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Maintenance-Free Cellulose Solvents Based on Onium Hydroxides

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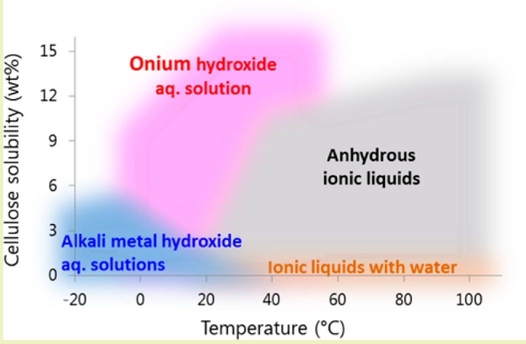
Ⓢ *Supporting Information*

ABSTRACT: Here, we report maintenance-free cellulose solvents that dissolve much cellulose within a few minutes under mild conditions even in the presence of water. We have examined a series of aqueous solutions of tetraalky-phosphonium and tetraalkyl-ammonium hydroxides to clarify the effect of cation species on cellulose dissolving. Aqueous solutions of the many hydroxides examined here were found to dissolve cellulose at room temperature, and electrostatic interaction and/or steric hindrance of component ions are suggested to affect the cellulose-dissolving ability. In spite of increasing water content after dissolution of wet cellulose, the water content automatically reduced to less than 60% just by keeping the filtrated solution in the air. The solvation state of cellulose in aqueous onium hydroxide solutions is discussed with ^{13}C NMR chemical shift of cellobiose signals in these solutions. They dissolve cellulose only when the ^{13}C NMR signal of the carbon atom at the 12 position of cellobiose is 64.8 ppm or larger in the hydroxide aqueous solution.



KEYWORDS: *Hydroxide solution, Cellulose, Maintenance-free, Dissolution, NMR spectroscopy*

■ INTRODUCTION

Cellulose is the most abundant polysaccharide in nature, but it is not extensively used as a food source. Accordingly, cellulose should be a starting material for alternatives to fossil-based chemicals or fuels. However, the bottleneck is the difficulty to dissolve cellulosic biomass in common solvents under mild conditions. Crystalline cellulose contains many intra- and intermolecular hydrogen bonds that assures its excellent chemical and physical stability,[1,2] and this stability also prevents the widespread use of cellulose, except for its use as fibrous materials. There have been many efforts to develop potential solvents for cellulose such as *N*-methylmorpholine-*N*-oxide monohydrate (NMMO·H_2O), sodium hydroxide (NaOH)/water with or without additives, lithium chloride/*N*,*N*-dimethylacetamide, and others.[3−13] These solvents have excellent ability to dissolve cellulose, but they still have several drawbacks such as toxicity, thermal instability, and high cost, and they require a heating or cooling process to dissolve cellulose, which prevents their practical relevance with the possible exception of NMMO·H_2O, which is used industrially to make cellulose fibers.[14] However, no solvent has so far been used to obtain energy from cellulose and/or cellulosic biomass.

Ionic liquids (ILs), organic salts having very low melting point, have been recognized as effective solvents for cellulose only when they have enough polarity. Because of these unique characteristics, ILs have been exploited as potential solvents by many industries.[15−17] In 2002, Swatloski et al. reported that a kind of ILs, 1-butyl-3-methylimidazolium chloride, dissolved cellulose at 100 °C, and its solubility was specifically attributed to the chloride anion.[18,19] After this report, many researchers have studied cellulose-dissolving ILs.[20−25] The role of the anion structure of ILs has also been investigated in our laboratory, and we have demonstrated that small and charge-localized anions have a strong proton accepting ability, resulting in high dissolution power for cellulose.[26] In this respect, we have identified both carboxylate (such as formate) and phosphonate (such as methylphosphonate) derivatives as the anions of choice for the development of cellulose-dissolving ILs at ambient temperature.[27−29]

