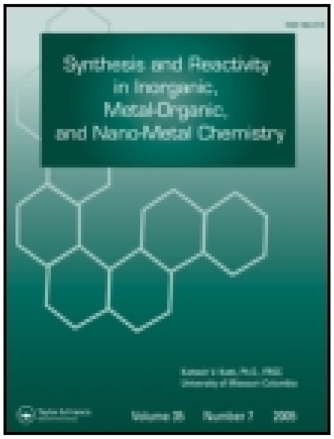
This article was downloaded by: [Tulane University]
On: 05 September 2014, At: 10:37
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

Esterification of Salicylic Acid Using Brønsted Acidic Ionic Liquid based on Keggin Heteropoly Acid

Fatemeh F. Bamoharram [a] , Majid M. Heravi [b] , Javad Ebrahimi [a] & Nilofar Tavakoli-Hoseini [a]

[a] Department of Chemistry , Mashhad Branch, Islamic Azad University , Mashhad , I. R. Iran

[b] Department of Chemistry , School of Science, Alzahra University , Vank , Tehran , I. R. Iran

Accepted author version posted online: 08 Aug 2013.Published online: 27 Sep 2013.

To cite this article: Fatemeh F. Bamoharram , Majid M. Heravi , Javad Ebrahimi & Nilofar Tavakoli-Hoseini (2014) Esterification of Salicylic Acid Using Brønsted Acidic Ionic Liquid based on Keggin Heteropoly Acid, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 44:1, 36-42, DOI: 10.1080/15533174.2013.768639

To link to this article: http://dx.doi.org/10.1080/15533174.2013.768639

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 44:36–42, 2014
Copyright © Taylor & Francis Group, LLC
ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533174.2013.768639

Esterification of Salicylic Acid Using Brønsted Acidic Ionic Liquid based on Keggin Heteropoly Acid

Fatemeh F. Bamoharram,[1] Majid M. Heravi,[2] Javad Ebrahimi,[1] and Nilofar Tavakoli-Hoseini[1]
[1]*Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, I. R. Iran*
[2]*Department of Chemistry, School of Science, Alzahra University, Vank, Tehran, I. R. Iran*

For the first time, a new water stable Brønsted acidic ionic liquid based on Keggin heteroployacid (HPA) was used as environmentally benign catalytic medium in the esterfication of salicylic acid with aliphatic alcohols, $C_nH_{2n+1}OH$ (n = 1-5) and benzylic alcohols, $RC_6H_4CH_2OH$ (R = H, NO_2, OCH_3). This ionic liquid (IL) afforded excellent yield in both thermal conditions and microwave irradiation. Maximum yields were observed under microwave irradiation. Different reaction runs were conducted by varying the reaction parameters such as molar ratio of reactants, weight of the IL, and reaction period in order to optimize the reaction. The IL was easily recovered and reused many times. No significant loss in catalytic activity was observed on recycling.

Keywords Brønsted-acidic ionic liquid, esterification, heteropoly-acid, Keggin, microwave, salicylic acid

INTRODUCTION

The search for catalytic processes involving environmentally benign catalysts has attracted much attention. In this area, ionic liquids (ILs) have been generating increasing interest over the last decade,[1] due to their particular properties[2] and applications in organic synthesis,[3] catalysis,[4] biocatalysis,[5] liquid-liquid separations,[6] extraction and dissolution processes,[7–9] nanomaterials synthesis,[10] polymerization reactions,[11] and electrochemistry.[12] Generally, they have investigated as green solvents and catalysts in different organic reactions.[13] They are made up at least two components including an anion and a cation and their merit lies in their special physical-chemical properties, which can be tuned by varying either the anion, cation, or its substitution pattern. By this means, an IL with optimal properties for a given application can be designed. In catalysis, this feature can be favorably exploited by rendering a homogeneous reaction mixture biphasic, thus combining the advantages of homogeneous and heterogeneous catalysis.

Thus, number of ILs grows daily and there is many examples of different ways in which ILs have been applied in catalysis (i.e. as the catalyst, cocatalyst, or catalyst activator) as the source of a new ligand for a catalytic metal center, or just as the solvent for the reactions.[13]

In general, ILs consists of a salt where one or both the ions are large, and the cation has a low degree of symmetry. These factors tend to reduce the lattice energy of the crystalline form of the salt, and hence lower the melting point.[14] ILs come in two main categories, namely simple salts (made of a single anion and cation) and binary ILs (salts where an equilibrium is involved).

The cations are generally bulky, asymmetric ammonium or phosphonium salts, or heteroatomics, with low symmetry, weak intermolecular interactions, and low charge densities.

The anions can be organic or inorganic and the combinations of the different cations and anions can dramatically change the physicochemical properties of the ILs.[15] The most typical anions are: Cl^-, Br^-, $[BF_4]^-$, $[SbF_6]^-$, $[AlCl_4]^-$, $[AuCl_4]^-$, $[NO_3]$, $[NO_2]^-$, $[SO_4]^{2-}$, $[AcO]^-$, $[Tf]^-$, $[N(OTf)_2]^-$, $[CF_3CO_2]^-$, $[CF_3SO_3]^-$, $[PhCOO]^-$, $[C(CN)_2]^-$, $[RSO_4]^-$, $[OTs]^-$, and $[SCN]^-$.

Although a variety of anions have been used, the application of heteropolyacids (HPAs) has been largely overlooked and very limited.

