PCCP

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

Journal Name
RSCPublishing

ARTICLE

Effects of polarity, hydrophobicity, and density of ionic liquids on cellulose solubility

Cite this: DOI: 10.1039/x0xx00000x

Mitsuru Abe,[§a,b,∥] Kosuke Kuroda,[§a,b,⊥] Daiki Sato,[a,b] Haruhito Kunimura,[a,b] and Hiroyuki Ohno*[a,b]

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

We have synthesised novel ionic liquids (ILs) to show both cellulose dissolution ability and LCST-type phase transition after mixing with water. To realise both polar and hydrophobic properties, tetraalkylphosphonium cations and a series of carboxylate anions were employed to assume hydrophobic and highly polar properties, respectively. Effects of their alkyl chain length on the water compatibility and cellulose solubility of the corresponding ILs were systematically examined. We succeeded in synthesise novel ILs which dissolve cellulose and separable with water at moderate temperature. Through the present study, we have clarified that not only polarity but also density of ILs are important factors to design the ILs for cellulose dissolution.

Introduction

Cellulose is the most abundant polysaccharide in nature, and this inedible biomass should be used as a starting material for sustainable energy. However, the bottleneck for the energy conversion is the difficulty to dissolve cellulosic biomass in common solvents under mild condition. Since there are many intra- and inter-molecular hydrogen bonds in crystalline cellulose, those assure excellent chemical and physical stability of plants together with lignin network.[1, 2] At the same time, this robust structural stability limits the widespread use of cellulose, except for fibrous materials. There have been many efforts to develop potential solvents for cellulose such as *N*-methylmorpholine-*N*-oxide monohydrate (NMMO·H_2O),[3] sodium hydroxide (NaOH)/water mixture with or without additives,[4-6] and lithium chloride/*N*,*N*-dimethylacetamide mixture.[7-9] These solvents have excellent ability to dissolve cellulose, but they still have several drawbacks such as toxicity, thermal instability, high cost, and applicable temperature range, that still prevent them from their practical relevance with the possible exception of NMMO·H_2O which is used in industries to make cellulose fibers.[10] However, no potential solvents have so far been proposed to get energy from cellulose and/or cellulosic biomass.

Ionic liquids (ILs), organic salts having melting point below 100 °C, have been recognised as effective solvents for cellulose only when they have sufficient polarity. In 2002, Swatloski et al. reported that 1-butyl-3-methyl-imidazolium chloride dissolved cellulose at 100 °C, and its solubility was specifically attributed to polar chloride anion.[11, 12] After that, many researchers have examined the cellulose dissolution in many ILs.[13-18] Role of anions has also been studied to find an important factor, i.e., small and charge-localised anions have a strong proton accepting ability, resulting in high cellulose dissolution power.[19] However, such small and charge localised anions are not suitable for IL preparation due to strong electrostatic interaction. In this respect, we have identified that carboxylates, phosphonates, and their derivatives are potential anions for the development of cellulose-dissolving ILs at ambient temperature.[20-22]

For the successive treatment of cellulose such as extraction (dissolution) and hydrolysis, it is desirable to dissolve cellulose in ILs containing small but enough amount of water for hydrolysis. However, solubility of cellulose in polar ILs decreased by increasing water content.[23-25] One candidate to solve this point is the design of hydrophobic ILs containing limited amount of water. However, all of existing cellulose solvents are polar and accordingly hydrophilic. They are freely miscible with water. Therefore, until now, such hydrophobic cellulose solvents are thought to be unfeasible due to their limited polarity.

ILs are known as designer's solvents, because their physico-chemical properties are tuneable with ion structure as well as selection of ion pair. Recently, we have succeeded in developing novel ILs showing high polarity and moderate hydrophobicity to show phase separation with water.[26] Kamlet-Taft parameters are known as quite useful parameters to discuss polarity of ILs.[27, 31] Especially, β value indicates proton accepting ability, in other words, hydrogen bond accepting ability, of the ILs.[28] The β value larger than 0.8 is semi-empirically known to be required for ILs to dissolve cellulose.[19] The question arises here that is it possible to design ILs showing both phase separation with water and cellulose dissolving ability or not. The present paper summarises the discussion on the effects of physico-chemical properties of a series of ILs such as polarity, hydrophobicity, and ion density on the cellulose dissolution to find ILs suitable for this objective.

Experimental

Materials

Tetra-*n*-butylphosphonium hydroxide ($[P_{4,4,4,4}]OH$) 40% aq. solution, tri-*n*-pentylphosphine, and tri-*n*-hexylphosphine were provided by Hokko Chemical Industry Co., Ltd. Formic acid, *n*-butyric acid, hexanoic acid, *n*-octanoic acid, capric acid, lauric acid, myristic acid, palmitic acid, behenic acid, 1-bromopentane, and 1-bromohexane were purchased from Tokyo Chemical Industry Co., Ltd. and these were used as received. Cellulose powder (Avicel® PH-101) and an anion exchange resin (Amberlite® IRN78 hydroxide form) were purchased from Sigma-Aldrich Co. LLC., and were used as received.

Preparation of ILs

An equal-weight mixture of pentylbromide and hexane was added into tri-*n*-pentylphosphine at room temperature (alkylbromide/phosphine was 1.1 by mol), and the mixture was stirred at 100 °C for 72 h. After that, an excess 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 hexane rich phase was removed. The hexane washing was repeated three times. The purified IL rich phase was collected and dried under vacuum, and tetra-*n*-pentylphosphonium bromide was obtained as white solid. The bromide anions were then converted into hydroxides with anion exchange resin in water/methanol mixture to prepare $[P_{5,5,5,5}]OH$ solution. Halide salt (10.0 g) was dissolved in 300 ml water/methanol 1:9 (v/v) mixture. Anion exchange resin (200 g) was added into the $[P_{5,5,5,5}]Br$ solution, and the mixture was moderately stirred for 3 days. Anion exchange was confirmed with nitric acid/silver nitrate solution test. After anion exchange, methanol was removed by moderate evaporation, and $[P_{5,5,5,5}]OH$ aq. solution was collected. Tetra-*n*-hexylphosphonium hydroxide ($[P_{6,6,6,6}]OH$) aq. solution was also prepared by the same process with hexylbromide and tri-*n*-hexylphosphine.