However, although some polar ILs are recognized to be good solvents for cellulose, they still have a serious problem, which is the effect of water. Addition of water significantly decreases the cellulose solubility in the ILs.[30−32] Since ILs easily absorb water from the atmosphere,[33] drying processes of ILs under vacuum are needed before use. It is therefore of great importance to develop novel ILs capable to dissolve cellulose under mild condition even in the presence of water. Recently, we found that both tetra-*n*-butylphosphonium hydroxide ($[P_{4,4,4,4}]$OH) and tetra-*n*-butylammonium hydroxide ($[N_{4,4,4,4}]$OH) aqueous solutions dissolved cellulose without heating.[34] Trimethylben-

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zyl-ammonium hydroxide was also reported to dissolve cellulose in the presence of water, but it was not applied as a cellulose solvent due to poor recyclability.[35] On the other hand, we have already confirmed that $[P_{4,4,4,4}]OH$ and $[N_{4,4,4,4}]OH$ are sufficiently stable throughout the cellulose-dissolving process and are usable repeatedly.[34] Also, it was confirmed that the dissolved cellulose was not degraded during the dissolution process, but their crystallinity decreased significantly. Quite recently, some researchers reported on tetraalkyl-onium hydroxide aq. solutions with/without additives for cellulose and lignocellulose dissolution.[36−39] However, the applicability of these solutions has not been discussed well. In this study, the temperature dependence of cellulose solubility was evaluated. The effect of cation species was evaluated with systematic investigation of several kinds of tetraalkyl-onium hydroxide aq. solutions. In addition, an easy quantitative evaluation method of solvation state of cellulose is also proposed.

EXPERIMENTAL SECTION

Materials. Tetra-*n*-butylphosphonium hydroxide ($[P_{4,4,4,4}]OH$) 40% aq. solution was provided by Hokko Chemical Industry Co., Ltd. Tetraethylphosphonium hydroxide ($[P_{2,2,2,2}]OH$) aq. solution (8 wt %), tri-*n*-butylmethylphosphonium iodide ($[P_{4,4,4,1}]I$), tri*n*-hexylphosphine, tetramethylammonium hydroxide ($[N_{1,1,1,1}]OH$) aq. solution (15%), tetraethylammonium hydroxide ($[N_{2,2,2,2}]OH$) aq. solution (10%), tetra-*n*-butylammonium hydroxide ($[N_{4,4,4,4}]OH$) aq. solution (25%), and tetra-*n*-hexyl bromide were purchased from Wako Pure Chemical Industries, Ltd. 1-Bromohexane, tri-*n*-hexylphosphine, and tetra-*n*-hexylammonium bromide ($[N_{6,6,6,6}]Br$) and D-(+)-cellobiose were purchased from Tokyo Chemical Industry Co., Ltd. These phosphine, amine, and alkyl halides were distilled before use. Halide salts were recrystallized before use. Cellulose powder (Avicel PH-101) and an anion exchange resin (Amberlite IRN78 hydroxide form) were purchased from Sigma-Aldrich Co. LLC., and these were used as received. Ethyl acetate, *n*-hexane, and methanol were purchased from Kanto Chemical Co., Inc. and were used as received. Deuterium oxide (D_2O) was purchased from Acros Organics and was used as received. 3-Trimethylsilyl-propanesulfonic acid sodium salt (DSS) was purchased from Merck KGaA and was used as received.

