rmim]+MX3- (R=n-butyl or n-lauryl; M=Zn, Cd; X=Cl, Br) were synthesised and then characterized by nuclear magnetic resonance spectroscopy and infrared spectroscopy. The catalytic activity was tested in glycolysis of poly(ethylene terephthalate) (PET) with ethylene glycol (EG) with the main product being bis-2-hydroxyethyl terephthalate (BHET). The following parameters were varied: the catalyst type, the catalyst loading and the molar ratio between PET and EG. For every reaction conversion and selectivity were calculated. All these reactions arose with high selectivity in the desired product, the conversion of PET being quasi-total.*

Keywords*: PET recycling, glycolysis, ionic liquids*

1. Introduction

Poly(ethylene terephthalate), often known as PET, is one of the most widely used plastics due to its durability, chemical resistance, light weight, and cheap market price. Textiles, photographic films, and primarily soft-drink plastic bottles are all examples of PET applications [1]. PET, on the other hand, is non-biodegradable, and global demand is expanding at an alarming rate, making this material one of the most plentiful post-consumer wastes [2]. As a result, scientists are focusing their efforts on ensuring that this material is recycled efficiently, PET can be recycled using either mechanical or chemical processes [3]. The traditional technique is a chemical recycling process that breaks down PET into its fundamental monomeric form as dimethylterephtalate (DMT), bis-(2-hydroxyethyl)terephthalate (BHET) or terephthalic acid (TA) by processes such as methanolysis [4, 5], glycolysis [6, 7] or hydrolysis [8]. These monomeric compounds can be then used to remanufacture PET [9].

Glycolysis, a widely used commercial technique, is the most economically viable, cost-effective, and future-oriented recycling method of plastic waste. Such reaction follows a transesterification mechanism in the presence of a catalyst, which can be a metal-based compounds [7], organic superbases [6] or ionic liquid [10, 11]. The use of ethylene glycol (EG) in this process produces BHET, a monomer used in repolymerizing PET, and other PET glycolyzates [9] which are used in manufacturing polyurethane foams, copolyesters, acrylic coatings and hydrophobic dyes [12-15]. Superior glycols can also be used as diols for PET glycolysis [16,17], depending on the targeted monomer or the targeted properties of the material that the glycolyzate is going to be used in.

Because of their unique properties, such as thermal stability, electrochemical stability, low flammability, and structural flexibility of the cation and anion, ionic liquids (ILs) have attracted researchers' attention as ideal green solvents and/or catalysts in various reactions [18, 19] including polymer breakdown [20, 21]. Degradation of PET using ionic liquids occurs quickly in low pressure and temperature environment, without releasing toxic substances. Adding water by filtration allows the ionic liquid to be separated from the compounds produced allowing the ionic liquid to be used again.

Wang et al. [22] explored the ability of acidic, basic, and neutral ionic liquids as novel catalysts in depolymerizing PET wastes using EG. The glycolysis method was enhanced by basic ionic liquids and

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acidic ionic liquids, but basic ionic liquid synthesis is relatively difficult and costly while acidic ionic liquids were discovered to be volatile at temperatures above 180°C. Using several basic ionic liquids as catalysts, Yue et al. [23] conducted the glycolysis of PET in which 1-butyl-3-methylimidazolium hydroxyl ([Bmim]OH) has shown the higher catalytic activity with 100% conversion of PET among various basic ionic liquids. Yue et al. [21] also proved that when opposed to the neutral ionic liquid ([Bmim]Cl), the Lewis acidic ionic liquid ([Bmim]$ZnCl_3$) possessed a high catalytic activity. Furthermore, Al-Sabagh et al. [24] achieved complete PET conversion and selectivity in BHET around 50% by using mixtures of $Zn(OAc)_2$, respectively $Cu(OAc)_2$ and [Bmim]Cl. Shuangjung et al. [25] achieved 100% conversion and almost 90% selectivity in BHET when they performed the PET glycolysis by using an equimolar mixture of [Hmim]$ZnCl_3$ and [Hmim]$CoCl_3$.

Our current goal in this work is to achieve total PET glycolysis in the presence of new metal containing ILs. To this aim, several metal-containing ionic liquids based on 1,3-N,N-disubtituted imidazolium salts and their precursors were synthesized (Figure 1). The metal-containing compounds were tested as catalysts in PET glycolysis with EG, and some optimum reaction parameters were also determined. To the best of our knowledge the use of [Bmim]$CdCl_3$, [Ddmim]$ZnCl_3$, and [Bmim]$ZnBr_3$ were not reported as catalysts for this reaction.

