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Volume 18 | Number 7 | 7 April 2016 | Pages 1821–2242

Green Chemistry

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ISSN 1463-9262

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DOI: 10.1039/C7GC00626H

Journal Name

COMMUNICATION

Induction of lignin solubility for a series of polar ionic liquids by the addition of small amount of water

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/greenchem

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Addition of small amount of water was found to induce lignin solubilizing ability of several polar ionic liquids which showed no lignin solubility in the absence of water. Similarly, addition of water was found to enhance lignin solubility in many polar ionic liquids. However addition of water lowered proton accepting ability of these ionic liquids, their proton donating ability was found to increase. The lignin dissolution by ionic liquids was newly found to be the function of both proton accepting ability and proton donating ability of the ionic liquids. Since water is a poor solvent for polysaccharides, water addition has been confirmed to be effective to improve selective extraction yield of lignin from cedar powder under mild condition.

Introduction

Lignocellulose, consisting mainly of cellulose, hemicellulose, and lignin, has attracted much attention as abundant and renewable feedstock.[1] As polysaccharides such as cellulose and hemicellulose have been utilized in pulp industry and currently used as a raw material for chemicals, lignin has also attracted attention as a renewable aromatic chemical stock.[2] However, utilization of lignin is still under development because insolubility of lignin in organic solvent limits the extraction of lignin from lignocellulose. Since the component of lignocellulose entangles with each other as well as crosslinking, many attempts have been made to extract each component by breaking these tough complexed structure.[3-10] The major method to extract each component is known as "kraft pulping process" in which biomass was added and treated in sodium hydroxide/sodium sulphide mixture to break the crosslinking of lignin. Throughout this method, cellulose is obtained as high quality pulp and lignin is obtained as a black liquor residue.[11] Though pulp is widely used to produce paper, the lignin recovered from black liquor is normally combusted to produce energy. Because black liquor contains depolymerised polysaccharides due to harsh treatment, lignin obtained as a precipitation after neutralization of black liquor is also contaminated by saccharide residues.[12] These impurities in lignin are unfavourable to obtain pure lignin for further application. Since it is economically difficult to produce value-added chemicals from lignin, lignin has been deemed as just a by-product and incinerated as a fuel for kraft pulping process. Thus, development of new methodology, which is able to separate lignin under milder condition expecting not to extract cellulose, is imperative for the effective use of lignin.

According to the method for lignocellulose treatment, lignins are classified into alkaline lignin (AL), Klason lignin, kraft lignin, organosolv lignin, lignosulfonate, and so on. Among these technical lignins, AL was chosen as a target in this work because of its moderately low molecular weight and simple structure. [13] In contrast to this, Klason lignin has large number of three-dimensional crosslinks and kraft lignin has thioether bond, respectively, which are different from lignin in nature.[14,15] In the case of organosolv lignin and lignosulfonate, these are soluble in organic solvents and water, respectively.[16,17] Accordingly, AL is considered to be a good model for the screening of novel solvents for lignin.

Recently, ionic liquids (ILs) have attracted attention as solvents for biomass processing.[18] ILs having high hydrogen donating ability can dissolve cellulose. In the initial stage, [C_4mim]Cl was found to dissolve cellulose at 100 °C.[19] We have previously shown that Kamlet-Taft parameters of ILs (α: hydrogen accepting ability and β: hydrogen donating ability) are quite useful to discuss dissolution ability of cellulose in ILs.[20, 21] Not only cellulose but also lignin is targeted to solubilise with ILs. It has been reported that some acidic ILs[22,23], imidazolium-type ILs[24,25], cholinium-type ILs[26,27] and amino acid ILs[28] are known as good solvents for fragmented lignin. Several ordinary ILs such as diazabicycro-type[29] and onium-type ILs[30] are also known as their solvents.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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DOI: 10.1039/C7GC00626H