One of the most important ILs, is SO_3-H-functionalized IL. For synthesis of these ILs, first a N-alkylimidazol (or N-alkylpyrrolidin, pyridine) is reacted with 1,4-butan(or propan) sultone to obtain a solid zwitterion. This zwitterion is then protonated with a Brønsted acid such as sulfuric acid and phosphoric acid to obtain corresponding IL. Although the mentioned IL shows satisfactory behavior, it needs hazardous acids as starting materials.

To the best of our knowledge, protonation of such zwitterions with HPAs has not been reported in the literature.

The principles of green chemistry have been introduced to eliminate or reduce the use of hazardous materials such as

---

Received 20 October 2011; accepted 16 January 2013.

Address correspondence to Fatemeh F. Bamoharram, Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, I. R. Iran. E-mail: abamoharram@yahoo.com

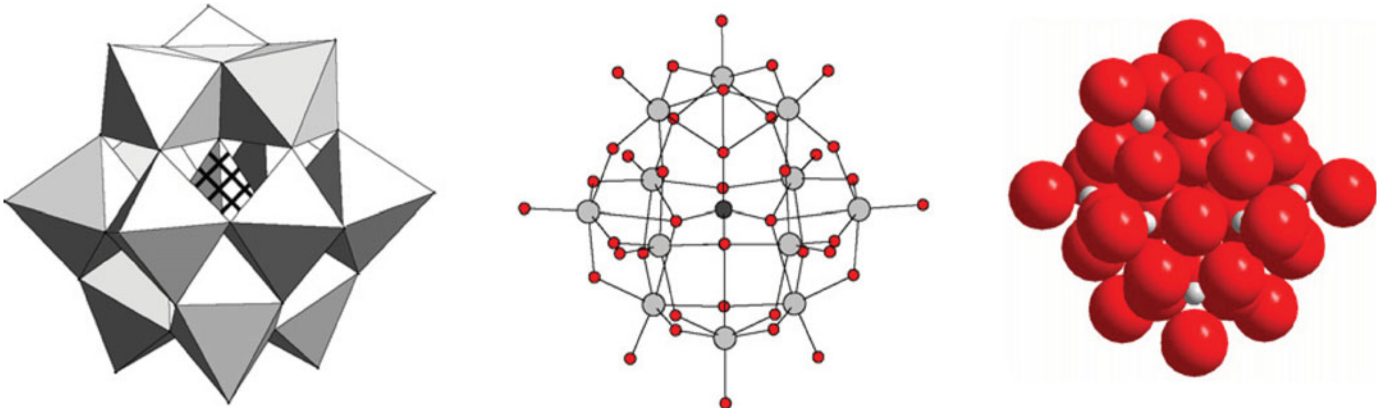


FIG. 1. The structure of the Keggin heteropoly anion $[XM_{12}O^{40}]^{n-}$ in polyhedral (left), ball-and-stick (middle) and space-filling (right) representations (color figure available online).

H_2SO_4 or H_3PO_4 in chemical processes. Cleaner technologies could be possible by making use of environmentally friendly materials involving the use of solid acids. It was shown that HPAs in the solid state are pure Brønsted acids and stronger acids than conventional acids such as SiO_2-Al_2O_3, H_3PO_4, HNO_3, H_2SO_4, HX, and HY zeolites.[16,17] These compounds have several advantages that make them economically and environmentally attractive.[18–22] These solid acids are green with respect to corrosiveness, safety, quantity of waste, and separability. Moreover, while some of the acid catalysts such as HCl, HNO_3, and H_2SO_4, can produce chlorated, nitrated, and sulfated by-products, HPAs do not produce any of these byproducts. HPAs have been extensively studied as green acid catalysts for many reactions and found industrial applications in several processes.[23] Many reactions catalyzed by Brønsted and Lewis acids, but proceeded more effectively under milder conditions with greater selectively, better yields, and shorter reaction times in the presence of HPAs.

Among HPAs, the application of Keggin structures have been extensively studied.[24–27] The Keggin structure with formula of $[XM_{12}O_{40}]^{n-}$, is shown in Figure 1.

In pursuing these studies and in continuation of our previous works on the applications of Keggin HPAs[28–30] and ILs[31–33] in the synthesis of organic compounds, in the present work for the first time we have used a Brønsted acidic IL based on Keggin HPA, for the esterification of salicylic acid with different alcohols, in both thermal conditions and microwave irradiation. Currently many reports are available in the literature on esterification using ILs.[34–38]

To the best of our knowledge there is no report with HPA-based ILs in esterification reactions.

The role of this IL will be to provide a medium for the catalyst and solubility for starting materials and products. Such combination of catalyst with medium has been found to be a viable alternative approach towards modern synthetic chemistry, especially when considering the growing environmental demands being placed on chemical processes.

EXPERIMENTAL

Chemicals and Instruments

All of the chemicals were commercially available.

IR spectra were obtained with a Brucker 500 scientific spectrometer. GLC analysis was performed on a Pu 4500 gas chromatograph with FID detector. Microwave (MW) irradiation was performed in MILESTONE ONE APC-55E.

Preparation of IL

Pyridine (0.2 mol) and 1,4-butane sultone (0.2 mol) were charged into a 100 mL round-bottom flask. Then, the mixture was stirred at 40°C for 10 h. The white solid zwitterion was washed repeatedly with ether to remove non-ionic residues and dried in vacuum.[39] Then, $H_3PW_{12}O_{40,}$ was added and the mixture stirred for 20 min at 60°C to form the IL.