Equimolar amount of carboxylic acids was added to tetraalkylphosphonium hydroxide aqueous solutions to prepare tetraalkylphosphonium carboxylates. After stirring for 12 h, water was preliminarily removed by evaporation and the resulting liquid was then dried *in vacuo* at 40 °C for 24 hours. The amount of water contamination of ILs was confirmed to be 0.20 wt% or less by Karl Fischer coulometric titration (Kyoto Electronics MKC-510N). Electrospray ionization-time-of-flight-mass (ESI-TOF-MAS) measurements were conducted with JEOL JMS-T100LC using methanol as solvent, and it clarified that these ILs were correctly synthesised. The structure of ILs was confirmed with both ^1H and ^{13}C NMR measurements using a JEOL ECX-400.

^1H NMR spectra of ILs used in this study

$[P_{4,4,4,4}][HCO_2]$: Tetrabutylphosphonium formate
^1H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.979 (t, J = 14.20 Hz, 12H, $P(CH_2)_3CH_3$), 1.503-1.550 (m, 16H, $PCH_2CH_2CH_2$), 2.323-2.396 (m, 8H, PCH_2), 8.868 (s, 1H, CH).
^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 13.46, 18.64 (d, J = 47.92), 23.74 (d, J = 4.79), 23.98 (d, J = 15.34), 167.93.

$[P_{4,4,4,4}][C_3CO_2]$: Tetrabutylphosphonium butyrate
^1H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.921 (t, J = 14.65 Hz, 3H, $CO_2(CH_2)_2CH_3$), 0.973 (t, J = 12.36, 12H, $P(CH_2)_3CH_3$), 1.512-1.528 (m, 16H, $PCH_2CH_2CH_2$), 1.588-1.684 (m, 2H $CO_2CH_2CH_2$), 2.146 (t, J = 16.49, 2H, CO_2CH_2), 2.370-2.439 (m, 8H, PCH_2).
^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 13.52, 14.60, 18.64 (d, J = 46.96), 20.49, 23.85 (d, J = 4.79), 24.03 (d, J = 15.34), 41.46, 179.26.

$[P_{4,4,4,4}][C_5CO_2]$: Tetrabutylphosphonium hexanoate
^1H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.869 (t, J = 13.74 Hz, 3H, $CO_2(CH_2)_4CH_3$), 0.973 (t, J = 13.74, 12H, $P(CH_2)_3CH_3$), 1.281-1.317 (m, 4H, $CO_2(CH_2)_2CH_2CH_2$), 1.497-1.553 (m, 16H, $PCH_2CH_2CH_2$), 1.590-1.666 (m, 2H, $CO_2CH_2CH_2$), 2.172 (t, J = 15.57, 2H, CO_2CH_2), 2.398-2.471 (m, 8H, PCH_2).
^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 13.53, 14.19, 18.71 (d, J = 46.96), 22.75, 23.87 (d, J = 4.79), 24.03 (d, J = 15.34), 26.97, 32.38, 39.22, 179.28.

$[P_{4,4,4,4}][C_7CO_2]$: Tetrabutylphosphonium octanoate
^1H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.858 (t, J = 13.74 Hz, 3H, $CO_2(CH_2)_6CH_3$), 0.974 (t, J = 13.28, 12H, $P(CH_2)_3CH_3$), 1.258-1.290 (m, 8H, $CO_2(CH_2)_2CH_2CH_2CH_2CH_2$), 1.513-1.711 (m, 18H, $PCH_2CH_2CH_2$, $CO_2CH_2CH_2$), 2.147 (t, J = 16.03, 2H, CO_2CH_2), 2.346-2.419(m, 8H, PCH_2).
^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 13.52, 14.16, 18.65 (d, J = 47.92), 27.73, 23.85 (d, J = 4.79), 24.02 (d, J = 14.38), 27.36, 29.44, 30.14, 31.97, 39.49, 179.65.

$[P_{4,4,4,4}][C_9CO_2]$: Tetrabutylphosphonium caproate
^1H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.865 (t, J = 13.74 Hz, 3H, $CO_2(CH_2)_8CH_3$), 0.966 (t, J = 12.36, 12H, $P(PCH_2CH_2CH_2)$, 1.244-1.282 (m, 12H, $CO_2(CH_2)_2(CH_2)_6$), 1.510-1.529 (m, 16H, $PCH_2CH_2CH_2$), 1.588-1711 (m, 2H, $CO_2CH_2CH_2$), 2.158 (t, J = 16.03, 2H, CO_2CH_2), 2.431-2.501 (m, 8H, PCH_2).
^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 13.56, 14.16, 18.68 (d, J = 46.96), 22.71, 23.94 (d, J = 4.79), 24.08 (d, J = 15.34), 27.57, 29.43, 29.77 (d, J = 9.58), 30.26, 31.97, 39.89, 179.44.

$[P_{4,4,4,4}][C_{11}CO_2]$: Tetrabutylphosphonium laurate
^1H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.879 (t, J = 13.28 Hz, 3H, $CO_2(CH_2)_{10}CH_3$), 0.981 (t, J = 14.20, 12H, $P(CH_2)_3CH_3$), 1.257-1.285 (m, 16H, $CO_2(CH_2)_2(CH_2)_8$), 1.510-1.557 (m, 16H, $PCH_2CH_2CH_2$), 1.591-1.664 (m, 2H, $CO_2CH_2CH_2$), 2.349 (t, J = 15.11, 2H, CO_2CH_2), 2.426-2.499 (m, 8H, PCH_2).
^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 13.57, 14.17, 19.09 (d, J = 46.96), 22.73, 23.95 (d, J = 4.79), 24.07 (d, J = 15.34), 24.68, 29.05, 29.27, 29.38, 29.49, 29.64, 31.96, 34.04, 172.61.