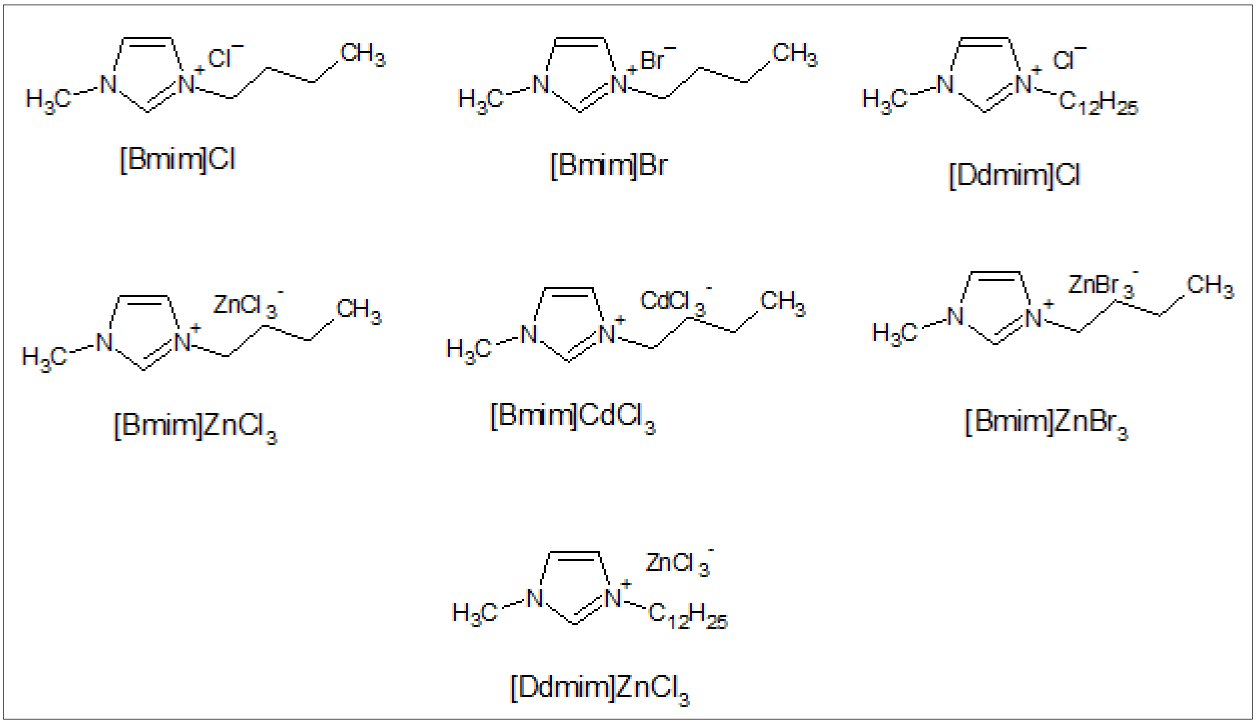
[Bmim]Cl
[Bmim]Br
[Ddmim]Cl
[Bmim]$ZnCl_3$
[Bmim]$CdCl_3$
[Bmim]$ZnBr_3$
[Ddmim]$ZnCl_3$

Figure 1. Structural formulas of synthesised ionic liquids (ILs)

2. Materials and methods

2.1. Material

PET waste was obtained from postconsumer bottles and cut into small flakes and cleaned thoroughly by washing with water containing detergent, then with distilled water and skimmed with benzene and dried in the laboratory oven at 80°C for 12 h. Butyl chloride, dodecyl chloride, butyl bromide, 1-methyl-imidazole, acetonitrile, zinc chloride, cadmium chloride, and zinc bromide were purchased from Sigma (Aldrich) and used as received.

2.2. Ionic liquids synthesis

Synthesis of 1-butyl-3-methylimidazolium chloride ([Bmim]Cl). The synthesis was carried out as described previously [26] with proper modifications. Briefly, a 100 mL round-bottom flask equipped with a reflux condenser, calcium chloride tube and magnetic stirring was loaded with 48.1 g butyl chloride (0.52 mol), 32.8 g 1-methylimidazole (0.4 mol) and 21.6 mL acetonitrile. The flask was immersed in an oil bath preheated at 85°C and refluxed for 48 h. The volatile compounds were then removed by evaporation and the reaction mixture was allowed to crystallize in the freezer. In order to obtain pure [Bmim]Cl the crude product was dissolved in 100 mL acetonitrile at 60°C and then added dropwise in 250 mL stirred ethyl acetate and the crystals formed were filtered affording 58.8 g of product. **Melting point**: 60°C; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 10.38 (s, 1H), 7.57 (s, 1H), 7.42 (s, 1H), 4.26 (t, *J* = 7.3 Hz, 2H), 4.04 (s, 3H), 1.89 – 1.75 (m, 2H), 1.38 – 1.23 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 137.62, 123.50, 121.79, 49.59, 36.40, 31.99, 19.28, 13.27. **FT-IR:** 3386; 3061; 2960; 2937; 2874; 2741; 1568; 1466; 1169.

Synthesis of 1-dodecyl-3-methylimidazolium chloride ([Ddmim]Cl) [26]. A 100 mL round-bottom flask equipped with a reflux condenser, calcium chloride tube and magnetic stirring was loaded with 25.4 g dodecyl chloride (0.12 mol), 10.82 g 1-methylimidazole (0.13 mol) and 28 mL acetonitrile. The flask was immersed in an oil bath preheated at 85°C and refluxed for 7 days. The volatile compounds were then removed by evaporation under reduced pressure and the reaction mixture was allowed to crystallize in the freezer. In order to obtain pure [Ddmim]Cl the crude product was dissolved in 60 mL acetonitrile at 60°C and decoloured using charcoal, followed by vacuum filtration and crystallization overnight. **Melting point:** 43°C; **^{1}H-NMR (300MHz, $CDCl_3$)** δ 10.69 (s, 1H), 7.46 (s, 1H), 7.41 (s, 1H), 4.29 (t, *J*=7.3 Hz, 2H), 4.11 (s, 3H), 1.94-1.80 (m, 2H) 1.30-1.22 (m, 18H), 0.85 (t, J=7.3 Hz, 3H). **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 138.14, 123.27, 121.49, 50.09, 36.58, 31.82, 30.26, 29.51, 29.41, 29.29, 29.25, 28.92, 26.20, 22.55, 14.05. **FT-IR:** 3443; 3377; 2916; 2848; 1574; 1562; 1463; 1168; 865; 767.

