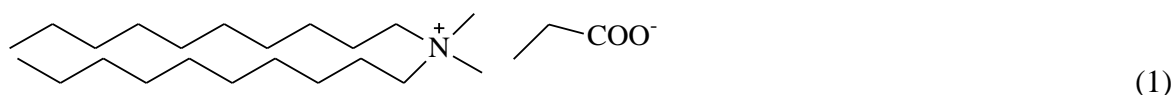


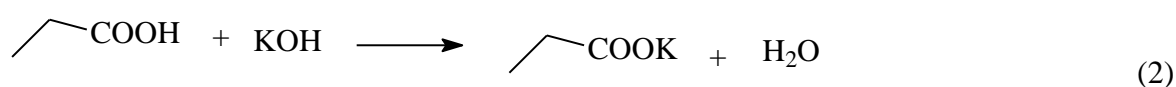
Supplementary Material

1. Synthesis of ILs

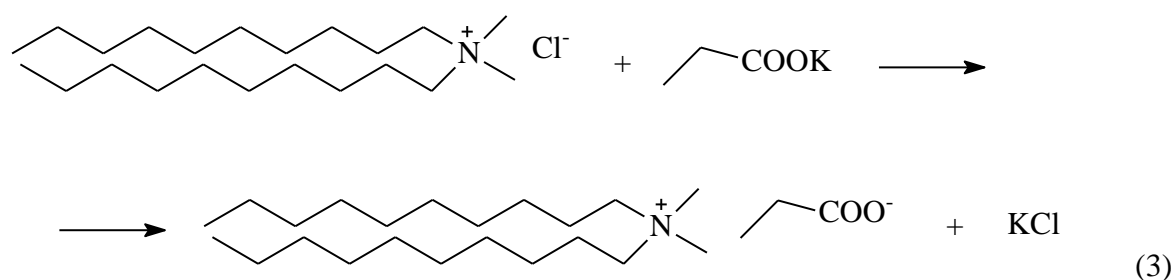
1.1. The synthesis of didecyldimethylammonium propionate $[N_{10,10,1,1}][C_2H_5COO]$, ($C_{22}H_{53}NO_2$), $M = 399.79$ g/mol



The reaction of propionic acid with potassium hydroxide



The reaction of didecyldimethylammonium chloride with potassium propionate



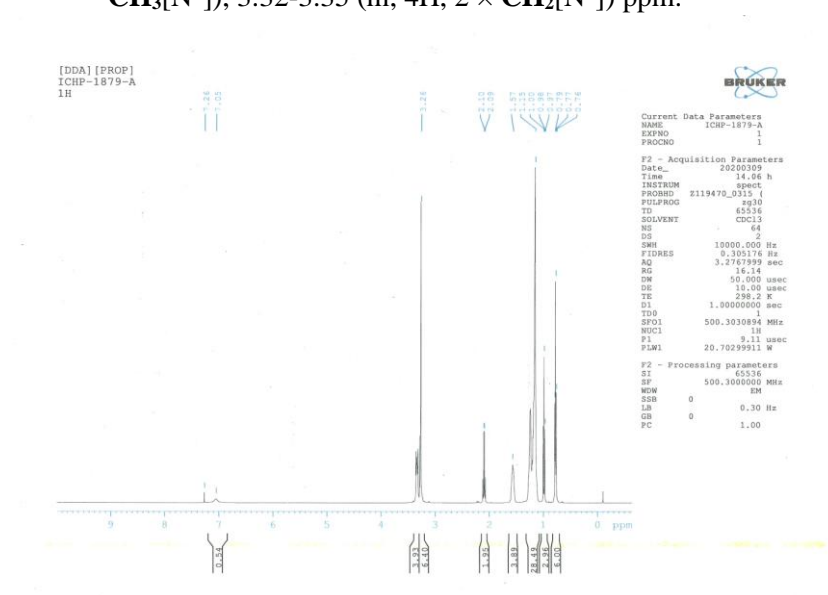
The 325.94 g of a 50% solution of didecyldimethylammonium chloride (162.97 g $[N_{10,10,1,1}][Cl]$, 0.45 mol) was added to potassium propionate obtained according to receipt: 33.33 g (0.45 mol) of propionic acid was added to 25.25 g (0.45 mol) of KOH and 75 cm³ of water, after mixing at the temperature $T = 333$ K for 5 h. The contents of the flask were stirred for 6 h at the temperature $T = 333 - 334$ K. Water was removed by distillation under reduced pressure and the residue was dried under the pressure 1.3 hPa ($T = 333$ K, 10 h). Next, 350 cm³ of methanol was added to the residue, mixed and left at the temperature $T = 253$ K for 20 h. The precipitated KCl was collected by the filtration and the filtrate was concentrated by the distillation of methanol under the reduced pressure. The IL was dried under the pressure 1.3

hPa for 10 h ($T = 333$ K). The 172.5 g (0.43 mol) of didecyldimethylammonium propionate was obtained. Yield 95.56%.