Furthermore, these solubility data cannot be compared because of different properties of these lignin samples. Accordingly, there is a strong request on the general understanding to obtain ILs with high lignin dissolution ability. It has been recently shown that addition of water to ILs enhances lignin dissolution[31] but the reason of positive effect of water addition on the improvement of lignin solubility remains unknown. Hart et al. have previously reported solubility of organosolv lignin in a series of ILs.[24] They have chosen ILs having different polarity to conduct systematic investigation. They have found that cation structure affected lignin dissolution greater than that of anion. We have focused on Kamlet-Taft parameters for quantitative study of lignin dissolution in ILs, especially on the effect of water addition.

Experimental

Materials

Alkaline lignin (AL) and cedar powder prepared from Japanese cedar were provided by Forestry and Forest Products Research Institute (FFPRI), Japan. AL was washed with water and filtrated three times to remove acid residue which was contaminated during extraction of AL. Absence of acid was confirmed by checking pH of the aqueous dispersion of AL. The AL and cedar powder were dried *in vacuo* at room temperature and sieved (75-150 μm). A series of [C_2mim] salts containing such anions as CH_3SO_3, dicyanamide ($N(CN)_2$), bis(trifluoromethanesulfonyl)imide ([Tf_2N]), and BF_4 were purchased from Tokyo Chemical Industry Co., Ltd. [C_2mim]$CH_3O(H)PO_2$ was purchased from Kanto Chemical Co., Inc. 1-Hydroxyethyl-3-methyimidazolium [Tf_2N] ([C_{2OH}mim][Tf_2N]), tetrabutylphosphonium dicyanamide ([P_{4444}]$N(CN)_2$), [P_{4444}]$CH_3O(H)PO_2$, and a series of [C_2mim] salts containing such anions as CH_3CO_2, CF_3CO_2, CF_3SO_3, as well as a series of CF_3CO_2 salts containing tetrabutylphosphonium ([P_{4444}]), *N*-butyl-*N*-methyl-piperidinium([Pip_{14}]), *N*-butyl-*N*-methylpyrrolidinium([Pyr_{14}]), and *N*-butyl-*N*-methylmorpholinium ([Mor_{14}]) were prepared as shown in the ESI.

Dissolution test of alkaline lignin

All ILs were dried *in vacuo* at 80 °C for 10 h. Water content of these ILs was confirmed to be less than 0.2 wt% by Karl Fischer titration. Then, Milli-Q® water was added to the ILs. To pristine ILs or IL/water mixtures, 10 wt% of AL was added and stirred at 60 °C for 30 min. Solubility was checked with optical microscope observation as well as by naked eyes. When added AL was dissolved completely, another 10 wt% of AL was added, and their solubility was evaluated in the same manner. To determine the maximum dissolution amount of AL, this procedure was repeated until undissolved AL was observed. For ILs having solubilisation ability of AL at 60 °C, the dissolution test was also carried out at room temperature. For this test under mild condition, 1.0 wt% of AL was added to IL and stirred for half a day. To confirm reproducibility of the obtained results, all the dissolution tests were conducted twice. Concentration of lignin in the liquid phase can be evaluated using UV-Vis spectroscopy. The absorption by phenolic groups of lignin at 280 nm is useful as Hart et al previously proposed[24]. In case of samples treated under harsh condition, some aromatic rings may be damaged and deviated from the relation between concentration of dissolved lignin and absorbance. We have checked this relation is effective for lignin dissolved in some ILs treated at 60 °C (see Fig. S2). For more direct measurement, we have checked the dissolution of lignin by naked eyes and optical microscopic observation.