Synthesis of 1-butyl-3-methylimidazolium bromide ([Bmim]Br) [27]. A 100 mL round-bottom flask equipped with a reflux condenser, calcium chloride tube and magnetic stirring was loaded with 54.8 g butyl bromide (0.4 mol), 32.8 g 1-methylimidazole (0.4 mol) and 28 mL acetonitrile. The flask was immersed in an oil bath preheated at 100°C and refluxed for 24 h. The volatile compounds were then removed by evaporation and the reaction mixture was allowed to crystallize in the freezer. **Melting point:** 73°C; **^{1}H-NMR (300 MHz, $CDCl_3$)** δ 10.17 (s, 1H), 7.59 (s, 1H), 7.47 (s, 1H), 4.25 (t, J = 7.3 Hz, 2H), 4.04 (s, 3H), 1.89 – 1.75 (m, 2H), 1.39 – 1.20 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H). **^{13}C-NMR (75 MHz, $CDCl_3$)** δ 137.04, 123.67, 122.08, 49.74, 36.66, 32.11, 19.39, 13.42. **FT-IR:** 3419; 3141; 3071; 2959; 2934; 2872; 1627; 1567; 1463; 1166; 843; 752.

Synthesis of 1-butyl-3-methylimidazolium trichlorozincate ([Bmim]$ZnCl_3$). The synthesis was carried out as described previously [1] with proper modifications. A 50 mL round-bottom flask equipped with magnetic stirring and a septum was loaded with 2.0 g [Bmim]Cl (11 mmol) and 1.558 g anhydrous $ZnCl_2$ (11 mmol). 20 mL methylene chloride were added through the septum. After an hour $ZnCl_2$ was dissolved and two layers were noticed. The stirring was maintained for 24 h. Afterwards, the volatile compounds were evaporated under vacuum. The flask was then introduced in the freezer for 48 h in order to obtain a viscous liquid. **^{1}H-NMR (300 MHz, DMSO-d_6)** δ 9.14 (s, 1H), 7.95 (s, 1H), 7.92 (s, 1H), 4.14 (t, *J* = 7.3 Hz, 2H), 3.84 (s, 4H), 1.87 – 1.73 (m, 2H), 1.39 – 1.24 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). **^{13}C-NMR (75 MHz, DMSO-d_6)** δ 137.51, 125.16, 123.76, 50.84, 37.46, 33.15, 20.54, 14.29. **FT-IR**: 3362; 3147; 3111; 2961; 2953; 2874; 1621; 1566; 1463; 1163; 838; 749.

Synthesis of 1-dodecyl-3-methylimidazolium trichlorozincate ([Ddmim]$ZnCl_3$). A 25 mL round-bottom flask equipped with argon inlet, thermometer and magnetic stirring was loaded with 2.025 g [Ddmim]Cl (7 mmol) and 0.952 g anhydrous $ZnCl_2$ (7 mmol). The flask was immersed in an oil bath preheated at 100°C. The stirring was maintained until the $ZnCl_2$ was entirely dissolved. **Melting point:** 57-58°C;

^{1}H-NMR (300 MHz, DMSO-d_6) δ 8.57 (s, 1H), 7.40 (s, 1H), 7.38 (s, 1H), 4.11 (t, J=7.3 Hz, 2H), 3.83 (s, 3H), 1.80 (m, 2H), 1.26 (m, 18H), 0.87 (t, *J* = 7.3 Hz, 3H) **^{13}C-NMR (75 MHz, DMSO-d_6)** 137.50, 125.15, 123.75, 51.08, 37.41, 33.18, 31.18, 30.88, 30.78, 30.64, 30.61, 30.18, 27.26, 23.95, 18.99, 15.00. **FT-IR:** 3405; 3144; 3102; 2924; 2854; 1630; 1464; 1165; 846; 752.

Synthesis of 1-butyl-3-methylimidazolium trichlorocadmiate ([Bmim]CdCl$_3$). A 25 mL round-bottom flask equipped with magnetic stirring was loaded with 2 g [Bmim]Cl (11 mmol), 2.013 g CdCl$_2$ (11 mmol) and 5 mL acetonitrile. The reaction mixture was allowed to stir for 24 h and then the acetonitrile was evaporated under reduced pressure. **^{1}H-NMR (300 MHz, DMSO-d$_6$)** δ 9.17 (s, 1H), 7.97 (s, 1H), 7.94 (s, 1H), 4.69 (t, *J* = 7.3 Hz, 2H), 4.39 (s, 3H), 2.37-2.29 (m, 2H), 1.72-1.79 (m, 2H), 1.47 (t, *J* = 7.3 Hz, 3H). **^{13}C-NMR (75 MHz, DMSO-d$_6$)** δ 137.33, 124.99, 123.59, 50.68, 37.31, 32.99, 20.39, 14.14. **FT-IR:** 3240; 3145; 2964; 2935; 2865; 1676; 1626; 1460; 1166; 837; 756.

Synthesis of 1-butyl-3-methylimidazolium tribromozincate ([Bmim]ZnBr$_3$). A 50 mL round-bottom flask equipped with magnetic stirring and a septum was loaded with 2.5 g [Bmim]Br (12 mmol) and 2.57 g anhydrous ZnBr$_2$ (12 mmol). 5 mL methylene chloride were added through the septum. The reaction mixture was allowed to stir for 24 h and then the acetonitrile was evaporated under reduced pressure. **^{1}H-NMR (300 MHz, DMSO-d$_6$)** δ 9.14 (s, 1H), 7.96 (s, 1H), 7.93 (s, 1H), 4.69 (t, *J* = 7.3 Hz, 2H), 3.56 (s, 3H), 2.42-2.30 (m, 2H), 1.9-1.75 (m, 2H), 1.48 (t, *J* = 7.3 Hz, 3H). **^{13}C-NMR (75 MHz, DMSO-d$_6$)** δ 137.34, 124.99, 123.60, 50.59, 37.32, 32.97, 20.38, 18.80, 14.12. **FT-IR:** 3380; 3145; 3110; 2959; 2934; 2873; 1611; 1564; 1462; 1162; 832; 744.