Catalytic Test

The utility of the IL was established in the esterification of salicylic with alcohols. In a typical reaction benzyl alcohol, salicylic acid and IL were taken in a 50 mL two-necked round bottom flask and the reaction mixture was stirred and refluxed for 3 h. At room temperature reactions were carried out with stirring for 6 h.

At regular intervals, Karl Fisher titration was performed for determination of produced water. The products were characterized by comparison of their spectroscopic data with those of authentic samples. Yields were determined by GC. Under MW irradiation a solution of salicylic acid, alcohol, and IL was irradiated for 2 min.

RESULTS AND DISCUSSION

The esterification of salicylic acid with aliphatic alcohols, $C_nH_{2n+1}OH$ (n = 1-5) and benzylic alcohols, $RC_6H_4CH_2OH$ (R = H, NO_2, OCH_3) was carried out in the presence of a new and green IL based on Keggin HPA with formula of $[XM_{12}O_{40}]^{3-}$.

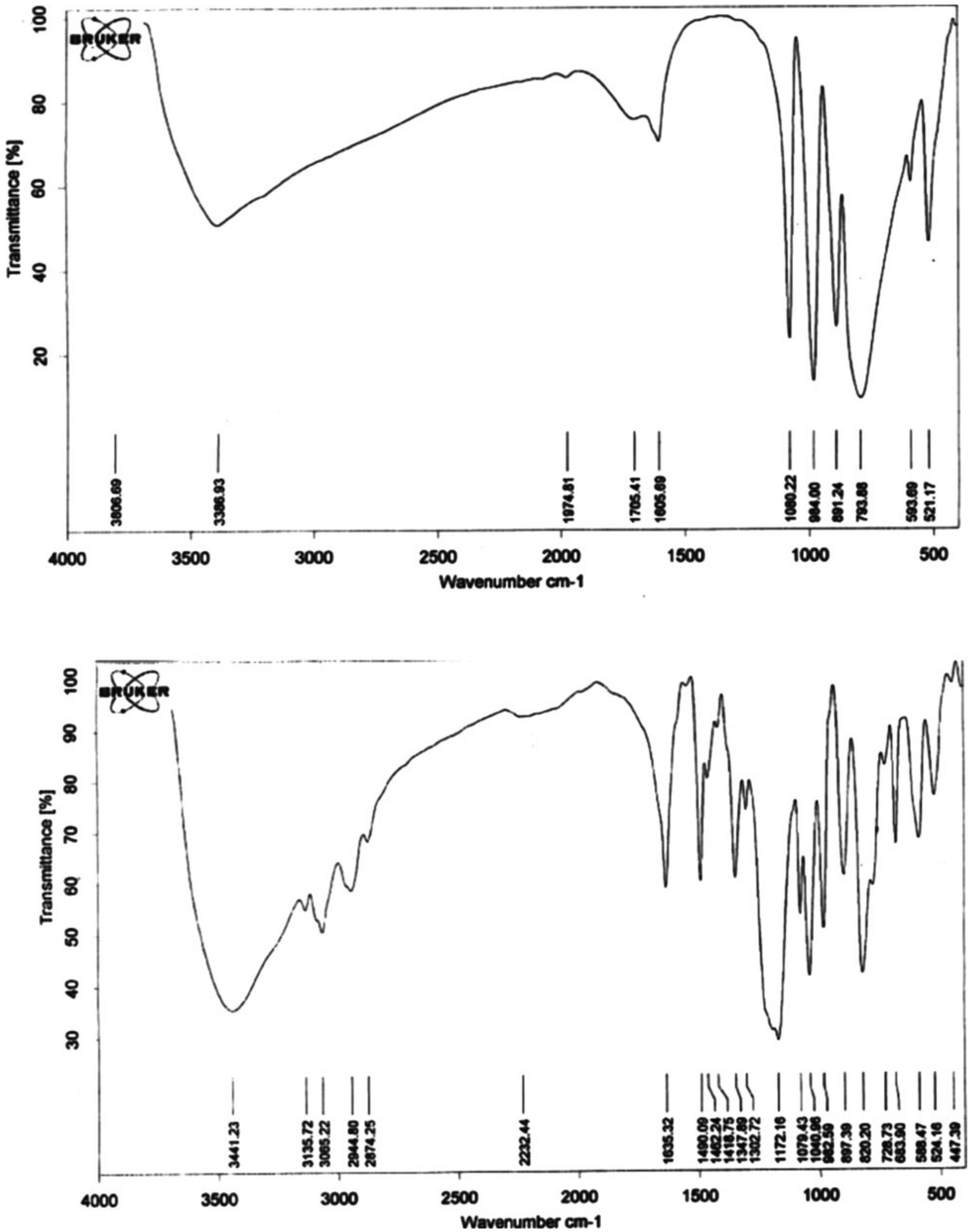


FIG. 2. (A) IR spectrum of the Keggin, $H_3 [PW_{12} O_{40]}$. (B) IR spectrum of IL formed via interaction of Keggin with **1**.

For preparation of this IL, first, pyridine was reacted with 1,4-butansultone to give solid zwitterions (**1**). Interestingly, when we mixed two solids including (**1**) and $H_3PW_{12}O_{40}$, a liquid formed after 20 min at 60°C. It is necessary to be mentioned that protonating of zwitterions (**1**) with H_2SO_4 as Brønsted acids need longer reaction time (6 h) and higher temperature (80°C).[37–39] Therefore, $H_3PW_{12}O_{40}$ not only reduced the time, but also the temperature. Figure 2 shows the IR spectra of $H_3PW_{12}O_{40}$ and prepared IL.