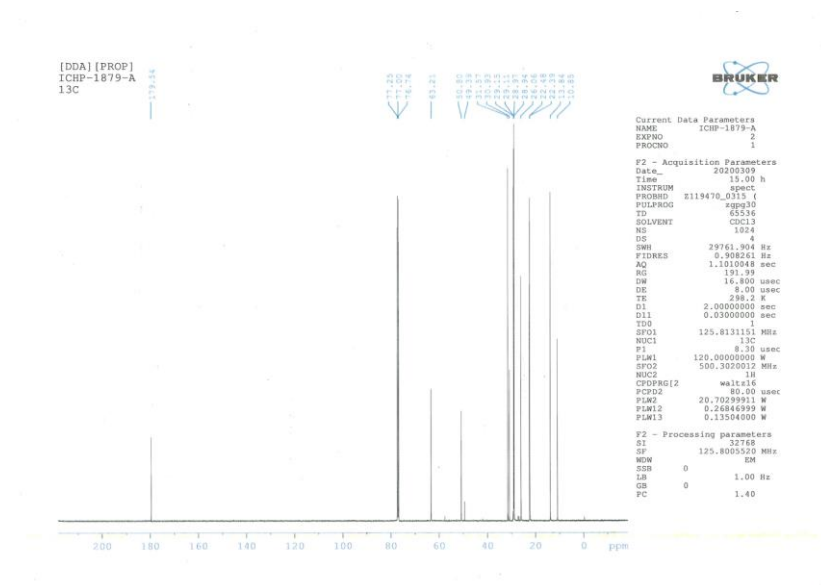
NMR spectra were recorded on the spectrometer 300 MHz in the presence of tetramethylsilane

Figure S1. NMR of didecyldimethylammonium propionate, $[N_{10,10,1,1}][C_2H_5COO]$: a) 1H NMR; b) ^{13}C NMR.

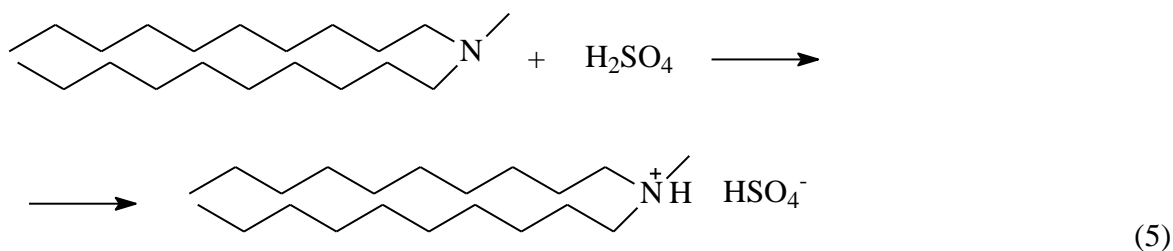
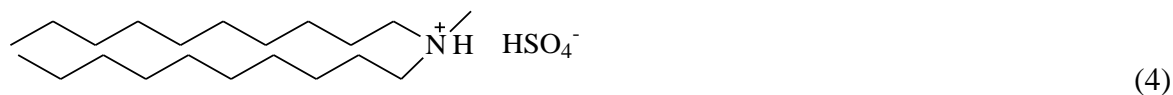
- a) 1H NMR ($CDCl_3$, 500 MHz), δ : 0.77 (t, 6H, $2 \times CH_3CH_2$, $J = 7.0$ Hz), 0.98 (t, 3H, $CH_3CH_2COO^-$, $J = 7.6$ Hz), 1.07-1.22 (m, 20H, $10 \times CH_2$), 1.22-1.31 (m, 8H, $4 \times CH_2$), 1.52-1.62 (m, 4H, $2 \times CH_2CH_2[N^+]$), 2.10 (q, 2H, $CH_3CH_2COO^-$, $J = 7.6$ Hz), 3.26 (s, 6H, $2 \times CH_3[N^+]$), 3.32-3.35 (m, 4H, $2 \times CH_2[N^+]$) ppm.