2.3. General procedure for glycolysis

A two-neck round-bottom flask equipped with a reflux condenser, calcium chloride tube, argon inlet and magnetic stirring was loaded with 2 g PET (10.42 mmol), catalyst, and EG in various ratios as noted in the following sections. The flask was then immersed in an oil bath preheated at 180°C and allowed to react. After 4 h the reaction mixture was filtered while hot and, in some experiments, PET-like material was isolated. The filtrate was added in water, and it was allowed to precipitate for 24 h in the freezer. The precipitate was filtered and dried in air. The outcome of each reaction was determined by calculating the conversion of PET and selectivity in BHET using the equations described by Al-Sabagh et al. [10].

2.4. Methods and techniques used to characterize the catalysts and glycolysis products

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Gemini Varian 300 MHz spectrometer at room temperature in deuterated solvents: chloroform-d (CDCl$_3$) and dimethylsufoxide-d$_6$ (DMSO-d$_6$); FT-IR spectra were recorded on a Bruker Vertex 70 Spectrometer, with a horizontal device for attenuated reflectance and diamond crystal, on a spectral window ranging from 4000 to 400 cm^{-1}.

3. Results and discussions

3.1. Catalyst selection

The efficacy of the organic catalyst synthesised above was determined in PET breakdown reactions using 1% molar of ILs with respect to PET, molar ratio PET:EG=1:10. The reaction mixture was processed according to the methodology mentioned above, and the resulting solid materials were analysed.

In the case of reactions where some PET-like material was isolated, the ^{1}H-NMR spectra of these solids (Figure 2) show two main signals at 8.11 ppm - TA from PET and 4.76 ppm - ethylene glycol interchain (EG$_{ic}$) confirming the presence of the PET. Beside the signals characteristic for PET, two small signals which are assigned to diethylene glycol interchain (DEG$_{ic}$) and the corresponding signal in the aromatic region at 8.07 ppm for TA substituted with DEG (added during the PET manufacturing process) are present. Comparing this spectrum with the one of the initial PET (Figure 2 inset), two new signals at 4.54 ppm and 4.17 ppm are assigned to ethylene glycol endchain (EG$_{ec}$), indicating a material with a lower degree of polymerization than the initial one. Additionally, this hypothesis is confirmed by its solubility in methylene chloride, while the raw material was insoluble.

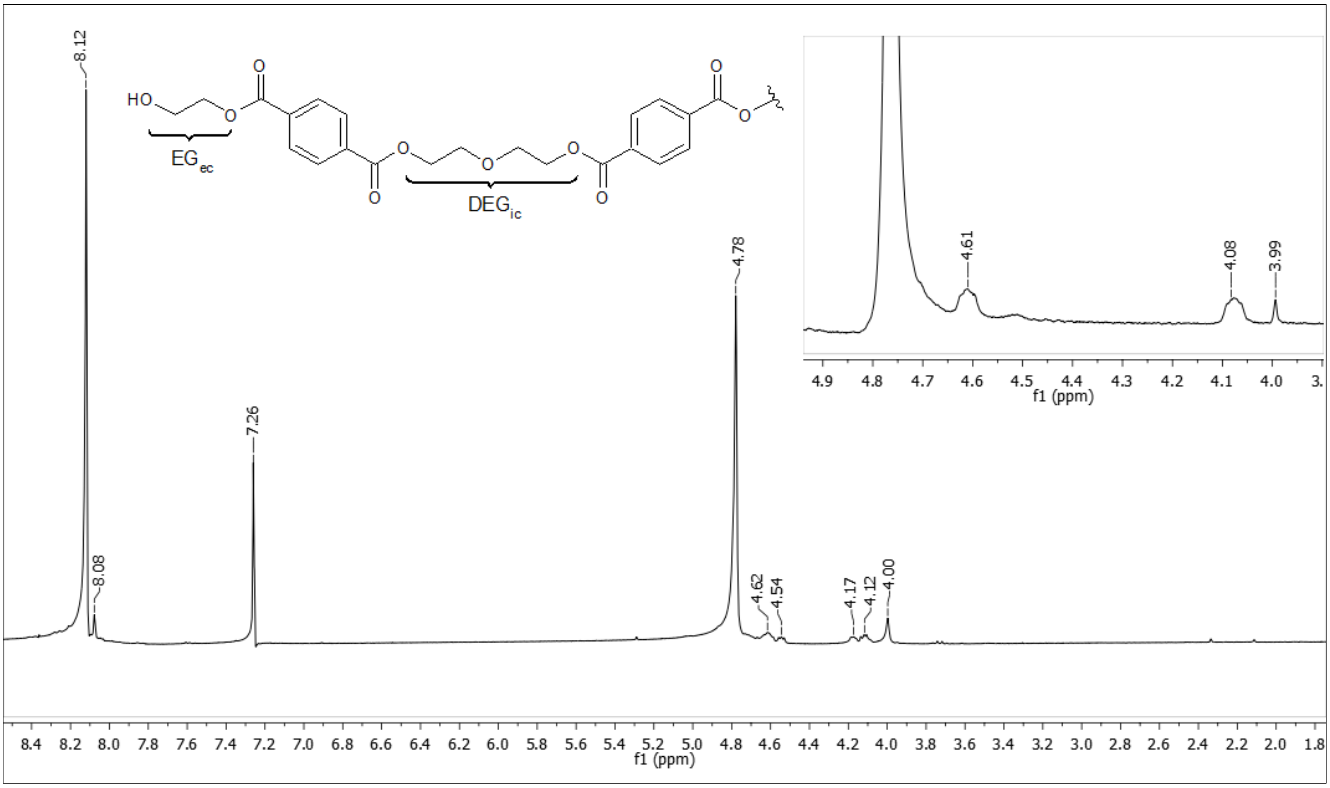

Figure 2. ^{1}H-NMR spectra of the isolated PET (inset: detail of initial PET spectra)

The ^{1}H-NMR spectra of the precipitate (Figure 3) exhibit signals belonging to two compounds. The major group of signals: 8.12 ppm, 4.51-4.48 ppm, 4.00-3.97 ppm is assigned to the main glycolysis product, bis(2-hydroxyethyl) terephthalate (BHET). The second group of signals: 8.11 ppm, 4.71 ppm and 3.74 ppm are assigned to BHET dimer (bisBHET). In addition, it should be noted that the precipitate contains 70-80% BHET. To the best of our knowledge this is the first time when bisBHET is reported in the precipitate.

