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Effect of water and methanol on the dissolution and gelatinization of corn starch in [MMIM][OAc]

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The effect of water and methanol on the dissolution and gelatinization of corn starch in [MMIM][OAc] was investigated by optical microscopy and differential scanning calorimetry. The presence of appropriate amount of water can accelerate the dissolution while the methanol is just opposite. The [MMIM][OAc]/water mass ratio of 7/3 is the best ratio for corn starch to disperse in [MMIM][OAc]/water mixture, since it can dissolve starch at lower temperature. When methanol was added to the mixture of [MMIM][OAc]/water 8/2 (w/w), methanol can accelerate the dissolving process of corn starch, since it can penetrate into the starch granules and swelled the out layer of granules with water. It is demonstrated that [MMIM][OAc]/water/methanol 8/2/3 (w/w/w) is a good mixed solvent like [MMIM][OAc]/water 7/3 (w/w) for corn starch.

Introduction

Starch is the second largest biomass produced on earth. It is a major storage product of many important economic crops such as maize (corn), rice, wheat, potato, and tapioca. It is composed of amylose and amylpectin molecules, and more importantly, amylose is mainly linear (1→4)-linked α-glucan, while amylpectin is (1→4)-linked α-glucan with α-(1→6) branch points. A large-scale starch processing industry has emerged since last century. Starch has a great prospect in the development of renewable resources.

Water, the most abundant and greenest solvent on the earth, is used for dissolving starch for thousands of years by human beings. However, water is limited to dissolving starch granule due to its semi-crystalline structure and extremely high molecular weight (higher than 10⁵ Da in some case). One of the most crucial challenges for producing starch-based materials is to find a suitable solvent for dissolving starch in a fast and efficient approach. When starch is dissolved in sodium hydroxide aqueous solution, the degradation of starch is non-negligible. Dimethylsulfoxide (DMSO) and N-methylmorpholine-N-oxide (NMMO) can be used for the dissolution and modification of starch. However, both DMSO and NMMO are poisonous and unrecyclable, from this point of view, researchers are searching for green solvent that can dissolve starch.

In recent 20 years, ionic liquid, a kind of green solvent, was invented and used as solvent for biomass such as cellulose and starch. Ionic liquid is also called room temperature ionic liquid, whose melting point is around or below 100 °C. Ionic liquid has been used to replace a wide range of common organic solvent due to its high thermal stability, negligible vapor pressure and wide electrochemical window. What’s more, ionic liquid has also been utilized as media for starch dissolution, since the anions and cations of the solvent can form hydrogen-bonding with hydroxy groups of starch and effectively break the hydrogen-bonding network of starch, whose mechanism is the same as that of cellulose. For example, in 2005, Liu et al. reported that 1-butyl-3-methylimidazolium dicyanamide ([BMIM][dca]) can dissolve amylose. Over the last few years, 1-butyl-3-methylimidazolium chloride ([BMIM]Cl), 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) and 1-ethyl-3-methylimidazolium acetate ([EMIM][OAc]) were usually used to dissolve starch. It is worth mentioning that 1,3-dimethylimidazolium methyl phosphonate ([MMIM][OAc]) is an excellent solvent for carbohydrates because it presents high polarity and remarkable high hydrogen bonding basicity. What’s more, as compared to [EMIM][OAc], [MMIM][OAc] is kind of IL which can be prepared easily. It can be prepared by one step quaternization of 1-methylimidazole with dimethyl phosphite. So it was used to dissolve starch in this study. An interesting discovery, which was firstly reported by Liu and Budtova, was that mixing water with ionic liquid could dissolve starch faster. Immediately after this discovery, Mateyawa et al. found that starch was mainly gelatinized in water-[EMIM][OAc] mixture with lower [EMIM][OAc] concentration while mainly dissolved in the same mixture with higher [EMIM][OAc] concentration. Sciarini et al. reported that...
depolymerization and dissolution happened when the [EMIM][OAc] concentration was higher. Among these works, the amount of water in ionic liquid-water mixture is important for the dissolving process of starch. Taking these into account, here we investigated the effect of water on the dissolution or gelatinization of corn starch in [MMIM][MeO]HPO$_4$2$\cdot$X.

Methanol is expected to stimulate a fast permeation to the non-crystalline area of starch and has better solubility for some organic compounds such as lipids in starch granule than water. So, innovatively, a small amount of methanol was added into ionic liquid-water mixture as solvent and the dissolving behavior and gelation process of starch in the ternary mixtures was observed via optical microscope equipped with a heating stage in real time in this paper.

