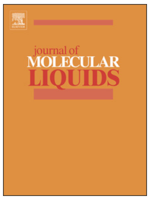
Journal of Molecular Liquids 268 (2018) 610–616

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq



Comparison of the alkalinity of hydroxypyridine anion-based protic ionic liquids and their catalytic performance for Knoevenagel reaction: The effect of the type of cation and the position of nitrogen atom of anion

Bin Xie [a], Yingjie Xu [a,*], Xiaochen Tang [a], Hegang Shu [a], Tingting Chen [a], Xiao Zhu [b]

[a] Department of Chemistry, Shaoxing University, Shaoxing, Zhejiang 312000, China
[b] School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, China

ARTICLE INFO

Article history:
Received 23 June 2018
Received in revised form 21 July 2018
Accepted 23 July 2018
Available online 24 July 2018

Keywords:
Ionic liquid
Alkalinity
Knoevenagel reaction

ABSTRACT

The design of acidity and alkalinity is an important characteristic of ionic liquids, and it also affects their application. For this reason, the alkalinity of six hydroxypyridine anion-based protic ionic liquids (PILs) was determined by potentiometric titration, and the effect of the type of cation and the position of nitrogen atom of anion on the alkalinity was discussed. Furthermore, six hydroxypyridine anion-based PILs were used as catalysts for Knoevenagel reaction, and the relationship between the catalytic performance and the alkalinity was investigated. The results indicate that the type of cation has little effect on the alkalinity of the studied PILs, while the position of nitrogen atom of anion has a significant influence on the alkalinity, and the order of the alkalinity is as follows: $[2\,Op]^- > [4\,Op]^- > [3\,Op]^-$, resulting from the positive cooperative interaction between electronegative nitrogen and oxygen atoms, which is confirmed by DFT calculation. Consequently, the PILs with $[2\,Op]^-$ anion showing stronger alkalinity exhibits better catalytic performance for Knoevenagel reaction.

1. Introduction

Ionic liquids (ILs) featured the designability of structure and physicochemical property via choosing cations and anions have attracted growing interest in the chemistry community due to their impressive performance in a wide range of chemical processes [1]. The alkalinity of ILs is one of the most important physicochemical properties and plays a significant role in the application of ILs, such as acidic gas absorption [2–5], catalytic process [6], and the dissolution of biopolymers [7]. For example, Wang et al. [8, 9] studied the effect of the alkalinity on the CO_2 absorption capacity of azole-based functionalized ILs and found the absorption capacity of CO_2 increased with the increasing the alkalinity of ILs. Moreover, the higher alkalinity of ILs often leads to a better catalytic performance during condensation and addition reaction when the functionalized ILs was used as an alkaline catalyst [3, 10]. Therefore, proper knowledge about the alkalinity of ILs is very significant for improving the efficiency of IL-based process, and it has become a critical issue in designing ILs [11].

Recently, the study of the influence of molecular structure and interaction between anion and cation on the alkalinity of ILs has attracted more and more attention, indicating that the type of anion was closely related to the alkalinity of ILs [8, 9, 11–14]. For example, Zhao et al. [12] used a series of azole-anion-based aprotic ILs as functional solvents and catalysts for atmospheric CO_2 transformation into various heterocyclic compounds, indicating that the type of anions played an important role in catalytic performance. To investigate the effect of the type of anion on the alkalinity of ILs, the pK_a value of the anion was employed to characterize the alkalinity qualitatively. Generally, and the alkalinity of ILs with the same cation increases with the increasing the pK_a value of the anion [8, 9]. However, the pK_a values of the anion reported in the literature was usually determined in the different solvent, such as DMSO and water, which increases the difficulty of evaluating of the alkalinity of ILs and its effect on acidic gas absorption capacity or catalytic performance. Therefore, to compare the alkalinity of ILs more accurately, the different methods were developed to characterize the alkalinity of ILs and used to investigate the relationship between the alkalinity and the structure of ILs [15–20]. Among them, potentiometric titration method is regarded as one of important methods for determination of experimental alkalinity values of ILs, because of its advantages, such as simple operation and good reproducibility [18–21]. For example, the alkalinity of four azole-based PILs was determined by potentiometric titration in our previous work, and the effect of the alkalinity on CO_2 capture behavior was carried out in detail aiming to give guidance for selection suitable PILs for efficient CO_2 capture and activation [4]. Up till now, compared with the physicochemical properties of ILs, such as density, viscosity, and conductivity [22–24], the study of the determination of experimental alkalinity values of ILs is relatively few.