$[P_{4,4,4,4}][C_{13}CO_2]$: Tetrabutylphosphonium myristate
^1H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.877 (t, J = 13.74 Hz, 3H, $CO_2(CH_2)_{12}CH_3$), 0.970 (t, J = 14.20, 12H, $P(CH_2)_3CH_3$), 1.242-1.297 (m, 20H, $CO_2(CH_2)_2(CH_2)_{10}$), 1.490-1.546 (m, 16H, $PCH_2CH_2CH_2$), 1.580-1.654 (m, 2H, $CO_2CH_2CH_2$), 2.172 (t, J = 15.57, 2H, CO_2CH_2), 2.389-2.464 (m, 8H, PCH_2).
^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 13.57, 14.17, 18.69 (d, J = 46.96), 22.73, 23.93 (d, J = 4.79), 24.08 (d, J = 15.34), 27.31, 29.41, 29.71, 29.75-29.85 (m), 30.20, 31.97, 39.31, 49.84, 179.48.

$[P_{4,4,4,4}][C_{15}CO_2]$: Tetrabutylphosphonium palmitate
^1H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.879 (t, J = 13.74 Hz, 3H, $CO_2(CH_2)_{14}CH_3$), 0.969 (t, J = 13.74, 12H, $P(CH_2)_3CH_3$), 1.242-1.317 (m, 24H, $CO_2(CH_2)_2(CH_2)_{12}$), 1.490-1.546 (m, 16H, $PCH_2CH_2CH_2$), 1.576-1652 (m, 2H,

$CO_2CH_2CH_2$), 2.175 (t, J = 15.57, 2H, CO_2CH_2), 2.393-2.466 (m, 8H, PCH_2).
^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 13.56, 14.16, 18.70 (d, J = 46.96), 22.73, 23.93 (d, J = 4.79), 24.08 (d, J = 15.34), 27.23, 29.40, 29.70-29.80 (m), 30.16, 31.96, 39.15, 179.37.

$[P_{4,4,4,4}][C_{21}CO_2]$: Tetrabutylphosphonium behenate
^{1}H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.879 (t, J = 13.74 Hz, 3H, $CO_2(CH_2)_{20}CH_3$), 0.969 (t, J = 14.20, 12H, $P(CH_2)_3CH_3$), 1.239-1.316 (m, 36H, $CO_2(CH_2)_2(CH_2)_{18}$), 1.466-1.545 (m, 16H, $PCH_2CH_2CH_2$), 1.578-1.666 (m, 2H, $CO_2CH_2CH_2$), 2.161 (t, J = 16.03, 2H, CO_2CH_2), 2.407-2.480 (m, 8H, PCH_2).
^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 13.60, 14.20, 18.74 (d, J = 46.96), 22.76, 23.99 (d, J = 4.79), 24.11 (d, J = 15.34), 27.45, 29.44, 29.73-29.83 (m), 30.26, 32.00, 39.62, 179.64.

$[P_{5,5,5,5}][HCO_2]$: Tetrapentylphosphonium formate
^{1}H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.914 (t, J = 14.20, 12H, $P(CH_2)_4CH_3$), 1.324-1.414 (m, 8H, $P(CH_2)_3CH_2$), 1.435-1.598 (m, 16H, $PCH_2CH_2CH_2$), 2.338-2.411 (m, 8H, PCH_2), 8.908 (s, 1H, CH).
^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 13.74, 18.85 (d, J = 46.96), 21.52 (d, J = 4.79), 22.01, 32.83 (d, J = 14.38), 168.04.

$[P_{5,5,5,5}][C_3CO_2]$: Tetrapentylphosphonium butyrate
^{1}H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.893-0.945 (m, 15H, $P(CH_2)_4CH_3$, $CO_2(CH_2)_2CH_3$), 1.315-1.404 (m, 8H, $P(CH_2)_3CH_2$), 1.426-1.576 (m, 16H, $PCH_2CH_2CH_2$), 1.593-1.686 (m, 2H, $CO_2CH_2CH_2$), 2.172 (t, J = 15.11, 2H, CO_2CH_2), 2.362-2.436 (m, 8H, PCH_2).
^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 13.82, 14.57, 18.90 (d, J = 46.96), 20.34, 21.67 (d, J = 4.79), 22.14, 32.94 (d, J = 15.34), 41.01, 179.31.

$[P_{5,5,5,5}][C_5CO_2]$: Tetrapentylphosphonium hexanoate
^{1}H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.855-0.927 (m, 15H, $P(CH_2)_4CH_3$, $CO_2(CH_2)_4CH_3$), 1.285-1.401 (m, 12H, $P(CH_2)_3CH_2$, $CO_2(CH_2)_2CH_2CH_2$), 1.425-1.573 (m, 16H, $PCH_2CH_2CH_2$), 1.595-1.670 (m, 2H, $CO_2CH_2CH_2$), 2.169 (t, J = 16.03, 2H, CO_2CH_2), 2.409-2.482 (m, 8H, PCH_2).
^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 13.84, 14.28, 18.93 (d, J = 46.96), 21.74 (d, J = 4.79), 22.18, 22.87, 27.18, 32.52, 32.99 (d, J = 15.34), 39.59, 179.59.

$[P_{5,5,5,5}][C_7CO_2]$: Tetrapentylphosphonium octanoate
^{1}H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.858 (t, J = 13.75 Hz, 3H, $CO_2(CH_2)_6CH_3$), 0.910 (t, J = 14.89, 12H, $P(CH_2)_4CH_3$), 1.262-1.300 (m, 8H, $CO_2(CH_2)_2(CH_2)_4$), 1.324-1.396 (m, 8H, $P(CH_2)_3CH_2$), 1.434-1.565 (m, 16H, $PCH_2CH_2CH_2$), 1.587-1.661 (m, 2H, $CO_2CH_2CH_2$), 2.162 (t, J = 16.04, 2H, CO_2CH_2), 2.393-2.453 (m, 8H, PCH_2).
^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 13.77, 14.17, 18.89 (d, J = 46.96), 21.69 (d, J = 4.79), 22.12, 22.76, 27.59, 29.50, 30.25, 32.01, 32.94 (d, J = 14.38), 39.91, 179.47.