Extraction of lignin from cedar powder

To ILs or their mixtures with water, 5.0 wt% of Cedar powder was added and stirred at 60 °C for 10 hrs. The mixture was centrifuged at 15,000 rpm for 10 min. to separate insoluble residue. Concentration of dissolved lignin (C_{lignin} in wt%) in the liquid phase was evaluated using UV-Vis spectroscopy, because of the absorption by phenolic groups of AL at 280 nm that was previously proposed by Hart et al[24]. The baseline was recorded using ILs or IL/water mixture stirred at 60 °C for 10 h. In order to obtain C_{lignin}, a standard line was determined by plotting the absorbance of [C_2mim]$CH_3O(H)PO_2$ dissolving defined amount of AL and added weight of AL. C_{lignin} was calculated by substituting measured absorbance for the linear equation (see Fig. S2). Weight of the extracted lignin (W_{lignin}) was then calculated from Eq.1, where W_{CP} is weight of the added cedar powder and $W_{solvent}$ is weight of used solvent.

$$W_{lignin} = (W_{CP} + W_{solvent}) \times C_{lignin} / 100 \cdots \text{Eq.1}$$

The W_{lignin} out of the quantity of lignin contained in the added cedar powder was defined as the extracted degree of lignin ($\%E_{lignin}$) as shown in Eq.2. The weight of lignin in the cedar powder was estimated to be 32.6% of W_{CP} according to Klason method.[32]

$$\%E_{lignin} = W_{lignin} / (W_{CP} \times 0.326) \cdots \text{Eq.2}$$

Results and discussion

Effect of water content on the solubility of AL in ILs

Solubility of AL in a series of [C_2mim] salts and their mixtures with water was evaluated. One of polar IL, [C_2mim]CF_3SO_3, could dissolve no AL at 60 °C, but it was newly found that this dissolved 40 wt% of AL at 60 °C when 10-20 wt% of water was added. It was also confirmed that [C_2mim]CF_3SO_3 dissolved lignin even at room temperature in the presence of water. Though there is a fact that addition of water dropped solubility of polysaccharides in ILs[33], addition of water induced dissolution of AL. Furthermore, addition of only 1.0 wt% water was confirmed to induce solubility of AL in [C_2mim]CF_3SO_3. Improvement of AL solubility was also observed as shown in Fig. 1(b) and Fig. S3 when [C_2mim]CH_3CO_2, [C_2mim]$CH_3O(H)PO_2$, and [C_2mim]CF_3CO_2 were used. In the case of [C_2mim]CH_3CO_2, up to 50 wt% of AL was dissolved in the presence of water. In contrast to this, induction and improvement of AL solubility was not observed for [C_2mim]BF_4 and [C_2mim][Tf_2N]. From these results, water addition was shown to be effective to dissolve AL only when certain ILs were used. Anion structure was also confirmed to strongly affect the solubility of AL even in the presence of water. The effect of cation structure on the solubility of AL was then analysed using a series of CF_3CO_2 salts. The CF_3CO_2 salts were selected by considering its high stability in the presence of water and low melting point compared to

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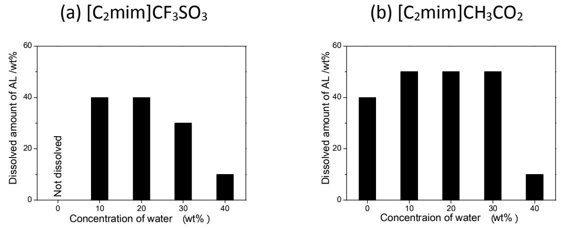

Fig. 1 Effect of water concentration on the solubility of AL in (a) $[C_2mim]CF_3SO_3$ and (b) $[C_2mim]CH_3CO_2$ at 60 °C.