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* Corresponding author.
E-mail address: xuyj@usx.edu.cn (Y. Xu).

https://doi.org/10.1016/j.molliq.2018.07.094
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Thus, it is of great important to investigate the experimental alkalinity values of ILs, which can provide guidance for the application and design of ILs.

Recently, hydroxypyridine anion-based ILs have been widely used for CO_2 capture and transformation, indicating that the charge distribution of nitrogen and oxygen atoms of anion is directly related to the interaction between CO_2 and hydroxypyridine anion-based ILs [3, 25–27], which also affects the alkalinity of hydroxypyridine anion-based ILs. In consideration of the alkalinity of ILs plays an important role on their practical applications, such as catalytic properties and CO_2 capture or transformation, it is necessary to comprehensively understand the alkalinity of this new type of hydroxypyridine anion-based ILs. For this purpose, six hydroxypyridine anion-based PILs (Scheme 1) were prepared by equimolar neutralization reaction of 1,8 Diazabicyclo[5.4.0]undec 7 ene (DBU) or tetramethylguanidine (TMG) with 2 hydroxypyridine (2 Op), 3 hydroxypyridine (3 Op), and 4 hydroxypyridine (4 Op), respectively. The alkalinity of the studied PILs was measured by potentiometric titration method [18–21] and compared with each other. The effect of the type of cation and the position of nitrogen atom of anion on the alkalinity of the studied PILs was discussed. The Mulliken atomic charges of nitrogen and oxygen atoms of hydroxypyridine anion is obtained by DFT calculation and used to explain the effect of the position of nitrogen atom of anion on the alkalinity. Furthermore, six hydroxypyridine anion-based PILs were employed as a catalyst for Knoevenagel reaction, and the relationship between the catalytic performance and the alkalinity was investigated, and the reaction mechanism of Knoevenagel reaction catalyzed by hydroxypyridine anion-based PILs is speculated.

2. Experimental and calculation section

2.1. Preparation and characterization of hydroxypyridine anion-based PILs

1,8 Diazabicyclo[5.4.0]undec 7 ene (99%), 1,1,3,3 tetramethylguanidine (99%), benzaldehyde (Redistillation, >99.5%), ethyl cyanoacetate (99%), and alcohol (>99%) were purchased from Aladdin Reagent Co., Ltd. 2 Hydroxypyridine (98 + %), 3 hydroxypyridine (98%) were supplied by Alfa, and 4 hydroxypyridine (99%) was purchased from Tci. Hydrochloric acid (36.5%) was purchased from Sinopharm Chemical Regent Co., Ltd.

[DBUH][2 Op], [DBUH][3 Op], [DBUH][4 Op], [TMGH][2 Op], [TMGH][3 Op], and [TMGH][4 Op] were synthesized by equimolar neutralization reaction of DBU or TMG with Pyr or Im, respectively [4, 28, 29]. In a typical synthesis of [DBUH][2 Op], 0.25 mol 2 Op was divided into several parts and added into 0.25 mol DBU in batches under vigorous stirring at room temperature for 24 h. Then the obtained hydroxypyridine anion-based PILs were dried under vacuum at 333.15 K for at least 24 h to remove possible trace of water. The water content of the studied PILs was determined with a Karl Fisher Coulometric Titration (Mettler Toledo C20S) and found to be <1000 ppm. The chemical structure of these hydroxypyridine anion-based PILs was characterized by using ^{1}H NMR, ^{13}C NMR, and FT-IR spectra, which were listed in Supporting Information, among which NMR spectra was measured on a Bruker AVANCE III spectrometer and FT-IR spectra was recorded by using a Nicolet 6700 Fourier transform infrared spectrometer equipped with ATR accessory.