The $[XM_{12}O_{40}]$ consists of one XO_4 tetrahedron ($X = Si^{IV}$, Ge^{IV}, P^{V}...) surrounded by four M_3O_{13} sets ($M = W^{VI}$, Mo^{VI}) linked together through oxygen atoms (named M-O_b-M).The XO_4 tetrahedron is assumed to vibrate almost independently from the rest of the anion. This assumption is particularly valuable for $X = P^V$. The symmetric and asymmetric stretching of the different kinds of M-O bonds are observed in the following spectral regions: M-O_d bonds (960–1000 cm^{-1}), M-O_b-M bridges (inter bridges between corner-sharing octahedral, 850–890 cm^{-1}) and M-O_c-M bridges (intra bridges between edge-sharing octahedra, 760–800 cm^{-1}). Only the M-O_d stretching can be considered as pure vibrations: the stretching involving O_b or O_c atoms present some bend character.[40,41]

In our study, the IR spectrum of the formed IL (Figure 2b) exhibits the characteristic frequencies of the Keggin structure in the range 600–1100 cm^{-1}. Compared with the initial Keggin structure (Figure 2a), the bands arising from the HPA change obviously either in intensity or position. Comparing the IR spectrum of the IL with the IR spectrum of $H_3[PW_{12}O_{40}]$ (Figure 2), the vibrational band of the M-O_c-M of the Keggin is split from 793.88 into two bands, including 728.73 and 820.20, due to difference in the M-O_c-M bonds. The vibrational band of the P-O is split from 1080.22 into two bands, including 1040.96 and 1079.43. This means that, the inter bridges between edge-sharing octahedra (760–800 cm^{-1}) and the P-O stretchings have been affected. These results indicate that many of the bonds were strengthened and the others were weakened. It means that the HPA has a interaction with (**1**).

It is suggested that, the Keggin HPA as a Brønsted acid generate acidic IL from its zwitterion to continuously and the produced IL acid, provides a medium for the catalyst and solubility for starting materials and products in esterification reaction.

Thermal Conditions

Initial attempts to optimize the esfterification of salicylic acid were performed with benzyl alcohol.

The mole ratio of salicylic acid to alcohol was varied as 1:1 to 1:6. The results are shown in Figure 3. All of the reactions were carried out in reflux conditions and 3 h. This figure shows the dependence of the molar ratio in the esterification reaction.

As we can see, the yield increases with that of the molar ratio up to 1:5. Any further increasing of the molar ratio does not have any appreciable effect on the reaction yield. By using some excess of acid the results were the same.

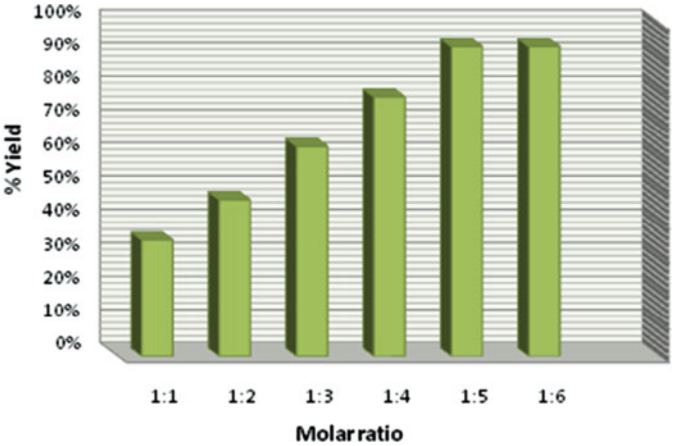


FIG. 3. Esterification of salicylic acid with benzyl alcohol with various molar ratio of acid:alcohol (solvent free) (color figure available online).

In order to check the amount of the IL we examined different amounts of used IL.

This attempt was performed with different amounts of IL (0.02–0.1 g) in molar ratio of 1:5 for salicylic acid: alcohol. The data are shown in Figure 4.

Our studies showed that under these conditions, the reaction yields were affected by changing the amount of the IL.

The yield increases up to 0.1 g and any further increasing for amount of the IL did not have any effect on the reaction yields.

Under optimum conditions, the esterification reactions were carried out in different temperatures. The results are shown in Figure 5.

The maximum yield of ester is reached at reflux temperature. This was expected, since increasing the temperature is apparently favorable for the acceleration of the forward reaction. The yield is lower when the reactions are carried out at room temperature.

Under the best conditions (0.1 g IL, 3 h, molar ratio 1:5, and reflux temperature) we have expended our study and investigated the application of the IL for esterification of salicylic acid with the other alcohols (Figure 6).

Our findings show that this IL is very active in these reactions.

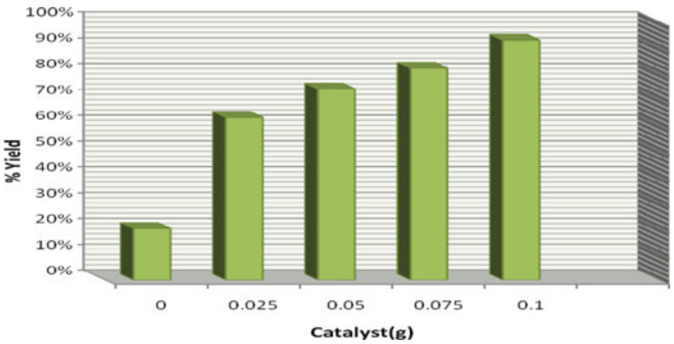


FIG. 4. Esterification of salicylic acid with benzyl alcohol using various amounts of the IL (solvent free) (color figure available online).