$[P_{5,5,5,5}][C_9CO_2]$: Tetrapentylphosphonium caproate
^{1}H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.867 (t, J = 13.74 Hz, 3H, $CO_2(CH_2)_8CH_3$), 0.912 (t, J = 14.65, 12H, $P(CH_2)_4CH_3$), 1.247-1.282 (m, 12H, $CO_2(CH_2)_2(CH_2)_6$), 1.314-1.404 (m, 8H, $P(CH_2)_3CH_2$), 1.426-1.561 (m, 16H, $PCH_2CH_2CH_2$), 1.572-1.660 (m, 2H, $CO_2CH_2CH_2$), 2.187 (t, J = 15.57, 2H, CO_2CH_2), 2.343-2.416 (m, 8H, PCH_2).
^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 13.81, 14.20, 18.89 (d, J = 46.96), 21.64 (d, J = 4.79), 22.12, 22.76, 27.05, 29.46, 29.74, 29.81, 30.10, 32.01, 32.93 (d, J = 14.38), 38.71, 179.39.

$[P_{5,5,5,5}][C_{11}CO_2]$: Tetrapentylphosphonium laurate
^{1}H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.857-0.928 (m, 15H, $P(CH_2)_4CH_3$, $CO_2(CH_2)_{10}CH_3$), 1.244-1.284 (m, 16H, $CO_2(CH_2)_2(CH_2)_8$), 1.313-1.404 (m, 8H, $P(CH_2)_3CH_2$), 1.426-1.564 (m, 16H, $PCH_2CH_2CH_2$), 1.582-1.658 (m, 2H, $CO_2CH_2CH_2$), 2.191 (t, J = 15.57, 2H, CO_2CH_2), 2.387-2.461 (m, 8H, PCH_2).
^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 13.76, 14.14, 18.86 (d, J = 46.96), 21.63 (d, J = 4.79), 22.09, 22.71, 27.13, 29.40, 29.70, 29.72-29.82 (m), 30.12, 31.95, 32.91 (d, J = 14.38), 38.90, 179.16.

$[P_{6,6,6,6}][HCO_2]$: Tetrahexylphosphonium formate
^{1}H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.896 (t, J = 14.20, 12H, $P(CH_2)_5CH_3$), 1.271-1.361 (m, 16H, $P(CH_2)_3CH_2CH_2$), 1.451-1.583 (m, 16H, $PCH_2CH_2CH_2$), 2.333-2.407 (m, 8H, PCH_2), 8.855 (s, 1H, CH).
^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 13.97, 18.94 (d, J = 46.96), 21.83 (d, J = 4.79), 22.37, 30.49 (d, J = 15.34), 31.09, 167.93.

$[P_{6,6,6,6}][C_3CO_2]$: Tetrahexylphosphonium butyrate
^{1}H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.877-0.945 (m, 15H, $P(CH_2)_5CH_3$, $CO_2(CH_2)_2CH_3$), 1.253-1.367 (m, 16H, $P(CH_2)_3CH_2CH_2$), 1.414-1.564 (m, 16H, $PCH_2CH_2CH_2$), 1.598-1.691 (m, 2H, $CO_2CH_2CH_2$), 2.168 (t, J = 15.11, 2H, CO_2CH_2), 2.391-2.464 (m, 8H, PCH_2).
^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 13.97, 14.50, 18.93 (d, J = 46.78), 20.21, 21.94 (d, J = 4.80), 22.40, 30.55 (d, J = 14.40), 31.17, 40.68, 178.94.

$[P_{6,6,6,6}][C_5CO_2]$: Tetrahexylphosphonium hexanoate
^{1}H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.857-0.916 (m, 15H, $P(CH_2)_5CH_3$, $CO_2(CH_2)_4CH_3$), 1.254-1.372 (m, 20H, $P(CH_2)_3CH_2CH_2$, $CO_2(CH_2)_2CH_2CH_2$), 1.414-1.556 (m, 16H, $PCH_2CH_2CH_2$), 1.569-1.661 (m, 2H, $CO_2CH_2CH_2$), 2.188 (t, J = 15.57, 2H, CO_2CH_2), 2.280-2.352 (m, 8H, PCH_2).
^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 14.00, 14.18, 18.89 (d, J = 46.96), 21.86 (d, J = 4.79), 22.41, 22.72, 26.49, 30.51 (d, J = 15.34), 31.16, 32.19, 38.23, 179.44.

$[P_{6,6,6,6}][C_7CO_2]$: Tetrahexylphosphonium octanoate
^{1}H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.844-0.915 (m, 15H, $P(CH_2)_5CH_3$, $CO_2(CH_2)_6CH_3$), 1.187-1.372 (m, 24H, $P(CH_2)_3CH_2CH_2$, $CO_2(CH_2)_2(CH_2)_4$), 1.414-1.557 (m, 16H, $PCH_2CH_2CH_2$), 1.567-1.661 (m, 2H, $CO_2CH_2CH_2$), 2.158 (t, J = 14.20, 2H, CO_2CH_2), 2.310-2.383 (m, 8H, PCH_2).
^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 14.02, 14.16, 18.89 (d, J = 46.96), 21.76 (d, J = 3.83), 22.46, 22.72, 25.54, 29.19, 29.44, 30.52 (d, J = 15.34), 31.15, 31.84, 35.55, 178.62.

$[P_{6,6,6,6}][C_9CO_2]$: Tetrahexylphosphonium caproate
^{1}H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.851-0.913 (m, 15H, $P(CH_2)_5CH_3$, $CO_2(CH_2)_8CH_3$), 1.182-1.357 (m, 28H, $P(CH_2)_3CH_2CH_2$, $CO_2(CH_2)_2(CH_2)_6$), 1.412-1.552 (m, 16H, $PCH_2CH_2CH_2$), 1.572-1.659 (m, 2H, $CO_2CH_2CH_2$), 2.194 (t, J = 15.57, 2H, CO_2CH_2), 2.341-2.415 (m, 8H, PCH_2).