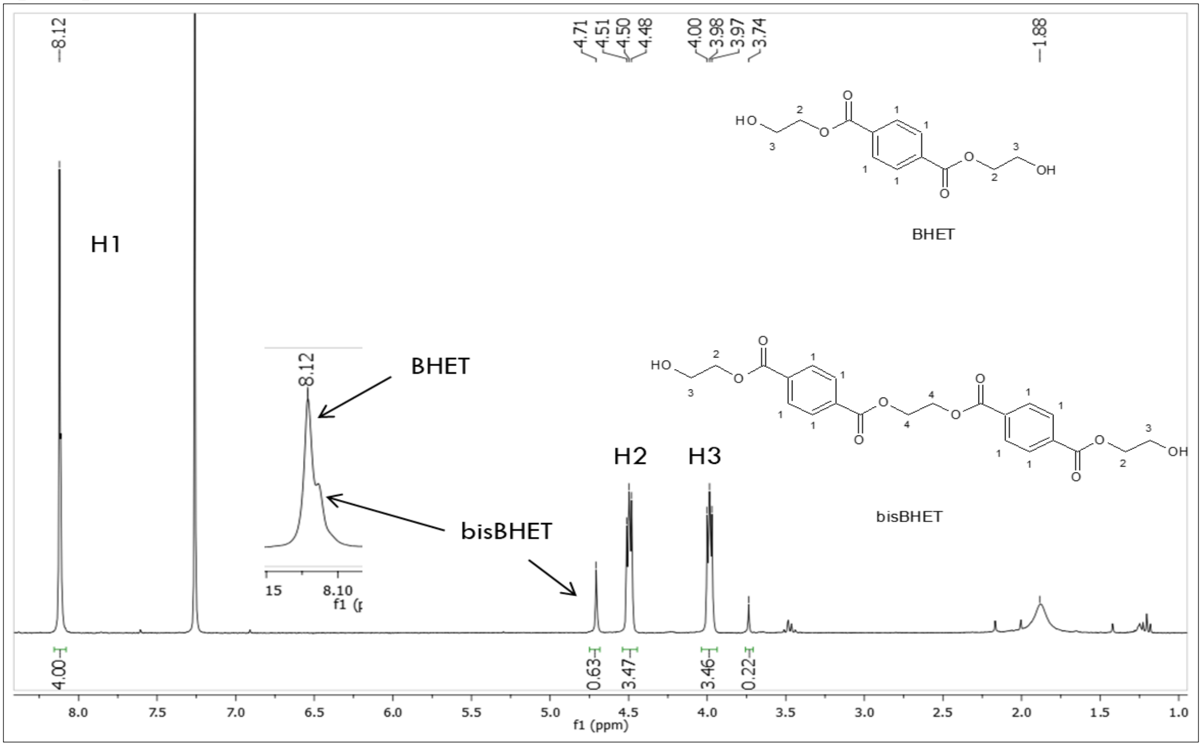

Figure 3. ^{1}H-NMR spectra of the precipitate

Considering that isolation of pure BHET is difficult, in the next sections only BHET quantity is considered.

The results obtained using the aforementioned equations are decreasing in the order [Ddmim]ZnCl$_3$> [Bmim]ZnCl$_3$≈[Bmim]ZnBr$_3$>[Bmim]CdCl$_3$ (Figure 4), the majority of them having above 80% conversion and 50% selectivity. The conversion and selectivity of [Ddmim]ZnCl$_3$ are slightly better than the ones of [Bmim]ZnCl$_3$. Even if the selectivity and the conversion are not much greater than the ones of the other two catalysts containing trihalozincate anion, [Ddmim]ZnCl$_3$ is solid at room temperature, hence easy to manipulate and at the same time its stability in air is better because of its lower hydrofilicity. Thus, [Ddmim]ZnCl$_3$ was selected for further experiments.