Results and discussion

Dissolution of corn starch in [MMIM][MeO]HPO$_4$2

It has been reported that [MMIM][MeO]HPO$_4$2 can dissolve cellulose in mild condition completely. In this paper, it was used to dissolve starch and its dissolution in [MMIM][MeO]HPO$_4$2 (10 wt%) at different temperature was investigated by the POM equipped with a hot stage. Corn starch was dissolved within 50 min at 80 $^\circ$C. When temperature increased, the starch was dissolved faster. At 90 $^\circ$C and 100 $^\circ$C, the corresponding dissolution time was shortened to only 22 and 5 min, respectively. Dissolving process at 80 $^\circ$C was shown in Figure 2, in which the starch granules were clearly identified by characteristic Maltese cross or birefringence. Corn starch was separated uniformly in the IL before heating. During the first 5 minutes, 30% of the starch granule disappeared from sight. 20 minutes later, only about 5% of corn starch had its basic structure. In the last 30 min, dissolution became slowly, which may be attributed to the increased concentration and viscosity of starch solution. Compared with our previous works, which had reported that it took 115 min for 6.25 wt% corn starch to dissolve in [EMIM][OAc] at 80 $^\circ$C, while 2 h for 10 wt% corn starch to dissolve in [AMIM][Cl] at the same temperature, it is obvious that [MMIM][MeO]HPO$_4$2 can dissolve starch faster than [EMIM][OAc] and [AMIM][Cl]. As shown Figure S1, [MMIM][MeO]HPO$_4$2 presents the lowest peak temperature, which again proves its better dissolving performance.

Hot stage microscopy without polarized light was performed for more concrete dissolution behavior of corn starch granule in [MMIM][MeO]HPO$_4$2, as shown in Figure 3. During heating in IL, granular erosion and corrosion appeared. Unlike the gelatinization of starch in water, neither of the starches have shown significantly swelling in [MMIM][MeO]HPO$_4$2. On the contrast, the size of starch granules decreased with time. As seen in Figure 3, “Granule a” and “Granule b” were eroded by [MMIM][MeO]HPO$_4$2 from external layers. The dissolution of “Granule c” started both from the center and periphery areas which was followed by the breakage of the granule. It was easier for solvents to dissolve the remaining fragmentations. This may be due to the openings (pores) on the surface of the corn starch granules. Fannon firstly found that these channels penetrated into the granule. Through these channels, ionic liquid could penetrate into the hilum of the starch granule where the structure was loosely packed. So the solvent could be accommodated in the hilum of the granule and the dissolution started from the hilum. This suggested that dissolution of the corn starch started from both the center and periphery of starch granules.

![Figure 1. Chemical structure of 1,3-dimethylimidazolium methyl phosphonate ([MMIM][MeO]HPO$_4$2).](image1)

![Figure 2. Dissolving process of corn starch in [MMIM][MeO]HPO$_4$2 at 80 $^\circ$C observed by POM equipped with a hot stage. The sample was heated to 80 $^\circ$C at a scanning rate of 100 $^\circ$C/min and then maintained at 80 $^\circ$C.](image2)

![Figure 3. Dissolution behavior of corn starch granule in [MMIM][MeO]HPO$_4$2 observed by POM equipped with a hot stage. The sample was heated from room temperature to 120 $^\circ$C at 5 $^\circ$C/min.](image3)
The regenerated materials were characterized by $^{13}$C NMR, wide-angle X-ray diffraction (WXRD) and thermogravimetric analysis (TGA). $^{13}$C NMR (Figure 4) was used to study the chemical change of starch after dissolution in [MMIM][MeO]HPO$_4$. Six signals of the regenerated starch appeared at $\delta$=100.5 (C-1), 79.2 (C-4), 73.6 (C-5), 72.4 (C-3), 72.0 (C-2), 60.9 (C-6) ppm, respectively, which were same as native starch dissolved in DMSO. It was thus concluded that the anhydroglucose unit was not modified when corn starch was dissolved in [MMIM][MeO]HPO$_4$. In other words, this IL was non-derivatizing solvent for starch.