Synthesis of Tetraalkyl-Onium Hydroxide Aqueous Solutions. $[P_{2,2,2,2}]OH$, $[P_{4,4,4,4}]OH$, $[N_{1,1,1,1}]OH$, $[N_{2,2,2,2}]OH$, and $[N_{4,4,4,4}]OH$ aq. solutions were used as received, and the water content was controlled by evaporation or addition of water. The water content was confirmed with Karl Fischer coulometric titration system (Kyoto Electronics; MKC-510N). Both $[P_{4,4,4,1}]OH$ and $[N_{6,6,6,6}]OH$ aq. solutions were prepared by anion exchange of corresponding halide salts, namely, $[P_{4,4,4,1}]I$ and $[N_{6,6,6,6}]Br$ were passed through anion exchange resin in water/methanol mixture. Ten grams of halide salt was dissolved in 500 mL of a water/methanol 1:9 (v/v) mixture. This was passed through a column that contains 200 g of anion exchange resin (drop speed: 0.1 mL/min). Anion exchange was confirmed with the nitric acid/silver nitrate solution test. After anion exchange, methanol was removed by evaporation, and the water content of these aq. solutions was controlled by evaporation or addition of water. $[P_{6,6,6,6}]OH$ aq. solution was synthesized by the following procedure. Both 1-bromohexane and tri-*n*-hexyl phosphine were mixed (bromohexane/phosphine = 1.2 by mol), and the mixture was stirred at 80 °C for 24 h. After that, an excess of hexane was added to the solution and stirred vigorously for 1 h followed by the process to keep it standing for 3 h. Then, the upper phase (hexane rich phase) was removed. The hexane washing was repeated three times. The purified solution (IL-rich phase) was dried under vacuum, and (tetra-*n*-hexylphosphonium bromide, $[P_{6,6,6,6}]Br$) was obtained as white solid. The bromide anions were then converted into hydroxides with anion exchange resin in water/methanol mixture to prepare the $[P_{6,6,6,6}]OH$ solution as well as $[P_{4,4,4,1}]OH$ and $[N_{6,6,6,6}]OH$ aq. solutions. After the anion exchange, methanol was removed by evaporation, and the water content was controlled by evaporation or addition of water. The cation species of those synthesized hydroxide aq. solutions were confirmed with NMR measurements. Nonexistence of any halogen ions were confirmed with the silver nitrate solution.

^{1}H NMR Data of Tetraalkyl-Onium Hydroxide Aqueous Solutions. $[P_{4,4,4,1}]OH$ aqueous solution (water/hydroxide = 20 (molar ratio)).

^{1}H NMR (400 MHz; D_2O; DSS) $\delta H = 0.860$ (9H, t, $J = 6.87$ Hz, CH_2CH_3), 1.427 (12H, m, $CH_2CH_2CH_2CH_3$), 1.727 (3H, d, $J = 13.28$ Hz, PCH_3), 2.085 (6H, m, PCH_2).

$[P_{6,6,6,6}]OH$ aqueous solution (water/hydroxide = 20 (molar ratio)).

^{1}H NMR (400 MHz; D_2O; DSS) $\delta H = 0.884$ (12H, t, $J = 6.41$ Hz, CH_2CH_3), 1.304 (16H, m, $CH_2CH_2CH_2CH_3$), 1.481 (16H, m, $PCH_2CH_2CH_2CH_2$), 2.186 (8H, m, PCH_2).

$[N_{6,6,6,6}]OH$ aqueous solution (water/hydroxide = 20 (molar ratio)).

^{1}H NMR (400 MHz; D_2O; DSS) $\delta H = 0.871$ (12H, t, $J = 6.41$ Hz, CH_3), 1.312 (16H, m, $CH_2CH_2CH_2CH_3$), 1.598 (16H, m, $NCH_2CH_2CH_2CH_2$), 3.157 (8H, m, NCH_2).

Cellulose Dissolution Test. Cellulose powder was dried under vacuum for 6 h at room temperature before use. Hydroxide aq. solution (300 mg) was put in a 3 mL vial. Cellulose powder (1.5 mg) was added to the hydroxide aq. solution (final concentration of cellulose was 0.5 wt %), and the mixture was gently stirred for 1 h at room temperature. After that, the cellulose dissolution was comfirmed with an optical microscope (Olympus BX51).

NMR Measurement of Cellobiose. Both ^{1}H and ^{13}C NMR measurements of D-(+)-cellobiose were carried out on a JEOL ECX-400 (^{1}H base frequency 400 MHz), and the analysis of NMR spectra was carried out with software JEOL Delta (version 5.0.1). D-(+)-Cellobiose (33 mg) was added to tetraalkyl-onium hydroxide aq. solutions (300 mg), and then, the samples were stirred to become clear (final concentration of cellobiose was 10 wt %). The resulting solutions were transferred into NMR tubes, and coaxial inserts containing DSS/D_2O mixtures (2 wt %) were subsequently fitted as an external standards (0 ppm). The sample tubes were capped with glass lids. All NMR measurements were conducted at 25 °C.