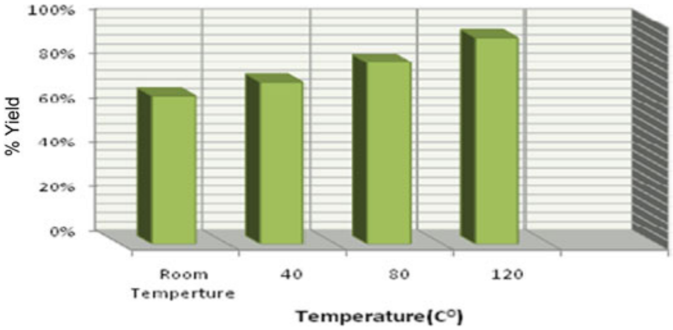


FIG. 5. Esterification of salicylic acid with benzyl alcohol in different temperatures (solvent free) (color figure available online).

Microwave-Assisted Esterification Reactions

During our on going study in thermal conditions using this IL, we interested in the combination of this IL with MW-assisted reaction. ILs consisting entirely of ions could absorb the MW energy efficiently.

Moreover, the risk of an explosion caused by rapid increase of vapor pressure of the solvent can be avoided, since ILs have no measurable vapor pressure.

Green chemistry is defined as the approach to synthesis, processing, and use of chemicals that reduces risks to humans and the environment.

Green chemistry has been one of the keywords when MW and especially ILs have been introduced. MW and ILs are green chemistry by themselves. Thus, there is enough room for new works to this field. The value of MW is that they usually reduce reaction time by efficient heating and ease the path to high temperature reactions.

Anyway, despite many reports in literature, there is no report for MW-assisted reactions using HPA-based ILs.

This work has been carried out with green chemistry principles in mind.

In this section we wish to report our preliminary results on the application of this IL in an MW-assisted reaction. Under optimum conditions, we investigated applicability of this IL for highly efficient esterification of salicylic acid with alcohols. The results are shown in Figure 7. As can be seen, this IL afforded excellent yields.

The two fundamental mechanisms for transferring energy from microwaves to the substance are dipole rotation and ionic conduction. Dipole rotation is an interaction in which polar molecules try to align themselves with the rapidly changing electric field of the microwave. Ionic conduction mechanism