WXRD patterns of starch are shown and compared in Figure 5. The native starch showed four diffraction peaks, that is, $20$=15.1°, 17.0°, 17.9° and 23.0°. After dissolution in [MMIM][MeO]HPO$_4$, the four peaks disappeared, indicating that the crystalline structure in starch was destroyed by IL completely and this change was irreversible. TGA curves are shown in Figure 6 for starch regenerated from [MMIM][MeO]HPO$_4$. The native starch was decomposed rapidly in a narrow temperature range from 300 to 325 °C. The onset temperature for decomposition of regenerated sample was about 10 °C lower, which might be explained by the irreversible unwinding of the amylopectin double helices when corn starch was dissolved. Another explanation was that the slight degradation existed in the solvation process, leading to the decreasing of starch molecular weight, so lower molecular weight had lower decomposition temperature. In Figure 6, the char yield after decomposition was higher. As Figure S2, the $^1$H NMR spectrum of regenerated starch shows no peak of [MMIM][MeO]HPO$_4$ in corresponding chemical shift, suggesting no ionic liquid exiting in regenerated starch. When comparing the starch regenerated from water, DMSO or [MMIM][MeO]HPO$_4$, it is found that starch regenerated from [MMIM][MeO]HPO$_4$ results in the highest char yield while that from water the lowest char yield. Thus it can be inferred that char yield of starch is highly related to its structure. When starch is dissolved or gelatinized in water, DMSO or [MMIM][MeO]HPO$_4$, its structure is destroyed to different extents. In detail, when dissolved in [MMIM][MeO]HPO$_4$, both crystalline structure and H bond of starch are totally destroyed, resulting in weaker intermolecular force, easier carbonization and higher char yield.

**Effect of water on the gelatinization and dissolution of corn starch in [MMIM][MeO]HPO$_4$**

When the corn starch was dispersed in the mixture of [MMIM][MeO]HPO$_4$ and water with different weight ratio, the phase transition (gelatinization, dissolution, or both) was analyzed by DSC, which revealed the interaction between starch, ionic liquid and water. The calorimetric response of corn starch as a function of [MMIM][MeO]HPO$_4$/water ratio is presented in Figure 7, and corresponding transition temperature and enthalpy value are summarized in Table 1. Gelatinization can be defined as the disruption of molecular orders (breaking of hydrogen bonds) within the granule, along with all concomitant and irreversible changes of properties such as water uptake, granular swelling, crystallite melting and...
birefringence loss. As shown in Figure 7, gelatinization was an endothermic process when starch was heated in water to higher temperature progressively. It had been suggested that gelatinization was a process during which energy was needed to break the intramolecular hydrogen bonds and disrupt the crystalline structure. As we demonstrated in the former part of this paper, the size of starch granules decreased from the external layer when starch was dissolved in [MMIM][MeO]HPO$_4$. This kind of dissolution behavior was absolutely different from the swelling behavior shown in gelatinization. It can be observed from Figure 7 that dissolution of corn starch in [MMIM][MeO]HPO$_4$ was also an exothermic process and the peak was between 70 °C and 103 °C. It was suggested that the anions and cations of [MMIM][MeO]HPO$_4$ can form strong hydrogen bonds with hydroxyl groups of starch, leading to a larger dissolving capacity of starch. Based on this hypothesis, the exothermic process might be attributed to the strong hydrogen bonding interaction between [MMIM][MeO]HPO$_4$ and starch.

When corn starch was dispersed in [MMIM][MeO]HPO$_4$-water mixture, two kind of phase transition as studied above, dissolution and gelatinization, should be taken into consideration. As shown in Figure 7 and Table 1, when adding specific amount of water into pure [MMIM][MeO]HPO$_4$, the ratio of [MMIM][MeO]HPO$_4$/water mixture was changed from pure ionic liquid to 8/2 and 7/3 (w/w) and the dissolution peak moved to lower temperature accompanied with decreased $\Delta H$. 7/3 (w/w) was the critical ratio at which both exothermic and endothermic transitions took place, indicating that both the gelatinization and dissolution occurred. Liu and Budtova reported the similar behavior of waxy corn starch in water-[EMIM][OAc] mixture and suggested that water penetrated into the granule firstly, then swelled the outer layers which facilitated penetration and dissolution of ionic liquid. So gelatinization of starch was inevitable when water was presented. When the [MMIM][MeO]HPO$_4$/water mixture changed from pure ionic liquid to 8/2 and 7/3 (w/w), dissolution was the main behavior of the starch granules. However, gelatinization became the main behavior of the starch granules as the mass ratio [MMIM][MeO]HPO$_4$/water was further decreased. With the mass ratio of [MMIM][MeO]HPO$_4$/water changed from 6/4 to 3/7, the gelatinization peak moved to a higher temperature, since dissolution can facilitate the swelling of starch and then further improve gelatinization. However, when mass ratio of [MMIM][MeO]HPO$_4$/water decreased from 3/7 to 0/10 (pure water), the gelatinization peak shifted to lower temperature. It had been explained that phosphonate is kosmotrope which will delay gelatinization, shifting gelatinization to lower temperature. Effect of methanol on the dissolution of corn starch in [MMIM][MeO]HPO$_4$.