RESULTS AND DISCUSSION

First, temperature dependence on the cellulose solubility of the $[P_{4,4,4,4}]OH$ aq. solution was examined. Cellulose was dissolved in 50% $[P_{4,4,4,4}]OH$ aq. solution over 10 wt % in a wide range of temperature, and the cellulose dissolution was comfirmed with an optical microscope (Figure S1, Supporting Information (SI)). Molecular weight distribution of cellulose did not change during dissolution even at 50 °C (Figure S2, SI). To highlight this very high cellulose-solubilization power, we have compared the solubility of cellulose in a series of media as the function of temperature (Figure 1). Polar ILs dissolve more cellulose at high temperature, but they scarcely dissolve cellulose without heating. In addition, it is commonly known that the cellulose-dissolving ability of these polar ILs decreased in the presence of water. Alkali metal hydroxide aq. solutions with/without urea are known as cellulose solvents, which dissolve cellulose in the presence of water. They can dissolve a certain amount of cellulose under cooling conditions, but the solubility of cellulose around room temperature is very low. On the other hand, the $[P_{4,4,4,4}]OH$ aq. solution dissolves more cellulose at the analyzed temperature range (0−50 °C) in the presence of water.

Next, automatic dehydration of the $[P_{4,4,4,4}]OH$ aq. solution was evaluated at room temperature. Commercially available $[P_{4,4,4,4}]OH$ aq. solution contains about 60 wt % water. The solution was left at rest, and its water content was periodically evaluated. The diluted aq. solution of $[P_{4,4,4,4}]OH$ was automatically condensed to optimum concentration to dissolve

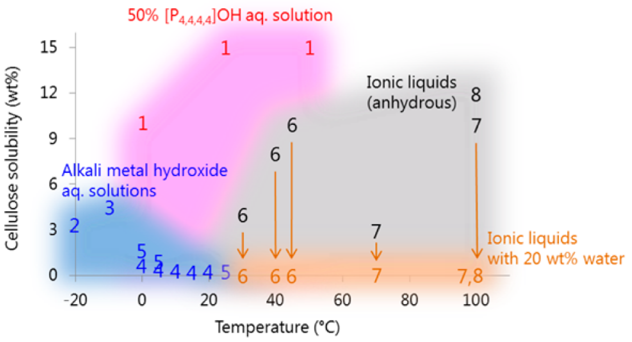

Figure 1. Cellulose solubility as the function of temperature in 50% $[P_{4,4,4,4}]OH$ aq. solution (**1**), NaOH aq. solution (**2**),[5] NaOH/urea aq. solution (**3**),[7] LiOH aq. solution (**4**),[10] LiOH/urea aq. solution (**5**),[10] 1-ethyl-3-methylimidazolium methylphosphonate (**6**),[28] 1-butyl-3-methylimidazolium chloride (**7**),[18] and 1-butyl-3-methylimidazolium acetate (**8**).[23] These ILs dissolve much cellulose under anhydrous condition (black), but they cannot dissolve cellulose in the presence of more than 20 wt % water (brown).[30−32]

cellulose (Figure 2), and the solvent is sufficiently stable at ambient temperature.[37] Regarding this issue, Hyvärkö et al. also reported that 50% $[P_{4,4,4,4}]OH$ aq. solution was stable after 24 h heating at 90 °C.[39] After dissolution of wet cellulose or extraction of cellulose from biomass, water content of the hydroxide solution should increase. However, as shown in Figure 2, excess water was easily autoevaporated by just putting the diluted $[P_{4,4,4,4}]OH$ aq. solution under air.

