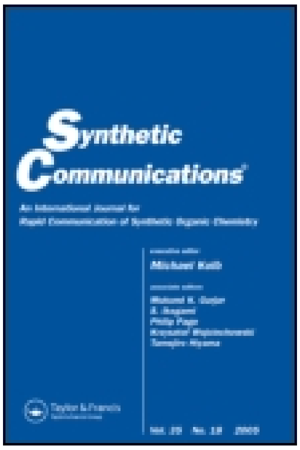

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Tao Jiang [a] , Yanhong Chang [a] , Guoying Zhao [a] , Buxing Han [a] & Guanying Yang [a]

[a] Center for Molecular Science, Institute of Chemistry, The Chinese Academy of Sciences, Zhongguancun, Beijing, 100080, P.R. China

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Tao Jiang,* Yanhong Chang, Guoying Zhao, Buxing Han,* and Guanying Yang

Center for Molecular Science, Institute of Chemistry, The Chinese
Academy of Sciences, Beijing, P.R. China

ABSTRACT

The esterification of carboxylic acids with alcohols catalyzed by paratoluene sulfonic acid (pTSA) was studied in different room temperature ionic liquids. The chemical equilibrium of esterification can be tuned by using ionic liquids as solvents.

Key Words: Carboxylic acid; Alcohol; Paratoluene sulfonic acid; Ionic liquid; Equilibrium.

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*Correspondence: Buxing Han and Tao Jiang, Center for Molecular Science, Institute of Chemistry, The Chinese Academy of Sciences, Zhongguancun, Beijing 100080, P.R. China; Fax: +86-10-62559373; E-mail: Hanbx@iccas.ac.cn.

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Room temperature ionic liquids (ILs) are organic salts consisting of cations and anions. They are good solvents for many kinds of organic chemicals. ILs have excellent thermal and chemical stability, almost undetectable vapor pressure at room temperature, wide electrochemical windows and a wide liquid range of about 300 K. The physical and chemical properties of ILs can be tuned by varying cations and anions. These special properties make them suitable replacement for volatile organic solvents in different chemical processes. They are regarded as clean solvents. Significant progress has been made in the application of ILs in catalysis and chemical synthesis in recent years. Several excellent reviews[1–6] have been published providing comprehensive information about the properties, preparation and applications of ILs in organic and catalytic reactions. In the past decade, a variety of typical organic reactions have been successfully conducted in ILs with high selectivity and yields, such as Friedel–Crafts reactions, alkylations, hydrogenations, hydroformylations, Diels–Alder reactions, Heck reactions, olefin dimerization and oligomerizations, and oxidations. Several papers have recently been published on the use of ILs as reaction media or catalyst for esterifications[7–10] and transesterifications.[11–14]

Tuning equilibrium of reversible reactions is one of the interesting topics in chemistry. In this work we probe the possibility to tune the equilibrium of a chemical reaction using an IL. The esterification reactions of carboxylic acids with alcohols in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), and 1-ethyl-3-methylimidazolium hexafluorophosphate ([emim][PF_6]) are studied, and the reactions are also carried out in the absence of the ILs. The results indicate that the equilibrium conversion can be enhanced by using some ILs. This opens up a new way to tune chemical equilibrium using green solvents.

ILs were synthesized according to the method in literature and dried at 40°C in vacuum until its mass was independent of drying time. Reactions were carried out in a stainless steel reactor of 11 mL with magnetic stirrer. Paratoluene sulfonic acid (pTSA) was used as catalyst.

The esterification was carried out with and without ILs. Only the experimental procedures with the IL are described because those in the absence of the IL are similar and simpler. In a typical experiment, suitable amount of IL, pTSA, alcohol and acid were added into the reactor after the reactor was purged with N_2. Then the reactor was put into a constant temperature bath. After a certain time, the reactor was cooled rapidly with iced-water for about one hour. Then the reactants and products in the IL were extracted six times with diethyl ether. Experiments indicated that all the reactants and products could be extracted because they were not detectable in the solvent after extracting six times. All analysis was carried out with an

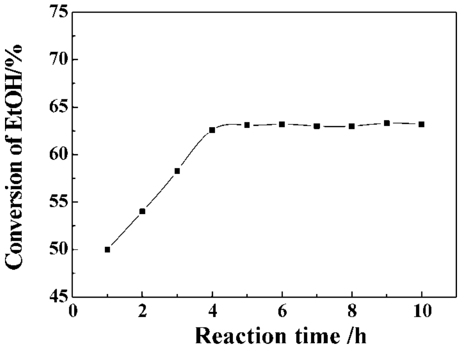

Figure 1. Dependence of ethanol conversion on reaction time for the reaction of ethanol and acetic acid at 60°C (ethanol : acetic acid : pTSA = 1 : 1 : 0.01 in molar ratio, ethanol 13 mmol).

Agilent 4890D GC equipped with a FID and an Innowax capillary column (30 m × 0.252 mm × 0.25 μm).