2.2. Characterization of the alkalinity of hydroxypyridine anion-based PILs

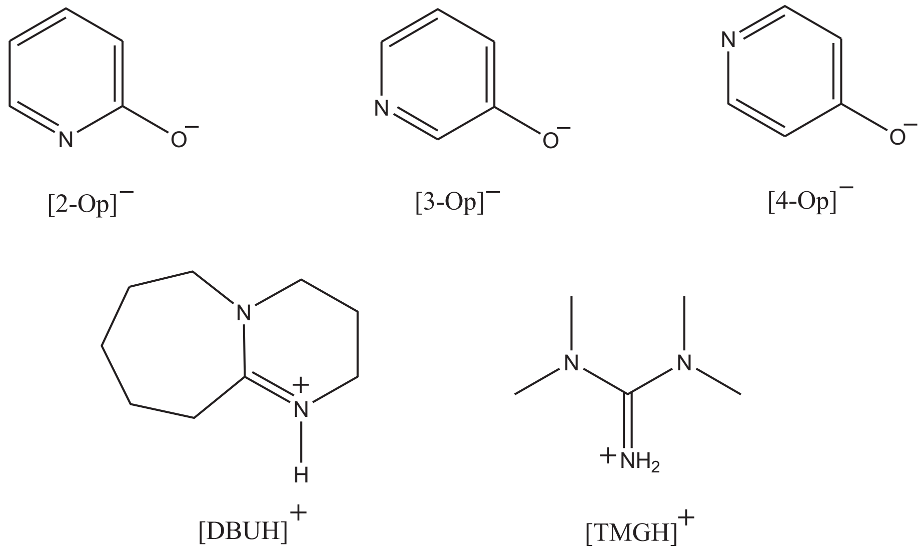
According to literature [18–21], the basicity dissociation constant pK_b values could use to characterize the alkalinity, which was determined by potentiometric titration method. Consequently, the alkalinity of six hydroxypyridine anion-based PILs was characterized by comparison of their pK_b values in the present work. The experiment of pK_b determinations can be referred to our previous work [4], which is briefly described below: a stock solution (0.100 mol L^{-1}) of hydroxypyridine anion-based PILs was prepared in high-purity water, which was then titrated with aqueous HCl solution (0.100 mol L^{-1}). The pH value of the solution was online measured using a calibrated glass electrode on a pH meter (Model pHS-25, Shanghai Precision Scientific Instrument) at 298.15 (±0.10) K. The titration curve of pH value versus titration volume (V) of aqueous HCl solution was plotted. The pK_b for each hydroxypyridine anion-based PILs was calculated using pH value and concentration of base ($[A^-]$) and its conjugated acid ([HA]), which was described as follows [21]:

$$pK_b = 14 - pH + \lg\frac{[A^-]}{[HA]} \tag{1}$$

when the titration volume was a half of the volume of titration end-point (0.5 V_e), the value of $[A^-]$ was equal to that of [HA], that was $[A^-] = [HA]$, so Eq. (1) could be rewritten as follows:

$$pK_b = 14 - pH \tag{2}$$

The volume of titration end-point (V_e) of PILs could be obtained from the extreme point of the first derivative curve of ΔpH versus ΔV, and



Scheme 1. Structures of the anion and the cation in hydroxypyridine anion-based PILs.

then the pH value corresponding to 0.5 V_e could be obtained from the titration curve. As a result, pK_b of PILs could be gained according to Eq. (2) accordingly. The titration curves of six hydroxypyridine anion-based PILs and their first derivative curves were illustrated in Fig. 1, and the obtained V_e and pK_b of the studied PILs were shown in Table 1.

2.3. Calculation of Mulliken atomic charge of hydroxypyridine anion-based PILs

The Mulliken atomic charge of the nitrogen and oxygen atoms in the anion of the studied PILs was calculated using the Gaussian 03 programs package [30]. For each set of calculations, we calculated geometry optimization for each PILs at the B3LYP/6-31G++(d,p) level. The calculated Mulliken atomic charges of the nitrogen and oxygen atoms in the anion of six hydroxypyridine anion-based PILs was listed in Table 1.

2.4. Knoevenagel reaction catalyzed by hydroxypyridine anion-based PILs

The experiment of Knoevenagel reaction (Scheme 2) was similar to the literature [31]. The simple process is as follows: a mixture of benzaldehyde (20 mmol), ethyl cyanoacetate (20 mmol), hydroxypyridine anion-based PILs (2 mmol), and alcohol (25 mL) was mixed and stirred at room temperature (25–30 °C) for 20 min, then the deionized water (50 mL) was added into the mixture and solid product was gradually precipitated. Light yellow solid and transparent filtrates were obtained by filtrating the mixture using sand core funnel. A white solid is obtained after recrystallization with 95% ethanol water solution and drying under vacuum at room temperature for at least 24 h. The melting point of product (ethyl (*E*) 2 cyano 3 phenyl 2 propenoate [32]) was measured by Buchi M-565, which was 49.3 °C (Lit. 47–48 °C [32, 33]). The chemical structure of the product was characterized by ^{1}H NMR, ^{13}C NMR, and IR spectra, respectively, which was presented in Supporting Information and in good agreement with the literature [32, 33]. Moreover, the effect of the type of hydroxypyridine anion-based PILs on catalytic performance of Knoevenagel reaction was investigated, which was listed in Table 1 and used to correlate with the alkalinity.