b) ^{13}C NMR (CDCl_3 , 125.8 MHz), δ : 10.85 (CH_3), 13.84 ($2 \times \text{CH}_3$), 22.39 ($2 \times \text{CH}_2$), 22.48 ($2 \times \text{CH}_2$), 26.06 ($2 \times \text{CH}_2$), 28.94 ($2 \times \text{CH}_2$), 28.97 ($2 \times \text{CH}_2$), 29.11 ($2 \times \text{CH}_2$), 29.15 ($2 \times \text{CH}_2$), 30.93 ($\text{CH}_3\text{CH}_2\text{COO}^-$), 31.57 ($2 \times \text{CH}_2$), 50.80 ($2 \times \text{CH}_3$), 63.21 ($2 \times \text{CH}_2$), 179.54 (COO^-) ppm.



1.2. The synthesis of didecylmethylammonium hydrogen sulphate $[N_{10,10,1,H}][\text{HSO}_4]$, $M = 409,67 \text{ g/mol}$

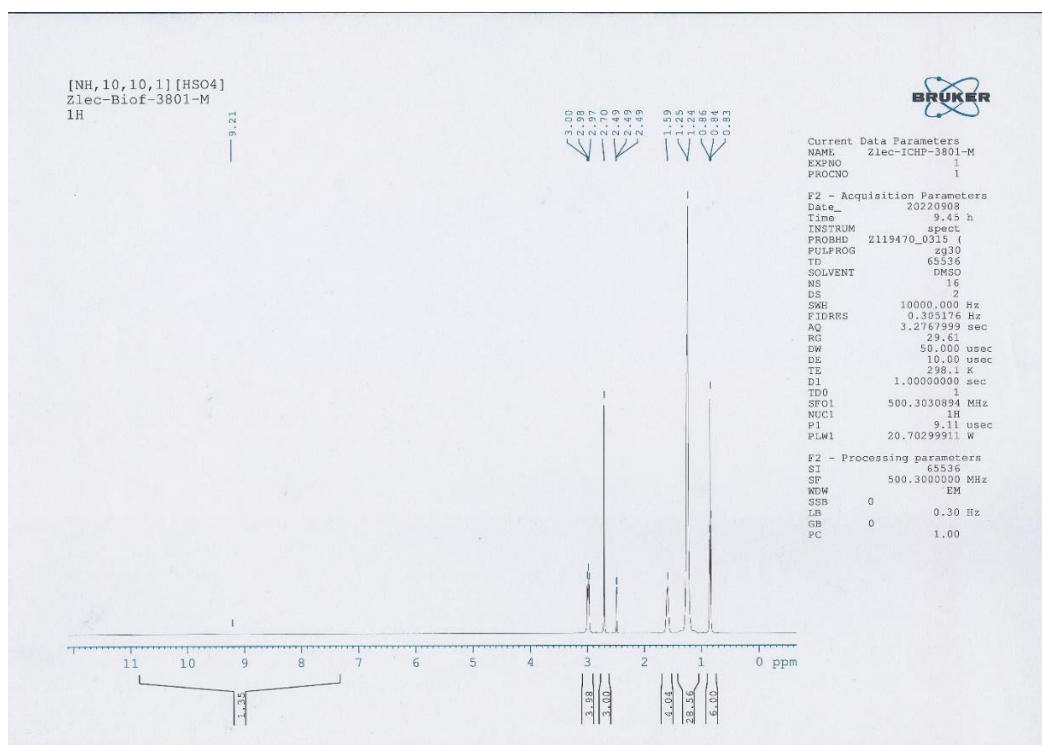


The 98.4 g of 95 wt % *N*-methyldidecylamine (0.3 mol) was placed in a 500 cm³ three-neck flask equipped with a thermometer, reflux condenser, dropping funnel, magnetic stirrer and cooled in an ice-water bath. The 30.65 g of 96 wt% sulphuric acid (0.3 mol) dissolved in 250 cm³ of water at the temperature $T = 293\text{-}298 \text{ K}$. A white solid product was formed during the addition of H_2SO_4 . After the completion of the dropwise addition, the reaction mixture was