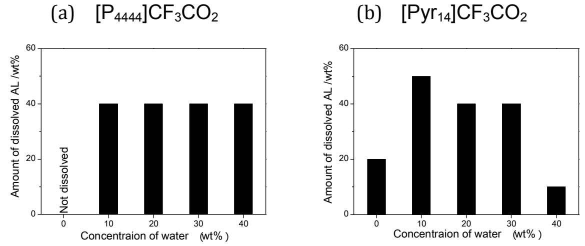

Fig. 2 Effect of water concentration on the solubility of AL in (a) $[P_{4444}]CF_3CO_2$, (b) $[Pyr_{14}]CF_3CO_2$ at 60 °C.

other salts we have investigated in this study. $[Pyr_{14}]CF_3CO_2$ dissolved AL after water addition (<40 wt%). Other ILs such as $[Mor_{14}]CF_3CO_2$, $[P_{4444}]CF_3CO_2$, and $[Pip_{14}]CF_3CO_2$ enhanced solubility of AL only after adding water (Figs. 2 and S4). All CF_3CO_2 salts investigated here dissolved AL even at room temperature when water was added.

Effect of water addition on the solubility of AL from the viewpoint of Kamlet-Taft parameters

Effect of Kamlet-Taft parameters of ILs on the solubility of AL was addressed. Kamlet-Taft parameters are often used to describe polarity of solvents, especially α and β values are known to denote the hydrogen donating ability and accepting ability, respectively. We have previously shown that ILs with high hydrogen accepting ability, i.e., high β value, are favourable for dissolution of cellulosic biomass.[20, 21] Because, in the case of cellulose dissolution, inter- and intra-molecular hydrogen bonds in cellulose crystals are broken by ILs having high β value. In addition to this, there are several reports suggesting that ILs with mid to high β value dissolve kraft lignin.[18] Considering that lignin also contains many OH groups, there are some contributions of hydrogen bonds between these OH groups. It is also considered to be necessary to break these hydrogen bonds for the dissolution of oligomeric lignin.

Table 1 shows β value of a series of ILs and solubility of AL in the ILs. Since solubility of AL in ILs mainly depended on the anion species and β value of ILs was also strongly influenced by anion species, we firstly focused on a series of $[C_2mim]$ salts. As shown in Table 1(a), β value of ILs strongly influenced the solubility of AL in ILs. However, when we focused on a series of CF_3CO_2 salts, clear correlation between β value and the solubility of AL could not be observed. The CF_3CO_2 salts showed β value greater than 0.6, but $[Mor_{14}]CF_3CO_2$, $[Pip_{14}]CF_3CO_2$, and $[P_{4444}]CF_3CO_2$ showed poor AL solubilisation ability in the absence of water. In addition to the irrelevance between β value and AL solubility, water addition is known to lower β value of ILs which is certainly unfavourable for AL dissolution. This strongly suggests the existence of other factors to affect solubility of AL in ILs. In spite that the α value has been empirically known to less affect the dissolution of these polymers containing lots of hydroxyl groups than β value, we have reached one point to check the effect of both α and β values for the dissolution of lignin.

Table 1 β value and solubility of 10 wt% AL in a series of (a) $[C_2mim]$ salts and (b) CF_3CO_2 salts.

(a) [C$_2$mim] salts					**(b) [CF$_3$CO$_2$] salts**				
#	**Anion**	**β value** (neat)	**Solubility of AL**		**#**	**Cation**	**β value** (neat)	**Solubility of AL**	
			neat	**10wt% aq.**				**neat**	**10wt% aq.**
1	$CH_3CO_2^-$	1.06	○	○	9	$[P_{4444}]^+$	1.06	×	○
2	$CH_3O(H)PO_2^-$	1.00	○	○	10	$[Pip_{14}]^+$	0.86	×	○
3	$CF_3CO_2^-$	0.75	○	○	11	$[Pyr_{14}]^+$	0.85	○	○
4	$CH_3SO_3^-$	0.72	○	○	3	$[C_2mim]^+$	0.84	○	○
5	$N(CN)_2^-$	0.61	○	○	12	$[Mor_{14}]^+$	0.71	×	○
6	$CF_3SO_3^-$	0.47	×	○					
7	BF_4^-	0.37	×	×					
8	$[Tf_2N]^-$	0.22	×	×					

Factors affecting the solubility of AL in ILs containing water

We then focused on the solubility of AL in the ILs containing water. Decrease of AL solubility at high water content is considered to be due to the dilution of ILs as well as poor solubilising properties of water. In contrast to this, improvement of AL solubility at low concentration of water is considered to be attributed to change in viscosity and/or solvent-solute interaction. However the effect of viscosity greatly affects the dissolution speed of AL, addition of water less affects on the dissolution amount. Considering this, the improvement of AL solubility may be triggered by the change of solvent-solute interaction.