^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 14.01, 14.19, 18.93 (d, *J* = 46.96), 21.94 (d, *J* = 4.79), 22.43, 22.76, 26.97, 29.47, 29.74, 29.80, 30.07, 30.56 (d, *J* = 14.38), 31.20, 32.01, 38.53, 179.27.

$[P_{8,8,8,8}][HCO_2]$: Tetraoctylphosphonium formate

^{1}H NMR (400MHz, $CDCl_3$, 25 °C, Me_4Si) δ_H = 0.888 (t, *J* = 13.75, 12H, $P(CH_2)_7CH_3$), 1.272-1.358 (m, 32H, $P(CH_2)_3CH_2CH_2CH_2CH_2$), 1.442-1.579 (m, 16H, $PCH_2CH_2CH_2$), 2.368-2.427 (m, 8H, PCH_2), 8.935 (s, 1H, C*H*).

^{13}C-NMR (100MHz; $CDCl_3$, 25 °C, Me_4Si) δ_C = 14.08, 18.98 (d, *J* = 47.98), 21.93 (d, *J* = 4.80), 22.61, 28.96, 28.98, 30.85 (d, *J* = 14.40), 31.71, 168.18.

Cellulose dissolution tests

Cellulose powder was dried under vacuum for 6 hours at room temperature before use. Dried cellulose powder was added to the dried ILs (the final concentration of cellulose was 0.10 wt%), and the mixture was gently stirred for 1 h at 130 °C. After that, the cellulose dissolution was comfirmed with an optical microscope (Olympus BX51). Structural characteristics of ILs before and after cellulose dissolution test were confirmed by both ^{1}H and ^{13}C NMR measurements.

Water miscibility and physico-chemical properties of ILs

Water miscibility was evaluated by the following procedure. Pure water and ILs were mixed (50/50 wt%) and gently stirred. After that, the mixtures were cooled or heated to the fixed temperature between 0 and 70 °C and the miscibility was confirmed by both naked eyes and optical micrograph.

Hydrogen bonding ability was evaluated with the Kamlet–Taft parameters.[27, 28] Density of ILs was measured at 40 °C with a density/specific gravity meter (DA-100, Kyoto Electronics Manufacturing Co.,LTD.).

Results and discussion

Effect of cation species of formate-type ILs on cellulose dissolution

Table 1 shows water miscibility of formate ($[HCO_2]$) type ILs after mixing with equal weight of water and 0.1 wt% cellulose solubility after stirring for 1 h at 130 °C. Formate anion was selected as a strong anion to improve hydrogen bonding ability of ILs. Density is another important factor for this experiment. When IL/water biphasic system is constructed, it is favourable that the IL locates at the upper phase to suppress the evaporation of water when IL was mixed with water. The density of ILs should therefore be lower than 1.0 g ml^{-1}. However, most organic cations such as imidazolium cations gave ILs with the density of over 1.0 g ml^{-1}. In addition, imidazolium type cations gave relatively hydrophilic ILs even long alkyl side chains were introduced.[26] Therefore, we focused on tetraalkylphosphonium cations because hydrophobic and low density ILs were empirically known to be obtained with these phosphonium cations.[29, 30] Effect of alkyl chain length were examined with these phosphonium cations. All ILs prepared in this study were found to have lower density than 1.0 g ml^{-1}. Both tetrabutylphosphonium formate ($[P_{4,4,4,4}]$ $[HCO_2]$, entry #**1**) and tetrapentylphosphonium formate ($[P_{5,5,5,5}][HCO_2]$, entry #**2**) are miscible with water regardless of temperature. On the other hand, tetrahexylphosphonium formate ($[P_{6,6,6,6}][HCO_2]$, entry #**3**) showed lower critical solution temperature (LCST) type phase transition; this IL is miscible with water at temperature below 10 °C but phase separated with water by heating. ILs with longer alkyl chain such as $[P_{8,8,8,8}][HCO_2]$ (IL **4**), showed phase separation with water at any temperature.

Table 1. Water miscibility after mixing with equal weight of water, and 0.1 wt% cellulose solubility at 130 °C for 1 h stirring of these $[HCO_2]$ salts. Number in parenthesis is the lower critical solution temperature.

Entry	Cations	Water miscibility	Cellulose solubility
1	$[P_{4,4,4,4}]$	Misc.	Sol.
2	$[P_{5,5,5,5}]$	Misc.	Insol.
3	$[P_{6,6,6,6}]$	LCST (10 °C)	Insol.
4	$[P_{8,8,8,8}]$	Immisc.	Insol.

Misc.: miscible with water, Immisc.: immiscible, Sol.: 0.1 wt% cellulose was soluble, Insol.: cellulose was insoluble. LCST: The mixture shows lower critical solution temperature (LCST) type phase transition after mixing the IL with water. Number in parenthesis is the lower critical solution temperature.

The alkyl chain length of the tetraalkylphosphonium cation was confirmed to have a considerable effect on not only the miscibility with water but also the cellulose dissolving ability of the ILs. Only IL **1** dissolved cellulose, but other ILs **2**-**4** did not dissolve it at temperatures between 0 and 130 °C. From this tendency, it was strongly suggested that the formate ILs lost the ability to dissolve cellulose before getting hydrophobicity to induce phase separation with water by increasing alkyl chain length on the cations. In other words, it seems to be quite difficult to construct formate ILs having ability to dissolve cellulose and to show phase separation with water by simple elongation of the alkyl chain on the phosphonium cations.