Methanol is the anti-solvent used for starch regeneration from a starch/ionic liquid mixture, like water. The effect of methanol on the solubility of starch in [MMIM][MeO]HPO$_4$ was investigated by POM equipped with a hot stage and DSC. Micrographs shown in Figure 8 clearly illustrate that significant swelling didn’t exist, meaning that gelatinization didn’t present when starch granule was dispersed in [MMIM][MeO]HPO$_4$/methanol (8/2 w/w) mixture. Starch granule began to disappear in pure ionic liquid and [MMIM][MeO]HPO$_4$-methanol mixture at 65 °C and 70 °C, and dissolved completely at 105 °C and 110 °C, respectively.

![Figure 7. DSC curves of corn starch in [MMIM][MeO]HPO$_4$-water mixture of different ratios. Aluminum crucibles are heated from 25 °C to 120 °C at scanning rate of 5 °C/min.](image1)

![Figure 8. Dissolution behavior of corn starch granule in [MMIM][MeO]HPO$_4$/methanol (8/2 w/w) observed by POM equipped with a hot stage. The sample was heated from room temperature to 120 °C at 5 °C/min.](image2)

<table>
<thead>
<tr>
<th>IL/water mass ratio</th>
<th>$T_o$ (°C)</th>
<th>$T_p$ (°C)</th>
<th>$T_e$ (°C)</th>
<th>$\Delta H$ (J g$^{-1}$)</th>
<th>Type of peak</th>
<th>IL/water molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure IL</td>
<td>70</td>
<td>90</td>
<td>103</td>
<td>14.02</td>
<td>Exo</td>
<td>--</td>
</tr>
<tr>
<td>8/2</td>
<td>52</td>
<td>69</td>
<td>76</td>
<td>3.54</td>
<td>Exo+</td>
<td>1/2.66</td>
</tr>
<tr>
<td>7/3</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>Exo+</td>
<td>1/4.57</td>
</tr>
<tr>
<td>6/4</td>
<td>59</td>
<td>65</td>
<td>71</td>
<td>1.26</td>
<td>Endo</td>
<td>1/7.11</td>
</tr>
<tr>
<td>5/5</td>
<td>70</td>
<td>74</td>
<td>79</td>
<td>1.26</td>
<td>Endo</td>
<td>1/10.66</td>
</tr>
<tr>
<td>3/7</td>
<td>82</td>
<td>87</td>
<td>91</td>
<td>1.13</td>
<td>Endo</td>
<td>1/24.88</td>
</tr>
<tr>
<td>1/9</td>
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<td>79</td>
<td>85</td>
<td>1.10</td>
<td>Endo</td>
<td>1/95.97</td>
</tr>
<tr>
<td>water</td>
<td>62</td>
<td>68</td>
<td>72</td>
<td>1.11</td>
<td>Endo</td>
<td>--</td>
</tr>
</tbody>
</table>

$T_o$: onset temperature; $T_p$: peak temperature; $T_e$: endset temperature; $\Delta H$: transition enthalpy.
which suggested that methanol impeded the dissolution process of corn starch in [MMIM][MeO]HPO$_2$. DSC curves in Figure 9 and data in Table 2 substantiate the decrease of the dissolution temperature as methanol was added to the [MMIM][MeO]HPO$_2$. This result can prove that methanol is a poor solvent for starch, so it inhibited the dissolution process of starch in [MMIM][MeO]HPO$_2$. Another possible reason is that methanol molecule is bulkier than water molecule, so it isn’t easy for methanol to penetrate into the starch granules through the pores on the corn starch granules. 