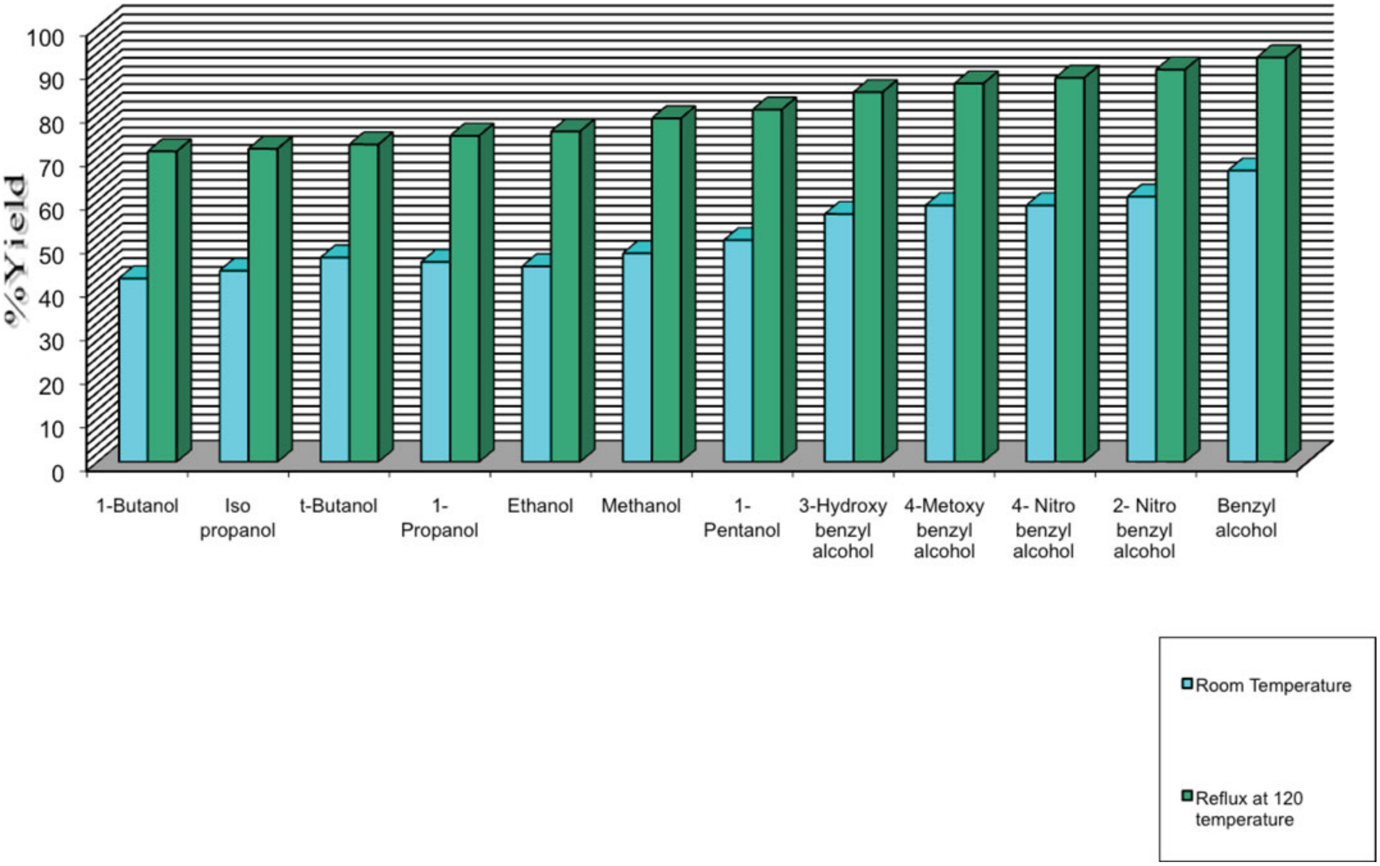


FIG. 6. Comparison between esterification of salicylic acid with alcohols at room temperature and reflux conditions (solvent free) (color figure available online).

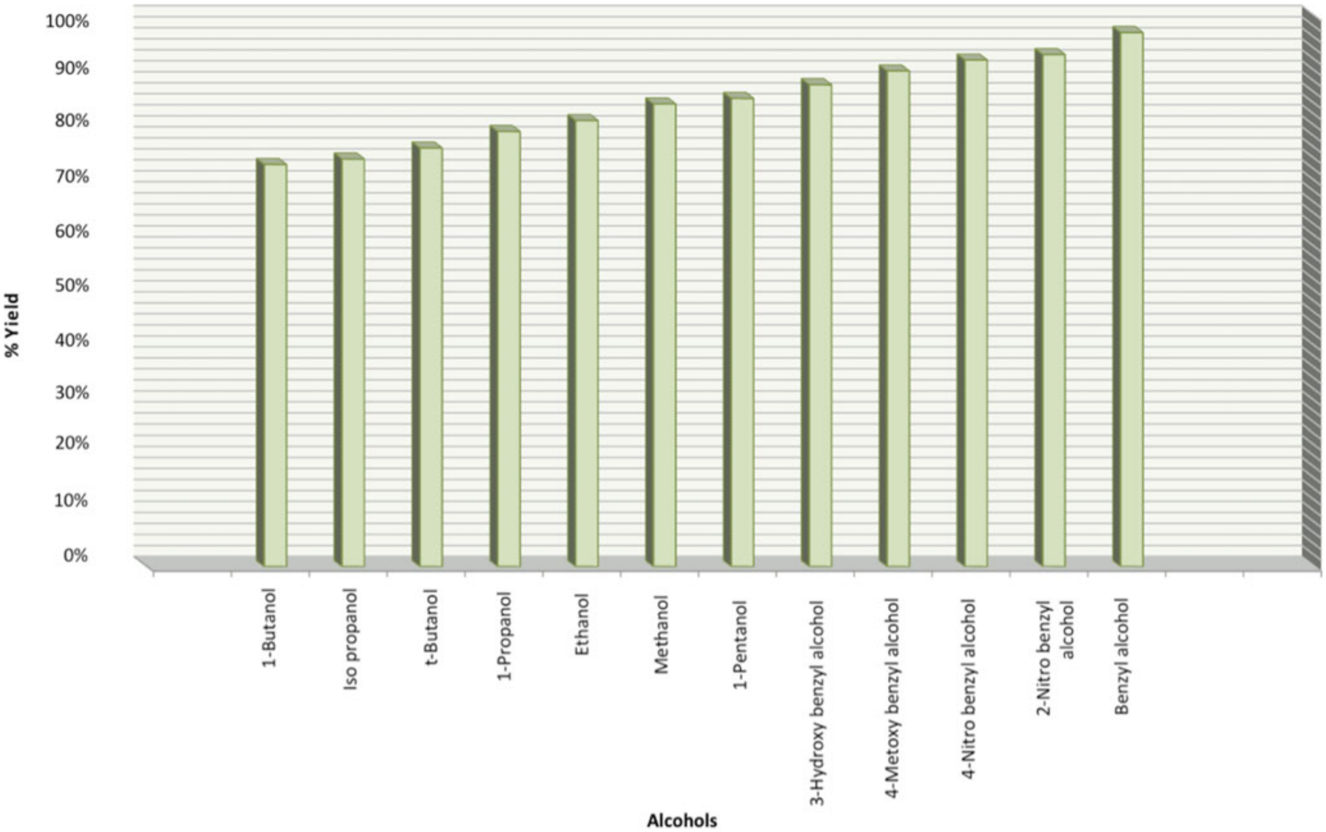


FIG. 7. Yields of esterification reactions in the presence of the IL, under microwave irradiation (solvent free) (color figure available online).

consists in the instantaneous superheating of the ionic substance due to the ionic motion generated by the electric field. When the temperature increases, the transfer of energy becomes more efficient.

Due to their ionic character, ILs absorb microwave irradiation extremely well and transfer energy quickly by ionic conduction.[42] Thus, can diminish reaction time, avoid side products, increase yield and simplify the course of reactions for combinatorial chemistry.[43]

Reusability of the IL

In the recycling study, this IL could be recovered and reused many times without any loss of catalytic activity. This result clearly indicates that this IL is quite stable upon both thermal conditions and MW irradiation.

CONCLUSIONS

In summary, a new and green Brønsted acidic IL based on Keggin anion were successfully used as effective and green medium for the esterification reactions under both thermal and MW irradiation. IL was readily recycled and reused to produce almost identical results. No organic solvent was used, resulting in eco-friendly process. The use of this new and novel IL in this reaction provides a better and practical alternative to the existing procedures and provides great promise toward further useful applications. This process will pave a way for large-scale applications of synthesis of other esters. Further applications for other reaction systems are currently under investigation.