Effect of anion species of $[P_{4,4,4,4}]$-type ILs on cellulose dissolution

Since IL **1** dissolved cellulose as shown in Table 1, we then change the anion species to realise the above-mentioned two conflicting properties. To evaluate the effect of alkyl chain length of carboxylic anion, some carboxylate anions having alkyl chains with different length were coupled with the $[P_{4,4,4,4}]$ cation. All of these $[P_{4,4,4,4}]$carboxylates prepared here were miscible with water regardless of the mixing ratio to water (see Table 2). Since the hydrophobic properties deeply depended on the alkyl chains, ILs with similar number of total carbon atoms were compared. For example, the number of carbon atoms of ILs **3** and **8** is 25 and 26, respectively. IL **3** shows the LCST-type phase transition with water as shown in Table 1, but IL **8** is water miscible at any temperature. The IL **3** is composed of hydrophobic cation and hydrophilic anion. On the other hand, IL **8** is composed of moderately hydrophilic cation and anion. The latter IL is strongly suggested to be less hydrophobic than the former one. This pushed us to prepare ILs with more hydrophobic anions. After introducing longer alkyl chain, the number of carbon atoms for ILs **11** and **12** are 32 and 38, respectively, but these ILs are also water miscible. This might be caused by the micelle formation of these ILs which has one long and linear alkyl chain on the anion. In any case, elongation of one alkyl chain on the carboxylate anion was found to scarcely affect the miscibility of ILs with water.

Therefore, it is suggested that design of cation containing four alkyl chains is more effective to increase the hydrophobicity of ILs without forming micelle structure in IL/water mixture.

A series of $[P_{4,4,4,4}]$carboxylate dissolved cellulose even though their alkyl chain was elongated. It dissolved cellulose with number of carbon atoms of anion up to 14 (IL **10**, in Table 2). On the other hand, ILs **11** and **12** did not dissolve cellulose at any temperature. According to these, it was suggested to be difficult to design ILs having both cellulose dissolving ability and hydrophobicity to induce phase separation with water by simply elongate the alkyl chains of anions. It should be noted here that there was no structural change for all ILs examined during cellulose dissolution tests (for example, see ESI for **IL 6**).

Table 2. Water miscibility after mixing with equal weight of water, 0.1 wt% cellulose solubility under 1 h stirring at 130 °C, and Kamlet-Taft β value of a series of $[P_{4,4,4,4}]$ salts at 25 °C.

Entry	Anions	Water miscibility	Cellulose solubility	Kamlet-Taft β value
1	$[HCO_2]$	Misc.	Sol.	1.26
5	$[C_3CO_2]$	Misc.	Sol.	-[a]
6	$[C_5CO_2]$	Misc.	Sol.	1.41
7	$[C_7CO_2]$	Misc.	Sol.	1.44
8	$[C_9CO_2]$	Misc.	Sol.	1.43
9	$[C_{11}CO_2]$	Misc.	Sol.	1.51
10	$[C_{13}CO_2]$	Misc.	Sol.	1.51
11	$[C_{15}CO_2]$	Misc.	Insol.	1.52
12	$[C_{21}CO_2]$	Misc.	Insol.	-[a]

[a] Not evaluated because it was solid at room temperature. Other abbreviations are the same as those in Table 1.

Hydrophobicity of ILs was considerably enhanced by introducing longer alkyl chains on the phosphonium cation, but it markedly decreased cellulose dissolving ability at the same time. On the other hand, elongation of alkyl chain of anions had a little effect to improve hydrophobicity of the corresponding ILs, but the ILs could still dissolve cellulose. Longer alkyl chain of carboxylate anion provided higher β value of the corresponding ILs (see Table 2). Alkyl chain, the electron-releasing substituent, increases the electron density of the ionic part of the carboxylate anion, and it may increase β value of the ILs.[31] Then, ILs containing long-chain carboxylates are illuminated as new starting materials for the purpose of this study.

Cellulose dissolution by ILs showing LCST-type phase transition after mixing with water

Considering above mentioned tendency, carboxylate anions with long alkyl chains were then coupled with relatively hydrophobic cations. Since slight increase in the chain length of four alkyl groups on the phosphate cation effectively improve hydrophobicity of ILs, here we use $[P_{5,5,5,5}]$ cation instead of $[P_{4,4,4,4}]$ cation. As shown in Table 3, ILs consist of $[P_{5,5,5,5}]$ cation and several carboxylate anions showed very high β values. ILs **13**, **14**, and **15** dissolved cellulose at 130 °C although formate type IL (IL **2**) did not. This difference should be explained by higher β value of the ILs consisting of long-chain carboxylates than that of the formate salt. On the other hand, ILs **16** and **17** did not dissolve cellulose in spite of longer alkyl chain on the anion and high enough β values. These results will be discussed with a new parameter, density of ILs, in the section after next. Next, water miscibility of these ILs was examined. When the carboxylate anions had pentyl or longer alkyl chains, the ILs showed LCST-type phase transition with water (see Table 3, Entry **14-17**). Therefore, it was found that ILs **14** and **15** had cellulose dissolving ability and they showed phase separation with water at temperature above the LCST. With fine selection and combination of ions, we succeeded in preparing ILs that solubilised cellulose and constructed a biphasic system with water. This is the first report about ILs that actually dissolve cellulose and they can make a phase separation with water. However, the ILs synthesised in this study certainly dissolved cellulose in the absence of water, but they could not dissolve cellulose after phase separation with water. For these IL/water mixtures, IL phase was always found in the upper layer, and the density of these ILs is easily speculated to be lower than 1.0 g ml^{-1}. Some polar and hydrophobic ILs prepared in this study did not dissolve cellulose in spite of their high β values as we mentioned above. Here there is a new question raised whether the β value is the essential and most effective parameter for the dissolution ability of the IL or not.

Table 3. Water miscibility after mixing with equal weight of water, 0.1 wt% cellulose solubility under 1 h stirring at 130 °C, and Kamlet-Taft β value of a series of $[P_{5,5,5,5}]$ salts at 25 °C.

Entry	Anions	Water miscibility	Cellulose solubility	Kamlet-Taft β value
2	$[HCO_2]$	Misc.	Insol.	1.29
13	$[C_3CO_2]$	Misc.	Sol.	1.44
14	$[C_5CO_2]$	LCST (18 °C)	Sol.	1.48
15	$[C_7CO_2]$	LCST (20 °C)	Sol.	1.53
16	$[C_9CO_2]$	LCST (12 °C)	Insol.	1.54
17	$[C_{11}CO_2]$	LCST (14 °C)	Insol.	1.55

*Number in parenthesis is the lower critical solution temperature. Other abbreviations are the same as those in Table 1.