Thus, here we address the changes of Kamlet-Taft parameters in more detail by focusing on both α and β values before and after adding water. Fig. 3 shows effect of α and β values on the AL solubility. The starting point of each arrow describes Kamlet-Taft parameters before adding water and the arrowhead describes those after addition of 10 wt% of water. Considering Kamlet-Taft parameters of water (α = 1.12 and β = 0.14)[35] into account, addition of water should decrease the β value. However, α value of ILs increased by the addition of water. For example, α and β values of $[P_{4444}]$ CF_3CO_2 were 0.28 and 1.06, and they were changed to 0.43 and 0.86 after adding 10 wt% water (see arrow #9 in Fig. 3), respectively.

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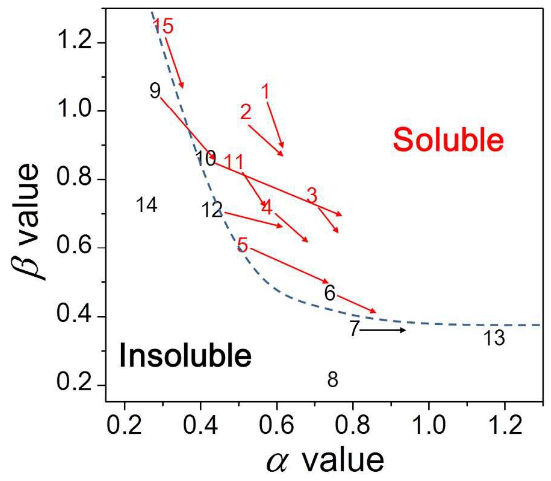

Fig. 3 Concerted effect of α and β values on the AL solubility of the ILs. Arrows describe the change in α and β values before (starting point) and after (arrowhead) addition of 10 wt% water. The color of number and arrow describes the solubility for these ILs before and after addition of water (red: soluble, black: insoluble). Each number corresponds to entry (#) 1-12 in Table 1. Others are as follows; #13: $[C_{2OH}mim][Tf_2N]$, #14: $[P_{4444}]N(CN)_2$, and #15: $[P_{4444}]CH_3O(H)PO_2$.

There is a threshold between AL soluble region and insoluble region as shown as a broken line in Fig. 3. The arrow (#9)started from insoluble region to soluble region. This might be a reason that solubility of AL increased after addition of water. The IL/water mixtures with improved α value may contribute to the dissolution of AL. Also, when the CF_3CO_2 salts are focused on (entry #3 and #9-12), AL dissolved in CF_3CO_2 salts having α value higher than 0.5 when no water was added. Similar trend was found in the two examples, i.e., $[C_2mim]N(CN)_2$ (entry #5), which has higher α value, dissolved AL, and $[P_{4444}]N(CN)_2$ (entry #14), which has lower α value, did not dissolve AL. From these results, it was strongly suggested that α value of ILs influences AL solubility in addition to β value.

Considering that $[C_{2OH}mim][Tf_2N]$ shows poor lignin solubilization ability in spite of its high α value (α: 1.17, β: 0.34) [35], it was suggested that there is a critical β value to dissolve AL, and ILs having very high α value cannot dissolve AL when their β value was lower than 0.40. As shown in Fig. 3, a threshold curve was depicted as the results of AL dissolution test. This clearly shows that addition of water was eminent only when the arrows start from AL insoluble region and reached to AL soluble region. This can explain the effect of water addtion to give AL dissolution ability to some ILs. Also this can explain the enhancement of AL dissolution ability of some ILs after addition of water. Decrease in solubility of lignin by ILs containing excess amount of water (see Figs. 1 and 2) should be attributed to the change of β value lower than the threshold shown in Fig. 3.