**Effect of methanol on the dissolution/gelatinization process of corn starch in [MMIM][MeO]HPO$_2$-water mixture**

The effect of methanol on the dissolution and gelatinization of corn starch in [MMIM][MeO]HPO$_2$-water mixture was analyzed by DSC and POM. The calorimetric responds of corn starch as a function of increased methanol ratio is shown in Figure 10 while maintaining the ratio of [MMIM][MeO]HPO$_2$ to water in the level of 8 to 2, and the corresponding transition temperature and enthalpy value are tabulated in Table 3. It is interesting to observe that the presence of methanol leads the dissolution of starch to happen at lower temperature, accompanied with decreased $\Delta H$. When methanol was added into the [MMIM][MeO]HPO$_2$-water mixture (8/2 w/w), dissolution temperatures decreased as the mass ratio of [MMIM][MeO]HPO$_2$-water-methanol changed from 8/2/0 to 8/2/3. But when mass ratio of methanol was further increased to 8/2/5, gelatinization became the main behavior of starch granules. [MMIM][MeO]HPO$_2$/water/methanol 8/2/3 (w/w/w) was the critical ratio at which both exothermic and endothermic transition took place, indicating that both the gelatinization and dissolution occurred. This illustrated that methanol molecules can be one of the factors controlling gelatinization and dissolution when methanol co-existed with water. After water swelled the outer layers of the granules, methanol could penetrate into the granules and swelled the granules further. Methanol affected the dissolution/gelatinization process of starch as the similar way as water molecule, facilitating the gelatinization process of corn starch. Another explanation is that some organics like starch lipids (including phospholipids) exist in corn starch granule and methanol has better dissolubility of organic matter than water. It accelerates the dissolution of corn starch through the disruption of hydrophobic effect of starch.
Microscopic images displayed in Figures 11, 12 and 13 could further support our speculation about methanol. In the mixture of [MMIM][MeO]HPO$_2$/water/methanol (8/2/1 w/w/w), the starch granule started to burst into fragments and started to dissolve at 39°C, during which the granule didn’t obviously swell, indicating that dissolution was the main behavior of starch granule. At 66°C, the starch granule dissolved completely. When the ratio of [MMIM][MeO]HPO$_2$/water/methanol was changed to 8/2/3 (w/w/w), the starch granule started to swell at 36°C.

When the ratio of [MMIM][MeO]HPO$_2$/water/methanol was changed to 8/2/5 (w/w/w), it was observed that the gelatinization process of starch granule was similar to that in water. Although methanol can’t penetrate into starch granules alone, when water existed, water firstly penetrated into the granule, swelled the outer layer and then methanol penetrated into the granule, accelerating the burst of starch granules into fragmentations. It was much easier for solvents to dissolve the fragmentations.

The effect of other alcohol on the dissolution and gelatinization of corn starch in [MMIM][MeO]HPO$_2$/water-alcohol mixture was also studied by DSC (Figure 14) and corresponding transition temperature and enthalpy value are summarized in Table 4. The DSC results showed that the presence of ethanol, n-propanol or isobutanol can also lead the dissolution to happen at lower temperature. However, when the same amount of alcohol was added into the [MMIM][MeO]HPO$_2$/water (8/2 w/w) mixture, the lowest dissolution temperature acquired in [MMIM][MeO]HPO$_2$/water/methanol. This result demonstrated that methanol was more efficient in accelerating the dissolution and gelatinization of corn starch in [MMIM][MeO]HPO$_2$/water mixture, which can be attributed to its smallest molecular size in alcohol.
Experimental

Materials

Corn starch (Aladdin, China, Reagent grade) was dried under vacuum for 48 h at 60 °C before use. N-methylimidazole (Linhai Kaile Chemical Factory, China) was dried with calcium hydride under stirring and then distilled under reduced pressure before use. Dimethyl phosphate was purchased from Xiya Reagent (Sichuan, China), and was distilled under reduced pressure before use. THF was purchased from Beijing Chemical Works (Beijing, China) and distilled under normal pressure from sodium benzophenone ketyl under argon immediately prior to use. Methanol (99.9%) and dimethyl sulfoxide (99.7%) were purchased from Aladdin (Shanghai, China). Other solvents were purchased from Beijing Chemical Works (Beijing, China). These chemicals were used as received.