REFERENCES

1. Wasserschied, P.; Welton, T. (Eds.). *Ionic Liquids in Synthesis*; VCH-Wiley, Weinheim, Germany, **2002**.
2. Forsyth, S. A.; Pringle, J. M.; MacFarlane, D. R. Ionic liquids: an overview. *Aust. J. Chem.* **2004**, *57*, 113–119.
3. Zhao, H.; Malhotra, S. V. Applications of ionic liquids in organic synthesis. *Aldrichim. Acta* **2002**, *35*, 75–83.
4. Zhao, D.; Wu, M.; Kou, Y.; Min, E. Ionic liquids: applications in catalysis. *Catal. Today* **2002**, *74*, 157–189.
5. Sheldon, R. A.; Maderia-Lau, L.; Sorgedrager, M. J.; Van Rantwijk, F.; Seddon, K. R. Biocatalysis in ionic liquids. *Green Chem.* **2002**, *4*, 147–151.
6. Visser, A.; Swatloski, R. P.; Rogers, R. D. pH-Dependent partitioning in room temperature ionic liquids provides a link to traditional solvent extraction behavior. *Green Chem.* **2000**, *2*, 1–4.
7. Zhang, S.; Zhang, Z. C. Novel properties of ionic liquids in selective sulfur removal from fuels at room temperature. *Green Chem.* **2002**, *4*, 376–379.
8. Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. Ionic liquids as green solvents for regeneration/engineering of cellulose based products. *J. Am. Chem. Soc.* **2002**, *124*, 4974–4975.
9. Liu, Y.; Hu, Y.; Wang, H.; Xu, C.; Ji, D.; Sun, Y.; Guo, T. Ionic liquids: novel solvents for petroleum asphaltenes. *Chin. J. Chem. Eng.* **2005**, *13*, 564–567.