Extraction of lignin from cedar powder

We have demonstrated that lignin solubility in ILs was induced or improved by the addition of water. Since water addition suppressed cellulose solubility in ILs,[33] the aqueous ILs prepared in this study are expected to be favourable for selective extraction of lignin from biomass. Here the extraction of lignin directly from CS has been tried (Table 2). From each group of ILs classified based on the solubility of AL, $[C_2mim]CH_3O(H)PO_2$, $[C_2mim]CF_3SO_3$, and $[C_2mim]BF_4$ were selected as extraction solvents. Among these ILs, $[C_2mim]CH_3O(H)PO_2$ is known to dissolve cellulose in the absence of water though others do not dissolve.[20] To confirm that addition of water reduced the solubility of cellulose in $[C_2mim]CH_3O(H)PO_2$, dissolution test of cellulose was carried out in advance. To $[C_2mim]CH_3O(H)PO_2$ containing 10 wt% water, 0.1 wt% of cellulose (Avicel® PH101) was added and stirred for 10 hrs. at 60 °C. The solubility was checked with the microscope and by naked eyes. Even the added amount of cellulose was quite small, the crystalline of cellulose was observed suggesting the cellulose solubility in the $[C_2mim]CH_3O(H)PO_2$/water mixture is less than 0.1 wt%. Consequently, the IL/water mixtures listed in Table 2 were confirmed not to dissolve cellulose.

Extraction was then attempted using these solvents. A lignin extraction degree ($\%E_{lignin}$) of pure $[C_2mim]CF_3SO_3$ and $[C_2mim]BF_4$ was less than 2%. On the other hand, $[C_2mim]CH_3O(H)PO_2$ extracted considerable amount of lignin with and without the presence of water, and $[C_2mim]CF_3SO_3$ extracted lignin only when water was added. Induction or improvement of lignin solubility by the addition of water was also observed when lignin was extracted from native wood. As a result, $[C_2mim]CH_3O(H)PO_2$/water and $[C_2mim]CF_3SO_3$/ water mixtures, which are poor solvents for cellulose, extracted 7.2 % and 4.9 % of lignin from cedar powder, respectively. It was confirmed that water addition is effective for not only dissolution of AL but also lignin extraction from biomass. Consequently, the IL/water mixtures were concluded to be potential media to extract lignin from native wood without contamination of cellulose. Of course, it is not easy to raise the extraction yield of lignin from natural wood powder treated under mild condition. Addition of water to some ILs should be one of powerful methods to improve extraction of lignin from biomass.

Table 2 Lignin extraction degree from cedar powder by IL/water mixtures.

Ionic liquid	$[H_2O]$ / wt%	Lignin extraction degree (%)
$[C_2mim]CH_3O(H)PO_2$	0	7.84 ± 0.58
$[C_2mim]CH_3O(H)PO_2$	10	7.23 ± 0.15
$[C_2mim]CF_3SO_3$	0	2.05 ± 0.02
$[C_2mim]CF_3SO_3$	10	4.86 ± 0.29
$[C_2mim]BF_4$	0	0.68 ± 0.11

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Conclusions

We have newly found that addition of water to ILs induces or improve AL solubility, in spite that water is poor solvent of biomass. Throughout the dissolution test of AL in the pure ILs, the effect of anion on the solubility was found to be stronger than that of cation of ILs. The AL solubility in pure ILs was found to be the function of both proton donating and accepting ability of ILs. Because anion structures affect strongly on the solubility, the improvement of the solubility triggered by water addition was observed when the ILs have moderate β value (> 0.4). Addition of water decreased β value but increased α value, and the improvement of α value supported the dissolution of AL in the ILs having moderate β value. In other words, when ILs were mixed with water, the polarity of ILs/water mixture changed from AL insoluble region to soluble one. Excess amount of water further changed the polarity of ILs outside the soluble region.