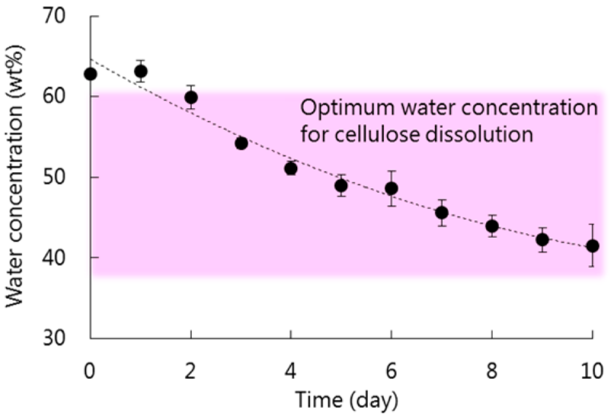

Figure 2. Automatic dehydration of $[P_{4,4,4,4}]OH$ aq. solution at 25 °C by keeping it under air (humidity: 40%). Twenty-five milliliter aq. solution was put into a 50 mL vial and was left at rest. Water concentration was determined with Karl Fischer coulometric titration. The solution was homogenized before evaluation.

Once-dissolved cellulose was precipitated by adding water and was easily collected.[37] There is no onium salt residue in the recovered cellulose after washing (Figure S3, SI). The recovered cellulose was not degraded during dissolution with these hydroxide aq. solutions.[34] In addition, we confirmed the reusability of the hydroxide aq. solution (SI).

There is a possibility that other alkyl-onium hydroxide aq. solutions also have a power to dissolve cellulose. A series of tetraalkyl-phosphonium or -ammonium hydroxides having different alkyl chains were prepared, and their cellulose-dissolving ability was tested as a function of water content at 25 °C (Table 1). Here, we use a new unit "a number of water molecules per hydroxide ion (N_w)" instead of wt % to discuss the effect of molar ratio of water to ion pair (wt % values are summarized in Table S1, SI). Most of the tetraalkyl-onium hydroxides examined here dissolved cellulose without heating in the presence of water. When these solutions were mixed with excess water ($N_w > 25$), they could not dissolve cellulose. However, as described above, the alkyl-onium hydroxide aq. solution was automatically condensed to optimum concentration to dissolve cellulose just by exposing it to the air. These results, as summarized in Table 1, suggest that many kinds of cations are usable to construct cellulose-dissolving onium hydroxide aq. solutions. There should be a variety of cations as candidates of component ions for this purpose. On the other hand, the optimum concentration of the solution slightly depended on the alkyl chain length of the cation. This cation structure dependence might be due to strong cation−anion interactions, hydrophobicity, and steric hindrance. Details of the correlation between cation structure and cellulose-dissolving ability will be discussed later.

Table 1. Effect of Cation Species on Cellulose Dissolution (0.5 wt %) at 25 °C

		N_w				
entry	cation	10	15	20	25	30
1	$[P_{2,2,2,2}]$	S	S	–	–	–
2	$[P_{4,4,4,1}]$	S	S	–	–	–
3	$[P_{4,4,4,4}]$	S	S	S	–	–
4	$[P_{6,6,6,6}]$	S	S	–	–	–
5	$[N_{1,1,1,1}]$	–	–	–	–	–
6	$[N_{2,2,2,2}]$	–	–	–	–	–
7	$[N_{4,4,4,4}]$	S	S	S	–	–
8	$[N_{6,6,6,6}]$	S	S	–	–	–

N_w: number of water molecules per hydroxide ion. S, soluble; –, insoluble.

Among them, tetra-*n*-butylphosphonium and -ammonium hydroxide aq. solutions (entries#3 and #7, Table 1) were found to dissolve cellulose in a wide range of water concentrations. Then the cellulose-dissolving ability of these tetraalkyl-onium hydroxide aq. solutions was evaluated in detail. Cellulose powders were added to $[P_{4,4,4,4}]OH$ and $[N_{4,4,4,4}]OH$ aq. solutions, and the required time for complete dissolution was measured under gentle stirring (Table 2). Both hydroxide aq. solutions could dissolve a large amount of cellulose within a few minutes. More amount of cellulose should be soluble in these hydroxide solutions, but an increase of viscosity during cellulose

Table 2. Correlation between Water Content of Tetra-*n*-butylphosphonium and -ammonium Hydroxide aq. Solutions and Their Cellulose-Dissolving Ability

entry	cation	N_w	cellulose (wt %)	time (min)
3	$[P_{4,4,4,4}]$	10	10	2
			15	3
		15	10	3
			15	5
		20	10	10
7	$[N_{4,4,4,4}]$	10	10	3
			15	5
		15	10	5
			15	10
		20	10	20

N_w: number of water molecules per hydroxide ion.