10. Cao, J. M.; Fang, B. Q.; Wang, J.; Zheng, M. B.; Deng, S. G.; Ma, X. I. Ionic liquids for the convenient synthesis of functional inorganic nanomaterials. *Prog. Chem.* **2005**, *17*, 1028–1033.
11. Pinkowska, H. Green chemistry of polymers. *Polymer.* **2006**, *51*, 836–842.
12. Yang, C.; Sun, Q.; Qiao, J.; Li, Y. lonic liquid doped polymer light-emitting electrochemical cells. *J. Phys. Chem. B.* **2003**, *107*, 12981–12988.
13. Welton, T. Ionic liquids in catalysis. *Coord. Chem. Rev.* **2004**, *248*, 2459–2477.
14. Freemantle, M. Designer solvents: ionic liquids may boost clean technology development. *Chem. Eng. News.* **1992**, *76*, 32–37.
15. Wasserschied, P.; Keim, W. (Eds.). *Ionic Liquids in Synthesis*; VCH-Wiley, Weinheim, Germany, **2004**.
16. Kapustin, G. I.; Brueva, T. R.; Klyachko, A. L.; Timofeeva, M. N.; Kulikov, S. M.; Kozhevnikov, I. V. A study of the acidity of heteropoly acids. *Kinet. Katal.* **1990**, *31*, 1017–1020.
17. Kozhevnikov, I. V. Catalysis by heteropoly acids and multicomponent polyoxometalates in liquidphase reactions. *Chem. Rev.* **1998**, *98*, 171–198.
18. Izumi, Y.; Urabe, K.; Onaka, M. *Zelite, Clay and Hetropolyacid in Organic Reaction*; Kodansha/VCH, Tokyo, Japan, **1992**.
19. Bamoharram, F. F.; Heravi, M. M.; Roshani, M.; Abrishami, F. Picolinic acid in the presence of heteropolyacids including Mo and W. *J. Mol. Catal. A: Chem.* **2007**, *267*, 241–244.
20. Bamoharram, F. F.; Heravi, M. M.; Roshani, M.; Tavakoli, N. N-oxidation of pyridine carboxylic acids using hydrogen peroxide catalyzed by a green heteropolyacid catalyst: Preyssler's anion, $[NaP_5W_{30}O_{110}]^{14-}$. *J. Mol. Catal. A: Chem.* **2006**, *252*, 219–225.
21. Kozhevnikov, I. V.; Paul, T. A.; Robert, H. C. (Eds.). *Handbook of Green Chemistry – Green Catalysis: Heterogeneous Catalysis*; VCH-Wiley, Weinheim, Germany, **2009**.
22. Misono, M.; Ono, I.; Koyano, G.; Aoshima, A. Heteropolyacids: versatile green catalysts usable in a variety of reaction media. *Pure Appl. Chem.* **2000**, *72*, 1305–1311.
23. Kozhevnikova, E. F.; Quartararo, J.; Kozhevnikov, I. V. Fries rearrangement of aryl esters catalyzed by hetropoly acid. *Appl. Catal.* **2003**, *245*, 69–78.
24. Li, G.; Ding, Y.; Wang, J.; Wang, X.; Suo, J. New progress of Keggin and wells: Dawson type polyoxometalates catalyze acid and oxidative reactions. *J. Mol. Catal. A: Chem.* **2007**, *262*, 67–76.
25. Nomiya, K.; Nemoto, Y.; Hasegawa, T.; Matsuoka, S. Multicenter active sites of vanadium-substituted polyoxometalate catalysts on benzene hydroxylation with hydrogen peroxide and two reaction types with and without an induction period. *J. Mol. Catal.* **2000**, *152*, 55–68.
26. Ono, Y.; Thomas, J. M.; Zamaraev, K. I. (Eds.). *Perspectives in Catalysis*; Blackwell Scientific, Oxford, England, **1992**.
27. Mansuy, D.; Bartoli, J. F.; Battioni, P.; Lyon, D. K.; Finke, R. G. Highly oxidation resistant inorganic-porphyrin analog polyoxometalate oxidation catalysts.2.Catalysis of olefin epoxidation and aliphatic and aromatic hydroxylations starting from alpha.2-$P_2W_{17}O_{61}(Mn^{+}\bullet Br)$ (n = 11) ($Mn^{+} =$ $Mn^{3}+$, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}), including quantitative comparisons to metalloporphyrin catalysts. *J. Am. Chem. Soc.* **1991**, *113*, 7222–7226.
28. Heravi, M. M.; Rajabzadeh, G.; Bamoharram, F. F.; Seifi, N. An eco-friendly catalytic route for synthesis of 4-amino-pyrazolo [3,4-d] pyrimidine derivatives by Keggin heteropolyacids under classical heating and microwave irradiation. *J. Mol. Catal. A: Chem.* **2006**, *256*, 238–241.
29. Heravi, M. M.; Behbahani, F.; Bamoharram, F. F. Acetylation of alcohols, phenols and salicylic acid by heteropoly acids in acetic anhydride: A green and eco-friendly protocol for synthesis of acetyl salicylic acid (aspirin). *Arkivoc* **2007**, *16*, 123–131.
30. Heravi, M. M.; Derikvand, F.; Bamoharram, F. F. Highly efficient, four-component one-pot synthesis of tetrasubstituted imidazoles using Keggin-type heteropolyacids as green and reusable catalysts. *J. Mol. Catal. A: Chem.* **2007**, *263*, 112–114.
31. Heravi, M. M.; Tavakoli-Hoseini, N.; Bamoharram, F. F. Brønsted acidic ionic liquids as efficient catalysts for the synthesis of amidoalkyl naphthols. *Synth. Commun.* **2011**, *41*, 298–306.
32. Heravi, M. M.; Tavakoli-Hoseini, N.; Bamoharram, F. F. Brønsted acidic ionic liquids: new, efficient, and green promoter system for the synthesis of 4(3H)-quinazolinones. *Synth. Commun.* **2011**, *41*, 707–714.
33. Davoodnia, A.; Heravi, M. M.; Rezaei-Daghigh, L.; Tavakoli-Hoseini, N. Brønsted-acidic ionic liquid $[HO_3S(CH_2)_4MIM][HSO_4]$ as efficient and reusable catalyst for one-pot synthesis of β-acetamido kotones. *Monatsh. Chem.* **2009**, *140*, 1499–1502.
34. Forbes, D. C.; Weaver, K. J. Brønsted acidic ionic liquids: the dependence on water of the Fischer esterification of acetic acid and ethanol. *J. Mol. Catal.A: Chem.* **2004**, *214*, 129–132.
35. Zhu, H.-P.; Yang, F.; Tang, J.; He, M.-Y. Brønsted acidic ionic liquid 1- methylimidazolium tetrafluoroborate: a green catalyst and recyclable medium for esterification. *Green Chem.* **2003**, *5*, 38–39.
36. Gu, Y.; Shi, F.; Deng, Y. Esterification of aliphatic acids with olefin promoted by Brønsted acidic ionic liquids. *J. Mol. Catal. A: Chem.* **2004**, *212*, 71–75.
37. Gui, J.; Cong, X.; Liu, D.; Zhang, X.; Hu, Z.; Sun, Z. Novel Brønsted acidic ionic liquid as efficient and reusable catalyst system for esterification. *Catal. Commun.* **2004**, *5*, 473–477.
38. Kirumakki, S. R.; Nagaraju, N.; Narayanan, S. A comparative esterification of benzyl alcohol with acetic acid over zeolites H beta, HY and HZSM5. *Appl. Catal. A: Gen.* **2004**, *272*, 1–9.
39. Wang, W.; Shao, L.; Cheng, W.; Yang, J.; He, M. Brønsted acidic ionic liquids as novel catalysts for Prins reaction. *Catal. Commun.* **2008**, *9*, 337–341.
40. Rocchiccioli-Deltcheff, C.; Thouvenot, R.; Dabbabi, M. Etude de la structure des niobotungstates $NbnW_6$- n=2- 19 au moyen des spectres de vibration. *Spectrochim. Acta* **1977**, *33*, 143–153.
41. Rocchiccioli-Deltcheff, C.; Thouvenot, R.; Franck, R. Spectresi r. et Rama d'hétéropolyanions α - $XM_{12}O_{40}$ n- de structure de type Keggin ($X{=}B^{III}$, Si^{IV}, Ge^{IV}, P^{V}, As^{V} et $M{=}W^{VI}$ et Mo^{VI}). *Spectrochim. Acta* **1976**, *32*, 587–597.
42. Martinez-Palou, R. Ionic liquid and microwave-assisted organic synthesis: a "green" and synergic couple. *J. Mex. Chem.* **2007**, *51*, 252–264.
43. Santagada, V.; Frecentese, F.; Perissutti, E.; Favretto, L.; Caliendo, G. The application of microwaves in combinatorial and high-throughput synthesis as new synthetic procedure in drug discovery. *OSAR Comb. Sci.* **2004**, *23*, 919–944.