Acknowledgements

The present work was supported by Cross-ministerial Strategic Innovation Promotion Program (SIP), Cabinet office government of Japan (project no. 14533483). Authors acknowledge Dr. T. Yamada of Forestry and Forest Products Research Institute (FFPRI), Japan for preparing alkaline lignin and cedar powder.

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Kamlet-Taft parameters of ionic liquid/water mixtures are the function of added water concentration. As water concentration increases, proton accepting ability of polar ionic liquids decreases but proton donating ability increases, respectively. This is the reason why some ionic liquids, that have no lignin dissolution ability, get lignin dissolution ability by the addition of suitable amount of water.

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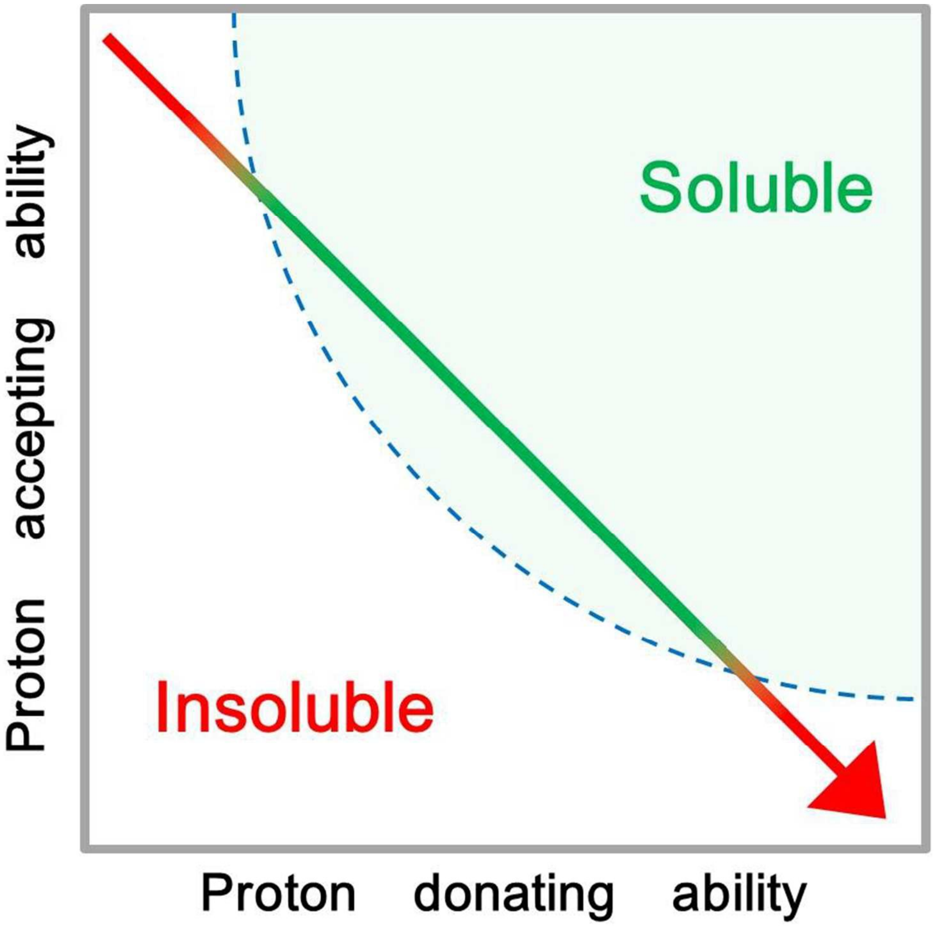

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