Preparation of [MMIM][MeO]HPO

1,3-dimethylimidazolium methyl phosphonate ([MMIM][MeO]HPO) was synthesized according to a previous report. To a THF solution of N-methylimidazole, dimethyl phosphate in THF was added dropwise under argon gas atmosphere at room temperature. The reaction mixture was stirred with reflux at 80 °C for 2 days. After removal of THF under reduced pressure, the resulting liquid was washed with an excess amount of ethyl acetate repeatedly. After removal of ethyl acetate, the obtained liquid was dried in a vacuum oven at 70 °C for 48 h. 1H NMR (400 MHz; CDCl3/Mes, 2H, d, J = 11.8 Hz), 4.04 (6H, o), 4.04 (6H, s), 6.90 (1H, d, J = 591.4 Hz), 7.54 (2H, s), 10.59 (1H, s).

Dissolution of corn starch in [MMIM][MeO]HPO

Dried corn starch (10 wt% of the IL) was added into [MMIM][MeO]HPO (2.0 g) with stirring at 80 °C until a transparent solution was formed. The dissolving process was observed in-situ by polarized light microscope (PLM) equipped with a hot stage. The sample was heated to 80 °C at a scanning rate of 100 °C/min and then maintained at 80 °C until all the starch granules disappeared from the view-window. Regenerated starch was precipitated by methanol, collected by filtration and then dried in a vacuum oven at 70 °C for 24 h. The final products were characterized by 13C NMR, wide-angle X-ray diffraction (WXRD) and thermogravimetric analysis (TGA).

DSC for dissolution/gelatinization observation

Differential scanning calorimetry (Mettler DSC 1 instrument, Germany) was used to investigate the thermal transition of native starches in [MMIM][MeO]PO2-water mixtures, [MMIM][MeO]PO2-methanol mixtures and [MMIM][MeO]PO2-water-methanol mixtures. Dried corn starch (10 wt%) was added above IL-water, IL-methanol or IL-water-methanol mixing solvents, which were mixed completely. 15-30 mg sample was weighed into 40 µL aluminum pan. An empty pan was used as a reference. The pans were heated from 20 °C to 120 °C at a scanning rate of 5°C/min. Each experiment was repeated at least two times to ensure the consistency of the results.

Optical microscope for dissolution/gelatinization observation

Optical microscope (Olympus BX53, Japan), equipped with Linkam hot stage (TMS94, Germany), was used to observe the behavior of the corn starch in IL, IL-water, IL-methanol and IL-methanol-water mixtures. Polarizing filters improved the contrast of images. Dried corn starch (10 wt% of solvent) was added into above IL-water, IL-methanol or IL-water-methanol mixing solvents, which were mixed completely. One drop of the sample was sandwiched between two pieces of cover glass. The edge of the cover glass was sealed by silicon adhesive to avoid evaporation of the water and methanol from the sample. The sample was quickly heated to 30 °C and then heated from 30 °C to 100 °C at a heating rate of 5 °C/min. The process of dissolution or gelatinization was monitored by a digital camera until the corn starch in the selected religion disappeared completely. Photos of 500× magnification were taken at every 1 °C during heating. Each experiment was repeated at least two times to ensure the consistency of the results.

Conclusions

In summary, [MMIM][MeO]HPO2 was found to be an effective solvent for starch, which could dissolve 10 wt% of starch completely in 50 min at 80 °C. The effect of water and methanol on the dissolution of starch was investigated in the presence of [MMIM][MeO]HPO2. The presence of appropriate amount of water can accelerate the dissolution while the methanol is just the opposite. The mass ratio of [MMIM][MeO]HPO2/water of 7/3 is the best ratio for corn starch to be dispersed in [MMIM][MeO]HPO2-water mixture, since it can dissolve starch at lower temperature. It is interesting that methanol can promote the dissolution of starch in the mixture of [MMIM][MeO]HPO2-water-methanol due to swelling of granules. When methanol was added to the mixture of [MMIM][MeO]HPO2/water 8/2 (w/w), methanol can accelerate the dissolving process of corn starch, since methanol can penetrate into the starch granules and swelled the outer layer of granules with water. It is demonstrated that [MMIM][MeO]HPO2/water/methanol 8/2/3 (w/w/w) is a good mixed solvent like [MMIM][MeO]HPO2/water 7/3 (w/w) for corn starch, since it can dissolve corn starch at low temperature. This finding improves the understanding about dissolution of starch and the methanol can be substituted by different acid, alcohol and other organic solvents to dissolve and gelatinize starch granule, thus promoting starch preparation in these new systems.

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Notes and references