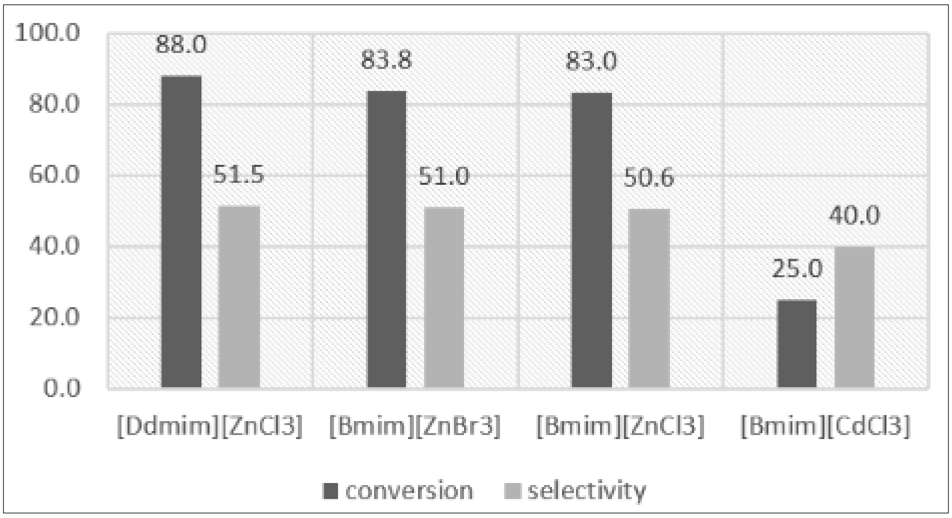

Figure 4. Effect of catalyst type

3.2. Effect of catalyst loading

In order to determine how the catalyst loading is influencing the outcome of the reactions there were performed PET destructions with [Ddmim]ZnCl$_3$ as catalyst, using different loadings, namely 1, 5 and 10% molar with respect to PET and PET:EG=1:10. The results (Figure 5) show an increase in the efficiency when the quantity of the catalyst increased from 1 to 5%, but as the catalyst amount increased to 10%, a decrease of the efficiency was noticed. This trend is in accordance with the results found for other ionic liquids used for glycolysis [28] and its explanation consists in the presumption that when more catalyst is used, BHET is produced more quickly, having then the opportunity to polymerize into oligomers as the glycolysis reaction proceeds.

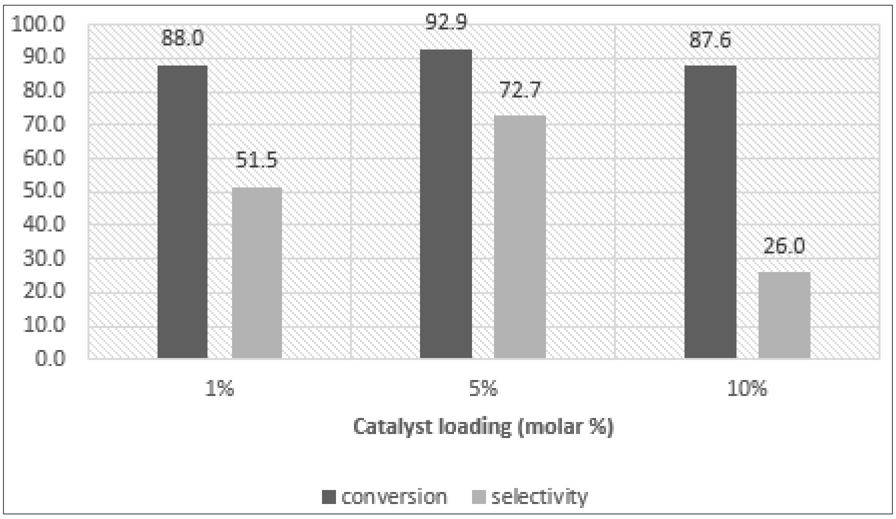

Figure 5. Effect of catalyst loading

3.3. Effect of EG amount

The amount of EG used in the glycolysis reaction is also crucial. PET destructions were performed using [Ddmim]ZnCl$_3$ as catalyst and various PET:EG ratios, namely 1:2.5, 1:5, 1:10 and 1:20 (Figure 6). The experiments, carried out at 180°C for 4h having 5% molar [Ddmim]ZnCl$_3$ as catalyst, showed that as the amount of the EG increases the efficiency of the reaction also increases, but the small increase in selectivity and conversion does not justify the usage of 1:20 ratio.

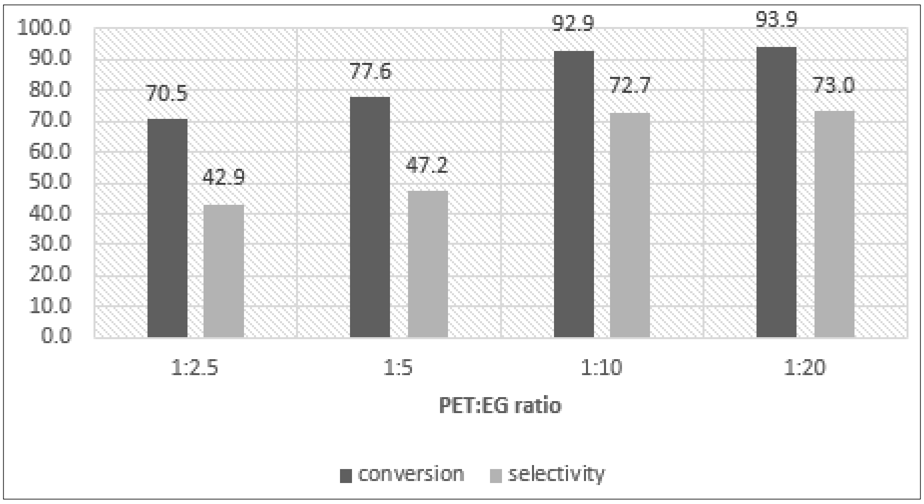

Figure 6. Effect of EG amount

3.4. Testing the effect of [Ddmim]Cl boosted – [Ddmim]ZnCl$_3$ on PET glycolysis

Considering the [Ddmim]ZnCl$_3$ behaviour and the literature data [23, 24], the effect that the Considering the [Ddmim]ZnCl$_3$ behaviour and the literature data [24, 25], the effect that the combination of pristine catalyst ([Ddmim]Cl) and the corresponding metal-containing compound has on the outcome of the reaction ([Ddmim]ZnCl$_3$) was studied. To this purpose mixtures of both compounds, containing 1% of [Ddmim]ZnCl$_3$ and the difference up to 5%, respectively 10% molar of [Ddmim]Cl, were used as catalyst for glycolysis at 180 °C and PET:EG=1:10 (molar ratio). In both cases the conversion was total and the selectivity in BHET was 80% in the first case, respectively 87% in the second case. The formation *in situ* of high catalytic activity species [Ddmim]$_2$[ZnCl$_4$], investigated before by computational and experimental studies [29, 30], could explain the synergic effect of both catalysts and the high selectivity in BHET.