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dissolution suppressed the stirring. Experiments with more amount of cellulose dissolution were not carried out in this study. $[P_{4,4,4,4}]OH$ aq. solutions dissolved cellulose relatively faster than $[N_{4,4,4,4}]OH$ aq. solutions, but the difference in solubility was small. It might be due to the difference in cellulose solvation ability of these solutions. Details of the correlation between water concentration and cellulose solvation ability will be discussed in later.

To understand the cellulose-dissolving ability, there is an easy and simple way to directly examine the solubilization of cellulose by adding different amounts of cellulose powder into the sample solutions. This empirical method, however, gives us only the Yes−No results, and the structural strategy for further design of cellulose solvent cannot be provided. To properly evaluate these solutions, it is necessary to define an easy-to-handle protocol to evaluate the solvation state. Kamlet−Taft parameters[40,41] have frequently been used to estimate cellulose solubilization ability of the ILs.[42,43] These parameters, however, cannot easily be calculated for the hydroxide aq. solutions used in this study since the UV−vis spectra of Kamlet dyes showed unusual peak splitting (Figure S4, SI). Accordingly, we have to find other parameters for this study.

Isogai et al. reported that the ^{13}C NMR chemical shift of sugar dissolved in alkaline solutions changed depending on the degree of proton dissociation of hydroxyl groups of the sugars.[44] This suggests that the solvation ability, including hydrogen bonding ability, of organic hydroxide aq. solutions can also be quantitatively evaluated with the NMR chemical shift. Cellobiose (Figure 3) was added to a series of hydroxide aq. solutions, and NMR chemical shifts were recorded. The NMR signals were similar to those observed in NaOH aq. solutions (Figures S5 and S6, SI). This also supports that the hydroxide ion plays an important role to cut down the interaction between sugar chains. Cellulose chains are known to form intermolecular hydrogen bonding of protons at the C6 position, while the corresponding carbons of cellobiose are both C6 and C12. Since the C6 one was affected by the aldehyde tautomerization of the C1 carbon atom, the chemical shift of C12 (δC12) was selected to evaluate the interaction between cellobiose and hydroxide anions.

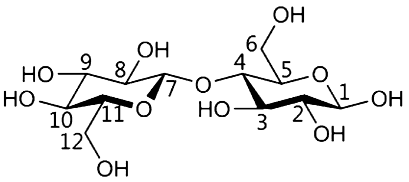

Figure 3. Structure and carbon numbers of D-(+)-cellobiose.

As shown in Table 1, hydroxide aq. solutions with N_w values larger than 25 did not dissolve cellulose. By comparing the cellulose dissolution and δC12 as the function of water content, we found a threshold of the δC12 to evaluate cellulose dissolution power. By decreasing water content, the δC12 became larger, and the solution turned to dissolve cellulose. We then found that the δC12 value of 64.8 is the threshold value for the cellulose dissolution (Figure 4). ^{13}C NMR measurement is a very useful tool to estimate the solvation state of cellulose in hydroxide aq. solutions, which in turn allows for estimating their cellulose-dissolving ability. To the best of our knowledge, this evaluation method, based on the correlation between the NMR chemical shift and cellulose dissolution, has not been demonstrated yet (SI).