The recovery process of hydroxypyridine anion-based PILs is as follows: PILs is obtained by removing ethanol and water from the transparent filtrate, then the recycled PILs is washed with ethyl acetate to remove a small amount of unreacted raw materials. After drying, the recycled PILs are used again for catalytic reaction.

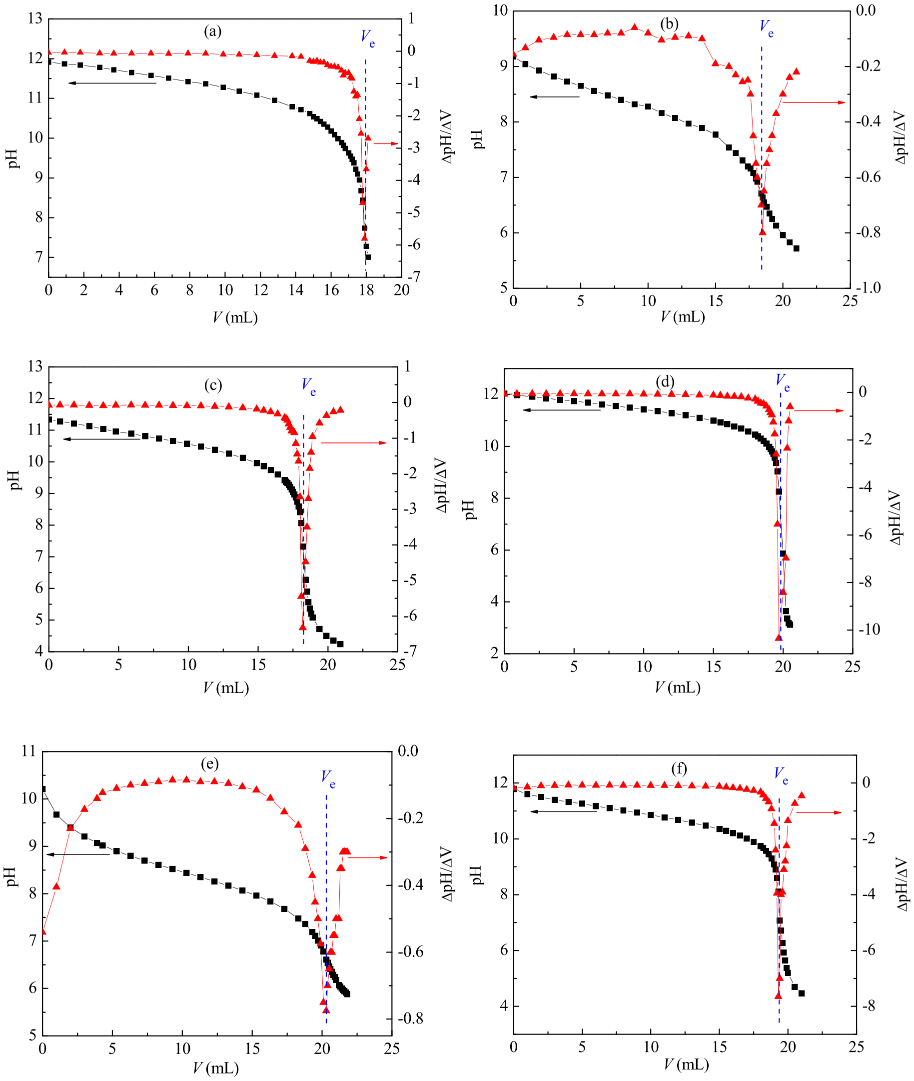


Fig. 1. Titration curves of six hydroxypyridine anion-based PILs and their first derivative curves. (a) [DBUH][2 Op]; (b) [DBUH][3 Op]; (c) [DBUH][4 Op]; (d) [TMGH][2 Op]; (e) [TMGH][3 Op]; (f) [TMGH][4 Op].

Table 1
Alkalinity, Mulliken atomic charges, and Knoevenagel reaction performance of six hydroxypyridine anion-based PILs.