4. Conclusions

This research presented an efficient way to break down PET into its fundamental monomeric form as bis-(2-hydroxyethyl)terephthalate (BHET) in the presence of some metal-containing ionic liquids as catalyst. The catalyst synthesis implies two steps, the first one is the obtaining of 1,3-N,N-disubstituted imidazolium salts starting from 1-methylimidazole and an organic halide and in the second step the compounds obtained in the previous stage were modified using and inorganic halide. The catalysts were tested in different conditions and showed good activity, the best results being obtained with [Ddmim]Cl boosted- [Ddmim]ZnCl$_3$, using a mixture of 1% [Ddmim]ZnCl$_3$ and 4% [Ddmim]Cl (molar percentages), and PET:EG=1:10 molar ratio, with a quasi-total conversion and selectivity in BHET around 87%.

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References

1.YUE, Q.F., YANG, H.G., ZHANG, M.L., BAI, X.F., Metal-containing ionic liquids: Highly effective catalysts for degradation of poly(ethylene terephthalate), *Adv. Mater. Sci. Eng.*, **2014**, 2014, https://doi.org/10.1155/2014/454756

2.SCHYNS, Z.O.G., SHAVER, M.P., Mechanical Recycling of Packaging Plastics: A Review, *Macromol. Rapid Commun.*, **42**(3), 2021, 1-27, https://doi.org/10.1002/marc.202000415.

3.SHEEL, A., PANT, D., *Recycling of Polyethylene Terephthalate Bottles*, Sabu Thomas, Ajay Rane, Krishnan Kanny and Martin George Thomas, Elsevier Inc., 2019, 61–84, doi:10.1016/b978-0-12-811361-5.00004-3.

4.KUROKAWA, H., OHSHIMA, M. A., SUGIYAMA, K., MIURA, H., Methanolysis of polyethylene terephthalate (PET) in the presence of aluminium tiisopropoxide catalyst to form dimethyl terephthalate and ethylene glycol, *Polym. Degrad. Stab.*, **79**(3), 2003, 529–533, https://doi.org/10.1016/S0141-3910(02)00370-1.

5.DU, J.T., SUN, Q., ZENG, X.F., WANG, D., WANG, J.X., CHEN, J.F., ZnO nanodispersion as pseudohomogeneous catalyst for alcoholysis of polyethylene terephthalate, *Chem. Eng. Sci.*, **220**, 2020, 115642, https://doi.org/10.1016/j.ces.2020.115642.

6.NICA, S., HANGANU, A, TANASE, A., DULDNER, M., IANCU, S., DRAGHICI, C., FILIP, P.I., BARTHA, E., Glycolytic depolymerization of polyethylene terephtalate (PET) wastes organic vs. metal-catalysis, *Rev. Chim.* **66**(8), 2015, 1105–1111.

7.LÓPEZ-FONSECA, R., DUQUE-INGUNZA, I., DE RIVAS, B., FLORES-GIRALDO, L. GUTIÉRREZ-ORTIZ, J. I., Kinetics of catalytic glycolysis of PET wastes with sodium carbonate, *Chem. Eng. J.*, **168**(1), 2011, 312–320, https://doi.org/10.1016/j.cej.2011.01.031.

8.AL-SABAGH, A. M., YEHIA, F. Z., ESHAQ, G., RABIE, A. M., ELMETWALLY, A. E. Greener routes for recycling of polyethylene terephthalate, *Egypt. J. Pet.*, **25**(1), 2016, 53–64, https://doi.org/10.1016/j.ejpe.2015.03.001.

9.SINHA, V., PATEL, M. R., PATEL, J. V., PET waste management by chemical recycling: A review, *J. Polym. Environ.*, **18**(1), 2010, 8–25, https://doi.org/10.1007/s10924-008-0106-7.

10.AL-SABAGH, A.M., YEHIA, F.Z., EISSA, A.M.M.F., MOUSTAFA, M.E., ESHAQ, G., RABIE, A.R.M., ELMETWALLY, A.E., Glycolysis of poly(ethylene terephthalate) catalyzed by the Lewis base ionic liquid [Bmim][OAc], *Ind. Eng. Chem. Res.*, **53**(48), 2014, 18443–18451, https://doi.org/10.1021/ie503677w.

11.YAO, H., LU, X., JI, L., TAN, X., ZHANG, S., Multiple hydrogen bonds promote the nonmetallic degradation process of polyethylene terephthalate with an amino acid ionic liquid catalyst, *Ind. Eng. Chem. Res.*, **60**(10), 2021, 4180–4188, https://doi.org/10.1021/acs.iecr.0c06073.

12.CHAEICHIAN, S., POURMAHDIAN, S., AFSHAR TAROMI, F., Synthesis of unsaturated poly-ester resins from PET wastes: Effect of a novel co-catalytic system on glycolysis and poly-esterification reactions, *Des. Monomers Polym.* **11**(2), 2008, 187-199, https://doi.org/10.1163/156855508X298080 .

13.CAKIĆ, S.M., RISTIĆ, I.S., M-CINCOVIĆ, M., NIKOLIĆ, N.Č., ILIĆ. O.Z., STOJILJKOVIĆ, D.T., B-SIMENDIĆ, J.K., Glycolyzed products from PET waste and their application in synthesis of polyurethane dispersions, *Prog. Org. Coatings*, **74**(1), 2012, 115-124, https://doi.org/10.1016/j.porgcoat.2011.11.024.