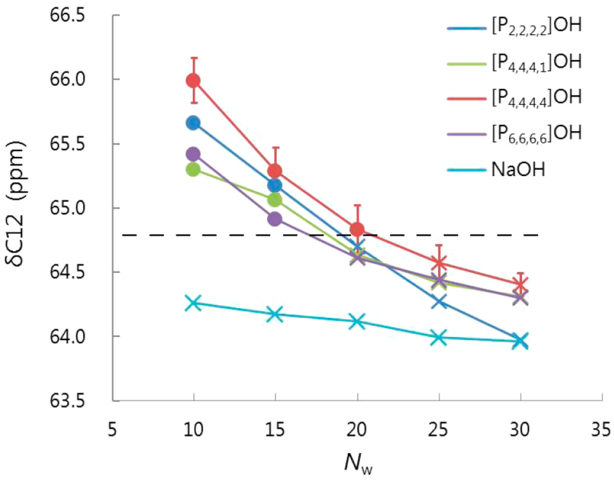

Figure 4. ^{13}C NMR chemical shift of C12 of cellobiose (10 wt %) in $[P_{2,2,2,2}]OH$ (blue), $[P_{4,4,4,1}]OH$ (green), $[P_{4,4,4,4}]OH$ (red), $[P_{6,6,6,6}]OH$ (purple), and NaOH (light blue) aq. solutions as the function of water content. Plots in the figure show the cellulose dissolution ability, i.e., ○ and x mean soluble and insoluble, respectively. To avoid overlapping, error bars were shown only for the case of $[P_{4,4,4,4}]OH$, but the experimental errors were comparable to all the tested solutions. N_w means number of water molecules per hydroxide ion.

We also discuss here in detail the correlation between the cation structure and the value of δC12. A $[P_{4,4,4,4}]OH$ aq. solution showed the largest shift of the signal, suggesting that this solution has excellent potential to dissolve cellulose. This solution may interact with cellobiose stronger than the $[P_{2,2,2,2}]OH$ or $[P_{4,4,4,1}]OH$ aq. solution. We believe that this difference may be due to electrostatic interactions between the onium cation and hydroxide anion. On the other hand, the C12 signal of the cellobiose in $[P_{6,6,6,6}]OH$ aq. solution showed a smaller shift than that in $[P_{4,4,4,4}]OH$ due to the steric hindrance of the larger cation. Too long alkyl side chains negatively affected the cellulose dissolution due to this steric hindrance that was also confirmed by Huo et al. by MD studies.[45] Also, the ion density in the $[P_{6,6,6,6}]OH$ aq. solution might affect the sugar-ion interaction (Table S2, SI, which is summarizing molarity). Swatloski et al. also reported that long alkyl chains are not good for cellulose dissolution in the case of imidazolium salts, and they suggested that this may be due to the reduced anion concentration or the hydrophobic interactions.[18] Tetraalkyl-ammonium hydroxide aq. solutions showed similar tendency to the tetraalkyl-phosphonium hydroxide ones (Figure S7, SI). However, there is not a direct correlation between δC12 and solubility of cellulose. At present, the threshold is quite effective for the evaluation of the aq. hydroxide solution to dissolve cellulose. However, there are additional factors such as viscosity to influence the cellulose solubility. Other parameters are required to clarify the whole interactions between cellulose and solvents. The effectiveness and limit of ^{13}C NMR are summarized in the SI. However, we still assume that the δC12 value of cellobiose in hydroxide aq. solutions should be quite effective to estimate the solvation state of cellulose in the hydroxide aq. solutions, similar to Kamlet−Taft parameters for ILs.

■ CONCLUSIONS

We have confirmed that the $[P_{4,4,4,4}]OH$ aq. solution dissolves cellulose at room temperature, and this is also effective to dissolve wet cellulose. After dissolution of wet cellulose, water content increased, but it was found that the water concentration of the diluted solution decreased due to vaporization just by putting the solutions under air to reach adequate value to recover the cellulose dissolution ability, i.e., we can call this "maintenance-free solvent for cellulose". In addition, we have developed the design basis of tetraalkylonium hydroxide aq. solutions with evaluation of the effect of cation species. We demonstrated that ^{13}C NMR measurement of cellobiose in these solutions correlated with the solvation state of cellulose in these hydroxide aq. solutions. The results mentioned here accelerate further development of the maintenance-free cellulose solvents, alkyl-onium hydroxide aq. solutions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Concentration of hydroxide solutions described in wt %, UV—vis spectra of Kamlet—Taft dyes, ^{1}H and ^{13}C NMR data of cellobiose, NMR spectroscopic studies of cellobiose in alkaline metal hydroxide solutions, molarity of hydroxide solutions, solubility of cellulose, correlation between δC12 and cellulose-dissolving ability of alkylammonium hydroxide aq. solutions, and the effectiveness and limit of ^{13}C NMR measurement. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00303.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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