PILs	V_e (mL)	pK_b	Mulliken atomic charges of anion		Yields of Knoevenagel reaction[a] (%)
			N	O	
[DBUH][2 Op]	18.9	2.6	−0.485	−0.636	96
[DBUH][3 Op]	18.5	5.7	−0.376	−0.690	83
[DBUH][4 Op]	18.2	3.4	−0.389	−0.680	90
[TMGH][2 Op]	19.7	2.6	−0.438	−0.658	94
[TMGH][3 Op]	20.3	5.5	−0.373	−0.665	84
[TMGH][4 Op]	19.3	3.1	−0.409	−0.650	89

[a] Reaction conditions: benzaaldehyde (20 mmol) and ethyl cyanoacetate (20 mmol) stirred in ethanol (25 mL) with 2 mmol hydroxypyridine anion-based PILs at room temperature for 20 min; Isolated yields of product.

3. Results and discussion

3.1. Comparison of the alkalinity of hydroxypyridine anion-based PILs

According to the titration curves and their first derivative curves of six hydroxypyridine anion-based PILs illustrated in Fig. 1, the pK_b values for the studied PILs calculated from Eq. (2) are obtained and listed in Table 1. As can be seen in Table 1, the pK_b values of six hydroxypyridine anion-based PILs are <6, which is similar to that of the azole-based PILs [4], whereas much smaller than that of traditional alkylimidazolium-based aprotic ILs and 1,1,3,3 tetramethylguanidinium-based PILs [21], indicating that the studied hydroxypyridine anion-based PILs has strong alkalinity. For example, the pK_b of 1,1,3,3 tetramethylguanidinium acetate PIL, which is usually used as basic solvent for the synthesis of porous metal-organic frameworks nanospheres [34, 35], is 9.61 and larger than that of the studied hydroxypyridine anion-based PILs. Clearly, the studied hydroxypyridine anion-based PILs exhibit much stronger alkalinity compared with the traditional ILs. Therefore, these hydroxypyridine anion-based PILs may be a suitable candidate for basic solvent and catalyst.

As shown in Table 1, one can see that the order of pK_b values of six hydroxypyridine anion-based PILs is as follows:

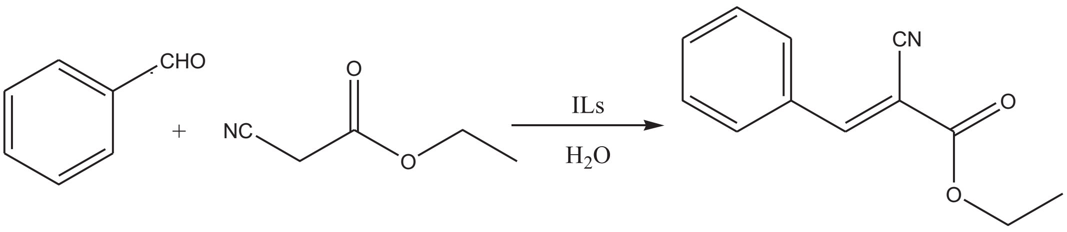
$$[\mathrm{TMGH}][2\ \mathrm{Op}] = [\mathrm{DBUH}][2\ \mathrm{Op}]<[\mathrm{TMGH}][4\ \mathrm{Op}]<[\mathrm{DBUH}][4\ \mathrm{Op}]<[\mathrm{TMGH}] \times [3\ \mathrm{Op}]<[\mathrm{DBUH}][3\ \mathrm{Op}]$$

indicating that the structure of anion has a significant influence on the alkalinity of the studied PILs, and the effect of the type of cation on the alkalinity can be neglected, which is consistent with the results obtained from the solvatochromic method for [$C_x$mim]-type ILs [36, 37] and the results obtained from the potentiometric titration method for azole-based PILs [4]. Why does the structure of anion affect the alkalinity of the studied PILs? By comparing with the structure of three anions of the studied PILs, it is clear that the position of nitrogen atom or the position of the substituent of oxygen atom on the pyridine ring (Scheme 1) is different, which will not only affect the change distribution of the anion, but also affect the alkalinity of the studied PILs. For [2 Op]$^-$ and [4 Op]$^-$ anions, the substituent of oxygen atom is located in the ortho-position and para-position of the pyridine ring, respectively. Consequently, the nitrogen atom may share the negative charge of the oxygen atom by formation the π-electron delocalization, thereby leading to the increase the stability of anions and the enhanced the alkalinity of PILs. However, for [3 Op]$^-$ anion, the substituent of oxygen atom is located in the meta-position of the pyridine ring, which will weaken the ability of the nitrogen atom to share the negative charge of the oxygen atom and lead to weaker alkalinity of PILs with [3 Op]$^-$ anion compared with PILs with [2 Op]$^-$ or [4 Op]$^-$. Therefore, we believe there must be lie in a positive cooperative interaction between electronegative nitrogen and oxygen atoms of anions of hydroxypyridine anion-based PILs [3], resulting in the significant increase of the alkalinity.