14.SABNIS, A., BHAVE, V.G., KATHALEWAR, M.S., MARE, S., RAUT, P.P., New polyester polyol derived from recycled poly (ethylene terephthalate) for coating application, *Arch. Appl. Sci. Res.* **4**(1), 2012, 85-93.

15.DULDNER, M. M., BARTHA, E., CAPITANU, S., NICA, S., COMAN, A.E., TINCU, R. SARBU, A., FILIP, P.I., APOSTOL, S. GAREA, S., Attempts to Upcycle PET Wastes into Bio-based Long-lasting Insulating Materials, *Rev. Chim.*, **70**(7), 2019, 2301-2307.

16.MANSOUR, S.H., IKLADIOUS, N.E., Depolymerization of poly(ethylene terephthalate) wastes using 1,4-butanediol and triethylene glycol, *Polym. Test.*, **21**(5), 2002, 497–505, https://doi.org/10.1016/S0142-9418(01)00115-5.

17.NICA, S., IONESCU, S., HANGANU, A., DULDNER, M., IANCU, S., SARBU, A., FILIP, P.I., BARTHA, E., Mechanistic investigations of the organocatalytic depolymerization of PET waste with isosorbide, *Rev. Chim.*, **69**(6), 2018, 1319–1326.

18.MARULLO, S., RIZZO, C., MELI, A., D'ANNA, F., Ionic Liquid Binary Mixtures, Zeolites, and Ultrasound Irradiation: A Combination to Promote Carbohydrate Conversion into 5-Hydroxy-methylfurfural, *ACS Sustain. Chem. Eng.*, **7**(6), 2019, 5818–5826, https://doi.org/10.1021/acssuschemeng.8b05584.

19.PLAYER, L. C., CHAN, B., TURNER, P., MASTERS, A. F. MASCHMEYER, T., Bromozincate ionic liquids in the Knoevenagel condensation reaction, *Appl. Catal. B Environ.*, **223**, 2018, 228–233, https://doi.org/10.1016/j.apcatb.2017.09.021.

20.CHANDA, M. Chemical aspects of polymer recycling. *Adv. Ind. Eng. Polym. Res.* **4**(3), 2021, 133–150, https://doi.org/10.1016/j.aiepr.2021.06.002.

21.YUE, Q. F., XIAO, L. F., ZHANG, M. L., BAI, X. F., The glycolysis of poly(ethylene terephthalate) waste: Lewis acidic ionic liquids as high efficient catalysts, *Polymers*, **5**(4), 2013, 1258–1271, https://doi.org/10.3390/polym5041258.

22.WANG, H., LIU, Y., LI, Z., ZHANG, X., ZHANG, S., ZHANG, Y., Glycolysis of poly(ethylene terephthalate) catalyzed by ionic liquids, *Eur. Polym. J.*, **45**(5), 2009, 1535–1544, http://dx.doi.org/10.1016/j.eurpolymj.2009.01.025.

23.YUE, Q.F., WANG, C. X., ZHANG, L. N., NI, Y., JIN, Y. X., Glycolysis of poly(ethylene terephthalate) (PET) using basic ionic liquids as catalysts, *Polym. Degrad. Stab.*, **96**(4), 2011, 399–403, https://doi.org/10.1016/j.polymdegradstab.2010.12.020.

24.AL-SABAGH, A.M., YEHIA, F.Z., EISSA, A.M.M.F., MOUSTAFA, M.E., ESHAQ, G., RABIE, A.R.M., ELMETWALLY, A.E., Cu- and Zn-acetate-containing ionic liquids as catalysts for the glycolysis of poly(ethylene terephthalate), *Polym. Degrad. Stab.*, **110**, 2014, 364–377, https://doi.org/10.1016/j.polymdegradstab.2014.10.005.

25.SHUANGJUN, C., WEIHE, S., HAIDONG, C., HAO, Z., ZHENWEI, Z., CHAONAN, F., Glycolysis of poly(ethylene terephthalate) waste catalyzed by mixed Lewis acidic ionic liquids., *J. Therm. Anal. Calorim.*, **143**(5), 2021, 3489–3497, https://doi.org/10.1007/s10973-020-10331-8.

26.DUPONT, J., CONSORTI., C.S., SUAREZ, P.A.Z., DE SOUZA, R.F., Preparation of 1-Butyl-3-Methyl Imidazolium-Based Room Temperature Ionic Liquids., *Org. Synth.* **79**, 2002, 236, https://doi.org/10.15227/orgsyn.079.0236.

27.ABDUL-SADA, A.K., ATKINS, M.P., ELLIS, B., HODGSON, G., MORGAN, M.LM., SEDDON, K.R., 1999, US Patent no. 5994602.

28.WANG, H., YAN, R., LI, Z., ZHANG, X., ZHANG, S., Fe-containing magnetic ionic liquid as an effective catalyst for the glycolysis of poly(ethylene terephthalate). *Catal. Commun.* **11**(8), 2010, 763–767, http://dx.doi.org/10.1016/j.catcom.2010.02.011.

29WANG, F., XU, C., LI, Z., XIA, C., CHEN, J., Mechanism and origins of enantioselectivity for [BMIM]Cl ionic liquids and $ZnCl_2$ co-catalyzed coupling reaction of CO2 with epoxides, *J. Mol. Catal. A Chem.*, **385**, 2014, 133–140, http://dx.doi.org/10.1016/j.molcata.2014.01.024.

30.WANG, Q., GENG, Y., LU, X., ZHANG, S., First-row transition metal-containing ionic liquids as highly active catalysts for the glycolysis of poly(ethylene terephthalate) (PET). *ACS Sustain. Chem. Eng.* **3**(2), 2015, 340–348, https://doi.org/10.1021/sc5007522.

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