Correlation between density of ILs and their cellulose dissolution power

Table 4 shows similar results as mentioned above but the used cation ($[P_{6,6,6,6}]$) is more hydrophobic than those used above. In the previous section, we succeeded in synthesising cellulose

Table 4. Water miscibility after mixing with equal weight of water, 0.1 wt% cellulose solubility under 1 h stirring at 130 °C, and Kamlet-Taft β value of a series of [$P_{6,6,6,6}$] salts at 25 °C.

Entry	Anions	Water miscibility	Cellulose solubility	Kamlet-Taft β value
3	[HCO_2]	LCST (10 °C)	Insol.	1.30
18	[C_3CO_2]	Immisc.	Insol.	1.47
19	[C_5CO_2]	Immisc.	Insol.	1.47
20	[C_7CO_2]	Immisc.	Insol.	1.48
21	[C_9CO_2]	Immisc.	Insol.	1.50

Abbreviations and note are the same as those in Table 1.

dissolving and water separable ILs consisting of tetrapentylphosphonium cation and hexanoate (IL **14**) or octanoate anion (IL **15**). However, tetrapentylphosphonium salts with longer chain carboxylates than that of IL **15**, namely, [$P_{5,5,5,5}$][C_9CO_2] (IL **16**) and [$P_{5,5,5,5}$][$C_{11}CO_2$] (IL **17**) did not dissolve cellulose in spite of their very high β values. In addition, ILs, consisting of phosphonium cations with longer alkyl chains, such as [$P_{6,6,6,6}$]carboxylate also did not dissolve cellulose in spite that they showed quite high β value of 1.30-1.50. Ions with longer alkyl chains such as [$P_{6,6,6,6}$] and [$C_{11}CO_2$] leaded lower bulk ion density. Sufficient anions are necessary to dissolve cellulose, and accordingly, we have to discuss the cellulose dissolving ability with not only the β value but also ion density.

It was strongly suggested that there is another parameter to affect cellulose dissolving ability of the ILs. It is well-known that the β value is essentially important parameter to govern the cellulose dissolution, but here we propose that the density of ILs is also an effective parameter. Figure 1 shows the effects of both Kamlet-Taft β value and density of the ILs on the cellulose solubilisation ability. IL **10**, [$P_{4,4,4,4}$][$C_{13}CO_2$], was found to dissolve cellulose, and IL **11**, [$P_{4,4,4,4}$][$C_{15}CO_2$], could not in spite of almost the same β value. Furthermore, IL **8**, [$P_{4,4,4,4}$][C_9CO_2], could dissolve cellulose in spite of lower β value than that of IL **11**. This contradiction was first comprehended by depicting Figure 1. When the density of the IL was about 0.90 g ml^{-1}, β value should be 1.40 or more to dissolve cellulose (ILs **7**, **8**, **13**, and **14**) according to our semi-empirical evaluations. On the other hand, when the density value is over 0.92 g ml^{-1}, the required β value is only 1.26 for cellulose dissolution (IL **1**). In other words, ILs with lower density need higher β value to dissolve cellulose. On the other hand, even if ILs do not have very high β value, the ILs can dissolve cellulose only when the density is high enough. This is the first report that the density of ILs affects cellulose dissolving ability. Here we succeeded in providing a novel guideline for developing cellulose dissolving ILs by clarifying the importance of the parameter, density. Hereafter, based on these results, we should consider not only the β value but also the density of ILs to design ILs to dissolve cellulose.

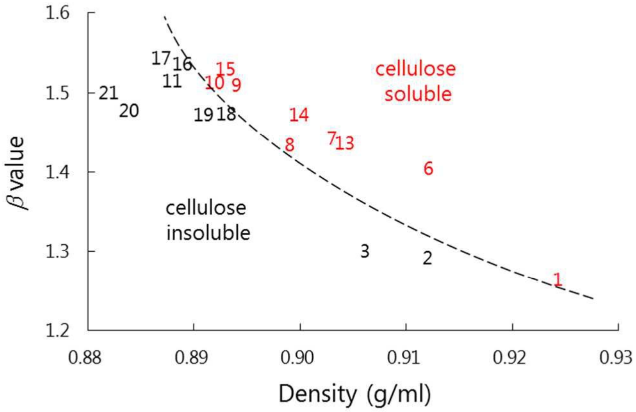


Figure 1. Effects of both Kamlet-Taft β value and density of ILs on the cellulose solubilising ability. The entry numbers of ILs are plotted on the figure. Red number means that the IL dissolves cellulose, and black one means no ability to dissolve cellulose. Broken line is proposed here to be the borderline between the ILs have power to dissolve cellulose and those of not.

Conclusions

Effects of alkyl chain length on cellulose dissolving ability and phase separation behaviour with water of ILs have been systematically examined. The elongation of alkyl group on the phosphonium cation significantly affects both hydrophobicity and cellulose dissolving ability of the ILs. ILs consisting of tetrapentylphosphonium cation and long-alkyl carboxylate anion dissolved cellulose and showed LCST-type phase transition after water addition. This is the first report on the cellulose dissolving and water separable ILs. In addition, we have succeeded in clarifying that the density of ILs greatly influences the cellulose dissolving ability through the present study. Not only the Kamlet-Taft β value but also the density of ILs should be considered to develop such polar ILs as solvent for cellulose. This finding will give us chance to propose totally new ILs as solvents for cellulose.

Acknowledgements

This study was supported by the Science and Technology Research Promotion Program for Agriculture, Forestry, Fisheries and Food Industry (26052A).