To confirm the above analysis, we calculated the Mulliken atomic charge of the nitrogen and oxygen atoms in the anion of six studied PILs using the Gaussian 03 program [30], which is listed in Table 1. As can be seen in Table 1, the order of the Mulliken atomic charge of the nitrogen atom in the anion of the studied PILs is as follows:

$$[2\ \mathrm{Op}]^- > [4\ \mathrm{Op}]^- > [3\ \mathrm{Op}]^-$$

which is much larger than that of the nitrogen atom in pyridine ($pK_b =$ −0.161 [3]). Interestingly, the order of the Mulliken atomic charge of the oxygen atom in the anion of the studied PILs is exactly opposite to that of the nitrogen atom, which is as follows: [2 Op]$^-$ < [4 Op]$^-$ < [3 Op]$^-$. For example, the Mulliken atomic charges of the nitrogen atom in [DBUH][2 Op], [DBUH][4 Op], and [DBUH][3 Op] are −0.485, −0.389, and − 0.376, respectively, while those of the oxygen atom is −0.636, −0.680, and −0.690, respectively. Therefore, it is certain that there is a positive cooperative interaction between electronegative nitrogen and oxygen atoms of anions of hydroxypyridine anion-based PILs by formation the π-electron delocalization, which effectively improves the alkalinity of PILs. Moreover, the position of the nitrogen atom of anion has a significant influence on the cooperative interaction. When the substituent of oxygen atom is located in the ortho-position or para-position of the pyridine ring of anion, the cooperative interaction between electronegative nitrogen and oxygen atoms is significant, transferring the negative charge of oxygen atom to the nitrogen atom by the conjugate effect to form the π-electron delocalization. Furthermore, in PILs with [2 Op]$^-$, the electronegativity of the nitrogen atom will also attract the negative charge of oxygen atom, leading to the cooperative interaction and the alkalinity of PILs with [2 Op]$^-$ slightly greater than those of PILs with [4 Op]$^-$, respectively. When the substituent of oxygen atom is located in the meta-position of the pyridine ring of anion, the cooperative interaction between electronegative nitrogen and oxygen atoms is relatively weak because of the lack of the conjugate effect between the electronegative oxygen and nitrogen atoms.



Scheme 2. Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate catalyzed by hydroxypyridine anion-based PILs.

Therefore, the positive cooperative interaction between electronegative nitrogen and oxygen atoms of anions can effectively improve the alkalinity of hydroxypyridine anion-based PILs, and the position of the nitrogen atom of anions plays an important role in the strength of the cooperative interaction. Thus, the alkalinity of hydroxypyridine anion-based PILs can be tumed by changing Mulliken atomic charge of the nitrogen and oxygen atoms in the anion, which is useful for the design of new highly strong alkalinity ILs for gas separation and catalysis process.

3.2. The effect of the alkalinity of hydroxypyridine anion-based PILs on Knoevenagel reaction

The above study shows that the hydroxypyridine anion-based PILs has strong alkalinity, which can be a good candidate for catalysis process. Therefore, to establish the relationship between the alkalinity and catalytic property of the studied PILs, Knoevenagel reaction is selected, which is a classic catalytic reaction with alkaline catalyst. The yields of Knoevenagel reaction between benzaldehyde and ethyl cyanoacetate catalyzed by hydroxypyridine anion-based PILs are listed in Table 1. As can be seen from Table 1, the hydroxypyridine anion-based PILs can effectively catalyze the Knoevenagel reaction with benzaldehyde and ethyl cyanoacetate, which is better than the results catalyzed by ethylammonium nitrate ILs [33] or solid base catalysts, such as fly ash supported calcium oxide [38], microporous carbon nitride [39], and nitrogen-doped carbon materials [40]. Moreover, by comparing the yields listed in Table 1, it can be clearly found that the catalytic performance of hydroxypyridine anion-based PILs for Knoevenagel reaction in a given condition increases with the increasing of alkalinity. For example, the yields of Knoevenagel reaction catalyzed by [DBUH][2 Op], [DBUH][4 Op], and [DBUH][3 Op] are 96%, 90%, and 83%, respectively, which is in good accordance with the alkalinity of PILs, indicating that the structure of anion is not only to related the alkalinity, but also directly affects the catalytic performance of PILs. Accordingly, the catalytic performance of the hydroxypyridine anion-based PILs is well correlated with the alkalinity.