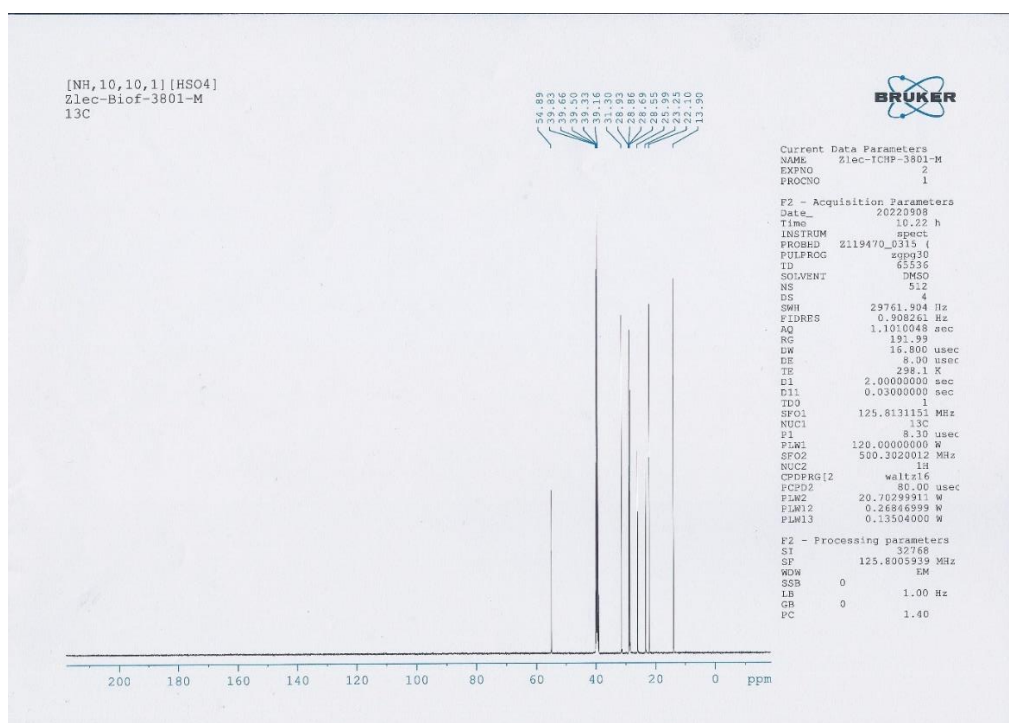
stirred at the temperature $T = 293$ - 298 K for 18 h. Next, water was separated by distillation under the reduced pressure. The residue was dried at the temperature $T = 333$ K under the pressure 1.3 hPa (10 h). The 122.3 g (0.298 mol) of didecylmethylammonium hydrogen sulfate was obtained as a white solid. The yield 99%.

Figure S2. NMR of didecylmethylammonium hydrogen sulphate, $[N_{10,10,1,H}][HSO_4]$,: a) 1H NMR; b) ^{13}C NMR,

1H NMR (DMSO- d_6 , 500 MHz), δ : 0.84 (t, 6H, $2 \times CH_3CH_2$, $J = 7.5$ Hz), 1.17-1.32 (m, 28H, $14 \times CH_2$), 1.56-1.64 (m, 4H, $2 \times CH_2CH_2[NH^+]$), 2.70 (s, 3H, $CH_3[NH^+]$), 2.97-3.00 (m, 4H, $2 \times CH_2[N^+]$), 9.21 (s, 2H, NH^+ and HSO_4^-) ppm.



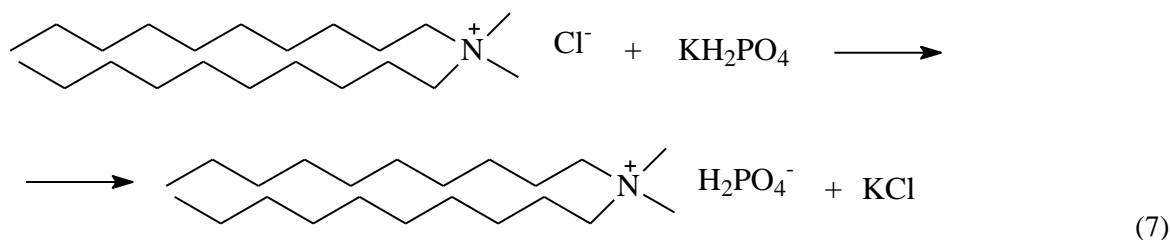
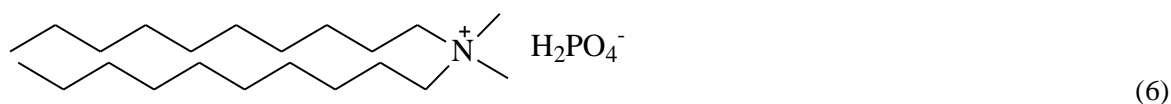
^{13}C NMR (DMSO- d_6 , 125.8 MHz), δ : 13.90 ($2 \times CH_3$), 22.10 ($2 \times CH_2$), 23.25 ($2 \times CH_2$), 25.99 ($2 \times CH_2$), 28.55 ($2 \times CH_2$), 28.69 ($2 \times CH_2$), 28.86 ($2 \times CH_2$), 28.93 ($2 \times CH_2$), 31.30 ($2 \times CH_2$), 39.33 ($CH_3[NH^+]$), 54.89 ($2 \times CH_2[NH^+]$) ppm.