Notes and references

[a] *Department of Biotechnology, Tokyo University of Agriculture and Technology, Naka-cho, 2-24-16, Koganei, Tokyo 184-8588, Japan. Fax: +81-42-388-7024; Tel: +81-42-388-7024; E-mail: ohnoh@cc.tuat.ac.jp*
[b] *Functional Ionic Liquids Laboratories, Graduate School of Engineering, Naka-cho, 2-24-16, Koganei, Tokyo 184-8588, Japan. Fax: +81-42-388-7024; Tel: +81-42-388-7024; E-mail: ohnoh@cc.tuat.ac.jp*

Present address:
‖ Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, Kyoto 606-8502, Japan
⊥ Faculty of Natural System, Institute of Science and Engineering, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan.
§ Equally contribution

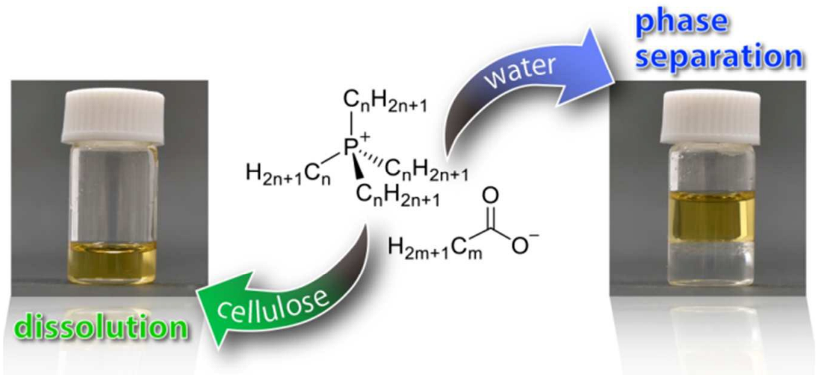
1. P. Zugenmaier, *Prog. Polym. Sci.*, 2001, **26**, 1341-1417.
2. Y. Nishiyama, P. Langan and H. Chanzy, *J. Am. Chem. Soc.*, 2002, **124**, 9074-9082.
3. H. Chanzy, A. Peguy, S. Chaunis and P. Monzie, *J. Polym. Sci. Pol. Phys.*, 1980, **18**, 1137-1144.
4. A. Isogai and R. H. Atalla, *Cellulose*, 1998, **5**, 309-319.

5. J. Cai and L. Zhang, *Macromol. Biosci.*, 2005, **5**, 539-548.
6. N. Isobe, K. Noguchi, Y. Nishiyama, S. Kimura, M. Wada and S. Kuga, *Cellulose*, 2013, **20**, 97-103.
7. C. L. Mccormick, P. A. Callais and B. H. Hutchinson, *Macromolecules*, 1985, **18**, 2394-2401.
8. T. R. Dawsey and C. L. Mccormick, *J. Macromol. Sci. R M C*, 1990, **C30**, 405-440.
9. Y. Nishio, S. K. Roy and R. S. Manley, *Polymer*, 1987, **28**, 1385-1390.
10. J. L. Wertz, O. Bédué and J. P. Mercier, *Cellulose Science and Technology*, EFPL Press, Lausanne, Switzerland, 2010.
11. R. P. Swatloski, S. K. Spear, J. D. Holbrey and R. D. Rogers, *J. Am. Chem. Soc.*, 2002, **124**, 4974-4975.
12. R. C. Remsing, R. P. Swatloski, R. D. Rogers and G. Moyna, *Chem. Commun.*, 2006, 1271-1273.
13. T. Heinze, K. Schwikal and S. Barthel, *Macromol. Biosci.*, 2005, **5**, 520-525.
14. H. Zhang, J. Wu, J. Zhang and J. He, *Macromolecules*, 2005, **38**, 8272-8277.
15. B. Kosan, C. Michels and F. Meister, *Cellulose*, 2008, **15**, 59-66.
16. J. Vitz, T. Erdmenger, C. Haensch and U. S. Schubert, *Green Chem.*, 2009, **11**, 417-424.
17. K. Ohira, Y. Abe, M. Kawatsura, K. Suzuki, M. Mizuno, Y. Amano and T. Itoh, *ChemSusChem*, 2012, **5**, 388-391.
18. A. W. T. King, J. Asikkala, I. Mutikainen, P. Jarvi and I. Kilpelainen, *Angew. Chem. Int. Edit.*, 2011, **50**, 6301-6305.
19. H. Ohno and Y. Fukaya, *Chem. Lett.*, 2009, **38**, 2-7.
20. Y. Fukaya, A. Sugimoto and H. Ohno, *Biomacromolecules*, 2006, **7**, 3295-3297.
21. Y. Fukaya, K. Hayashi, M. Wada and H. Ohno, *Green Chem.*, 2008, **10**, 44-46.
22. M. Abe, Y. Fukaya and H. Ohno, *Green Chem.*, 2010, **12**, 1274-1280.
23. M. Mazza, D.-A. Catana, C. Vaca-Garcia and C. Cecutti, Cellulose, 2008, 16, 207–215.
24 L. K. Hauru, M. Hummel, A. W. King, I. Kilpeläinen and H. Sixta, Biomacromolecules, 2012, 13, 2896–2905.
25 C. Olsson, A. Idstrom, L. Nordstierna and G. Westman, Carbohydr. Polym., 2014, 99, 438–446.
26. Y. Fukaya and H. Ohno, *Phys. Chem. Chem. Phys.*, 2013, **15**, 4066-4072.
27. M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, 1976, **98**, 377-383.
28. L. Crowhurst, P. R. Mawdsley, J. M. Perez-Arlandis, P. A. Salter and T. Welton, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2790-2794.
29. C. J. Bradaric, A. Downard, C. Kennedy, A. J. Robertson and Y. Zhou, *Green Chem.*, 2003, **5**, 143-152.
30. J. Kagimoto, S. Taguchi, K. Fukumoto and H. Ohno, *J. Mol. Liq.*, 2010, **153**, 133-138.
31. Y. S. Wu, T. Sasaki, K. Kazushi, T. Seo and K. Sakurai, *J. Phys. Chem. B*, 2008, **112**, 7530-7536.

Effects of polarity, hydrophobicity, and density of ionic liquids on cellulose solubility.

Mitsuru Abe,§ Kosuke Kuroda,§ Daiki Sato, Haruhito Kunimura and Hiroyuki Ohno*

§ *Equally contribution*



Density of ionic liquids deeply affects their cellulose dissolving ability, and hydrophobic cellulose dissolving ionic liquids were synthesised for the first time.