Comparing the yields of Knoevenagel reaction listed in Table 1, it can be found that the catalytic effect of studied PILs with [2 Op]$^-$ anion is much better than that of other studied PILs with [3 Op]$^-$ or [4 Op]$^-$ anions. In view of the good catalytic ability of [DBUH][2 Op] or [TMGH][2 Op] for Knoevenagel reaction, as well as the positive cooperative interaction between electronegative nitrogen and oxygen atoms of [2 Op]$^-$ anion, the possible reaction mechanism of Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate catalyzed by the studied PILs with [2 Op]$^-$ anion is presented and illustrated in Fig. 2. As shown in Fig. 2, in addition to the negative oxygen atom of [2 Op]$^-$ anion, we believe that the electronegative nitrogen atom of [2 Op]$^-$ anion also participate in the reaction through the formation of the interaction with the acidic alkyl hydrogen of ethyl cyanoacetate, which is beneficial to stabilize the active hydrogen and the formation of the reaction intermediate. Therefore, this may be the main reason why the studied PILs with [2 Op]$^-$ anion has better catalytic properties than other PILs with [3 Op]$^-$ or [4 Op]$^-$ anions, resulting from the positive cooperative interaction between electronegative nitrogen and oxygen atoms of [2 Op]$^-$ anion.

It is well-known that the recycling ability is an important factor in evaluating the performance of catalysts. Therefore, taking [DBUH][2 Op] as an example, its recycling ability of Knoevenagel reaction is investigated, and the results are plotted in Fig. 3. As shown in Fig. 3,

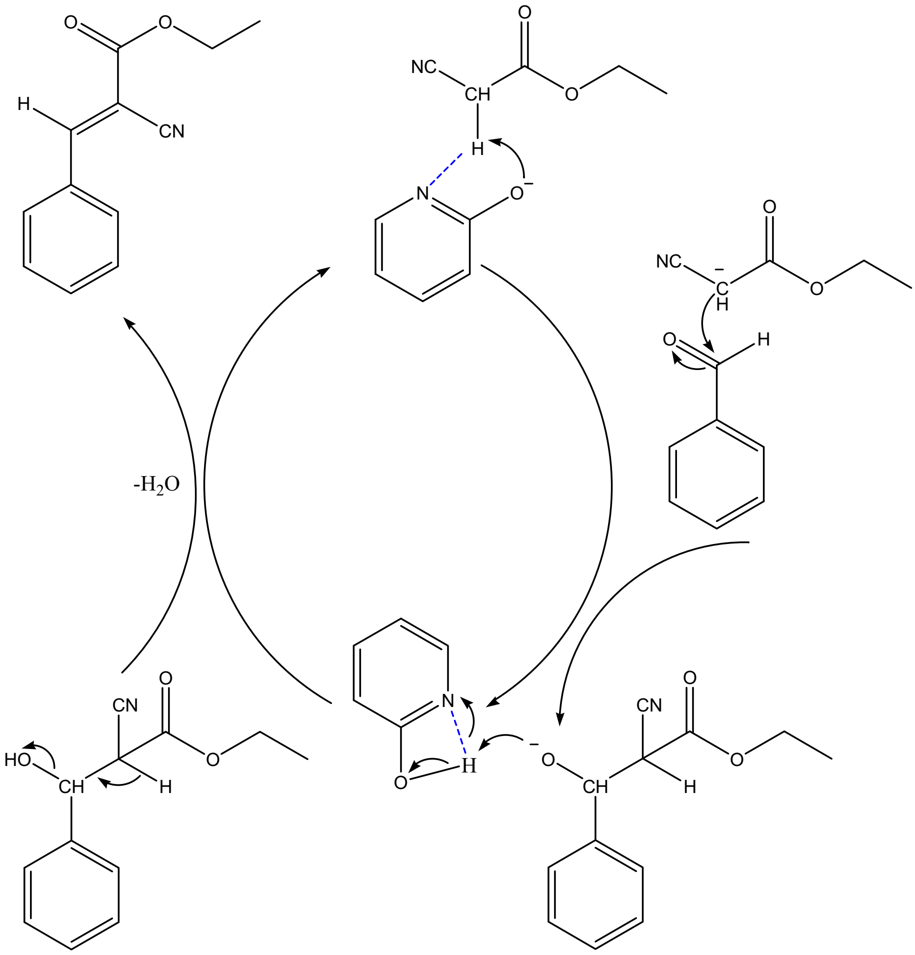


Fig. 2. The possible reaction mechanism of Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate catalyzed by PILs with [2 Op]$^-$ anion.