Effect of reaction time on conversion was first investigated. Figure 1 illustrates the conversion of the reaction of ethanol and acetic acid as a function of reaction time without solvent, which demonstrates that chemical equilibrium can be reached in 5 h. The effect of reaction time on conversion of ethanol in [bmim][PF_6] is shown in Table 1. The data indicate that reaction equilibrium can be reached after 20 h at 60°C, which is longer than that in the absence of the IL. The main reason is that the viscosity of ILs is larger than ordinary organic liquids.[15] It is easy to understand that the higher the viscosity, the longer the time is needed for reaching equilibrium.

The equilibrium conversions of the reactions are presented in Table 2. Entries 1–6 show that the equilibrium conversion of the reaction of ethanol

Table 1. Conversion at different reaction times in [bmim][PF_6].[a]

No.	Reaction time/h	Ethanol conv./%
1	16	69.2
2	20	73.1
3	24	73.2

[a] Ethanol : acetic acid : pTSA = 1 : 1 : 0.01 in molar ratio; ethanol 13 mmol; [bmim][PF_6] 3.3 g; temperature 60°C.

Table 2. Equilibrium conversion of esterification of carboxylic acids with alcohols in different ionic liquids.[a]

No.	Acids	Alcohols	Ionic liquids	IL/g	Alcohol conv./%	Selectivity/%[b]	Time/h
1	Acetic acid	Ethanol	Without	0	63.3	100	6
2	Acetic acid	Ethanol	[bmim][PF_6]	1.3	69.2	100	24
3	Acetic acid	Ethanol	[bmim][PF_6]	2.3	72.0	100	24
4	Acetic acid	Ethanol	[bmim][PF_6]	3.3	73.2	100	24
5	Acetic acid	Ethanol	[bmim][PF_6]	4.6	73.7	100	24
6	Acetic acid	Ethanol	[bmim][PF_6]	6.2	73.1	100	24
7	Acetic acid	Ethanol	[emim][PF_6]	3.5	83.8	100	24
8	Acetic acid	Ethanol	[emim][PF_6]	6.2	84.9	100	24
9	Acetic acid	Iso-Pentanol	Without	0	68.1	>98	16
10	Acetic acid	Iso-Pentanol	[bmim][PF_6]	3.3	78.4	>98	24
11	Acetic acid	Iso-Pentanol	[emim][PF_6]	3.3	74.9	>98	28
12	Acetic acid	n-Butanol	Without	0	69.2	100	16
13	Acetic acid	n-Butanol	[bmim][PF_6]	3.3	87.6	100	24
14	Acrylic acid	Methanol	Without	0	39.7	100	16
15	Acrylic acid	Methanol	[bmim][PF_6]	3.3	73.7	100	24
16	Acrylic acid	Methanol	[emim][PF_6]	2.1	83.4	100	28
17[c]	Lauric acid	n-Butanol	[bmim][PF_6]	3.3	91.6	100	24
18[c]	Lauric acid	1-Dodecanol	[bmim][PF_6]	3.3	69.8	100	24
19[c]	Lactic acid	1-Dodecanol	[bmim][PF_6]	3.3	65.3	100	24
20	Acrylic acid	Methanol	[bmim][BF_4]	3.3	2.3	100	24
21	Acetic acid	Ethanol	[bmim][BF_4]	3.3	38.2	100	24

[a] Alcohol : acid : pTSA = 1 : 1 : 0.01 in molar ratio; alcohol 13 mmol; temperature 60°C.

[b] The selectivity is the ratio of “moles of alcohol converted to ester” to “total moles of alcohol converted.”

[c] At 80°C.

and acetic acid in the absence of the ILs is 63%, and increases with the amount of the IL in the reactor and then keeps constant after the amount of IL is more than 3 g. The equilibrium conversion can reach 73% as 3.3 g IL is used. In other words, the equilibrium conversion can be enhanced by using the IL as a reaction medium.

The data of entries 1–8 indicate that the equilibrium conversion of esterification of ethanol with acetic acid in [emim][PF_6] is considerably higher than that in [bmim][PF_6], suggesting that the properties of the ILs affect the reaction considerably. Esterification of acetic acid with iso-pentanol or n-butanol (entries 9–13) is performed in [bmim][PF_6] and [emim][PF_6], respectively. Conversion of iso-pentanol or n-butanol can also be enhanced significantly. Esterification of methanol with acrylic acid is conducted in [bmim][PF_6] and [emim][PF_6] (entries 14–16). The increase in conversion is more pronounced for the acid containing C=C double bond. Results of esterification of alcohols and acids with longer carbon chains are shown by entries 17–19, which show that the reactions have high conversion in [bmim][PF_6]. Entries 1, 14, 20 and 21 demonstrate that [bmim][BF_4] reduces the conversion of the reactions. One of the possible reasons is that [bmim][BF_4] is miscible with water, while [bmim][PF_6] can dissolve little amount of water. Therefore, some water produced in the reaction comes out from the solvent as [bmim][PF_6] is used, which shifts the chemical equilibrium to higher conversion.

In summary, equilibrium conversion of the esterification of alcohols with carboxylic acids can be tailored by using ionic liquids as solvents.

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