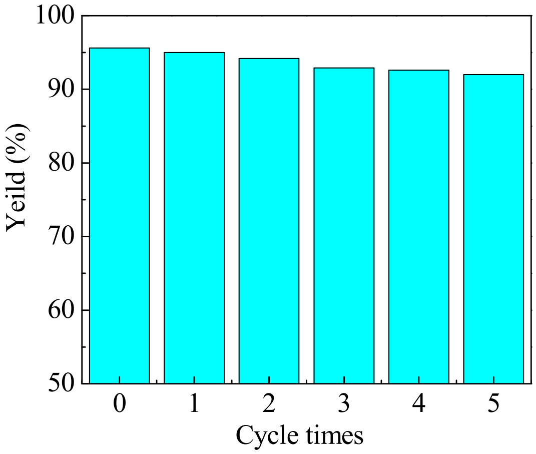


Fig. 3. Reuse of [DBUH][2 Op] for Knoevenagel condensation between benzaaldehyde and ethyl cyanoacetate.

[DBUH][2 Op] can be reused 5 times without noticeable loss of its activity, indicating that [DBUH][2 Op] has good recovery and reuse properties. To investigate the effect of recovery process on the performance of the catalyst, FT-IR spectra of [DBUH][2 Op] before and after Knoevenagel reaction is measured and compared in Fig. 4. Clearly, the absorption peaks of the recovered [DBUH][2 Op] is in good agreement with those of the fresh [DBUH][2 Op], exhibiting that the structure of [DBUH][2 Op] is not destroyed during the recovery process, thus effectively ensuring its activity.

4. Conclusions

In this work, the effects of the type of cation and the position of nitrogen atom of anion on the alkalinity of six hydroxypyridine anion-based PILs were carried out in detail aiming to give guidance for selection suitable PILs as catalysts for Knoevenagel reaction. The results exhibit that the structure of anion has much greater influence on the alkalinity of the studied PILs than the type of cation. Moreover, the position of nitrogen atom of anion is well correlated with the alkalinity of the studied PILs and the order is as follows: $[2\ Op]^- > [4\ Op]^- > [3\ Op]^-$, resulting from the positive cooperative interaction between electronegative nitrogen and oxygen atoms, which is confirmed by the Mulliken atomic charges obtained from DFT calculation. Moreover, the alkalinity of hydroxypyridine anion-based PILs has significant influence on the catalytic performance, and the PILs with $[2\ Op]^-$ anion exhibiting good catalytic and recycling properties can be used as a good candidate for Knoevenagel reaction, and the possible reaction mechanism of Knoevenagel condensation catalyzed by PILs with $[2\ Op]^-$ anion is presented.

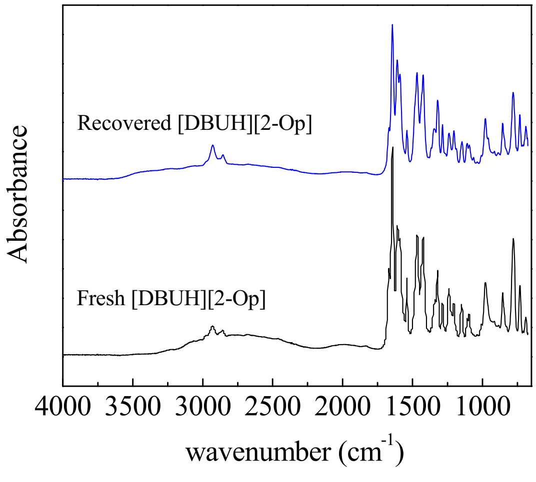


Fig. 4. FT-IR spectra of [DBUH][2 Op] before and after Knoevenagel reaction.

Acknowledgments

We are grateful to the Natural Science Foundation of Zhejiang Province (Y18B060014), National Natural Science Foundation of China (21406140), and National Under-graduate Training Program for Innovation and Entrepreneurship (No. 201810349013) for financial support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2018.07.094.

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