NMR spectra were recorded on spectrometer Avance Bruker 500 MHz in the presence tetramethylsilane (TMS) as an internal standard.

1.3. The synthesis of didecyldimethylammonium dihydrogen phosphate $[N_{10,10,1,1}][H_2PO_4]$

$(C_{22}H_{50}NO_4P)$, $M = 423.7 \text{ g/mol}$



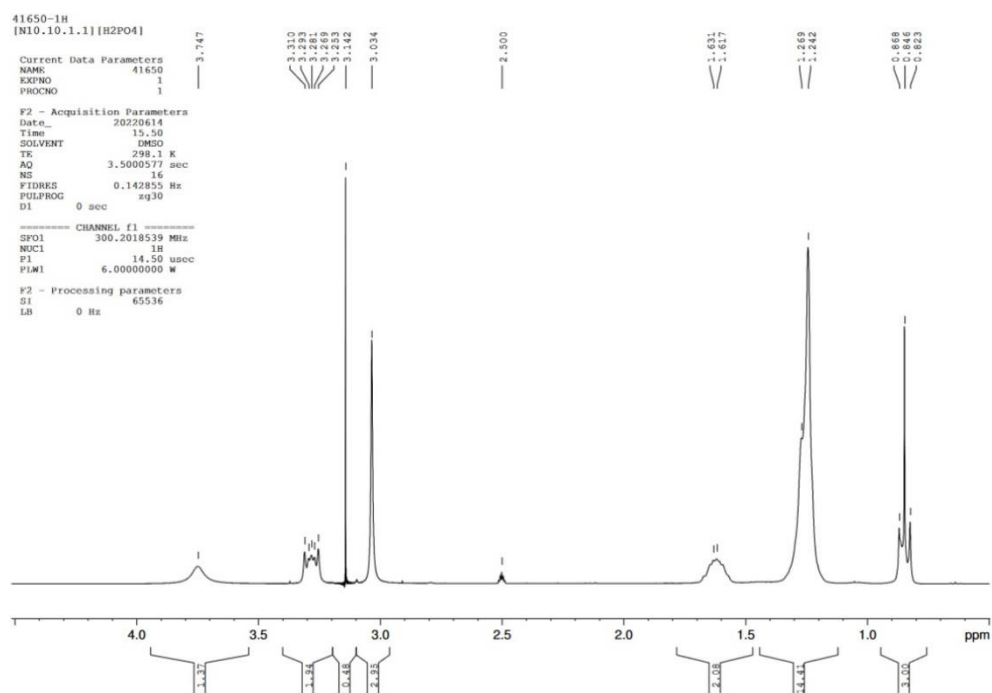
The 27.22 g (0.2 mol) of potassium dihydrogen phosphate was placed in 500 cm³ reaction flask. Next 75 cm³ of deionized water was added and heated to the temperature $T = 333 \text{ K}$. Then, 144.86 g of a 50 wt% solution of didecyldimethylammonium chloride (72.43 g $[N_{10,10,1,1}][\text{Cl}]$, 0.2 mol) was added. The contents of the flask were stirred for 8 h at the temperature $T = 343 \text{ K}$.

Cloudiness occurred upon stirring and two phases appeared. The mixture was cooled to the temperature $T = 303$ K and next two phases were separated. The upper phase containing IL was concentrated by the distillation of water under the reduced pressure and the residue was dried under the pressure 1.3 hPa (333 K, 10 h). 80 cm³ of methanol was added to the residue, mixed and frozen to the temperature $T = 253$ K and left for 15 h. The precipitated KCl was collected by the filtration and the filtrate was concentrated by the distillation of methanol under the reduced pressure. The IL was dried under pressure 1.3 hPa for 10 h (333 K). 68.2 g (0,161 mol) of didecyldimethylammonium dihydrogen phosphate was obtained. Yield 80.5%.

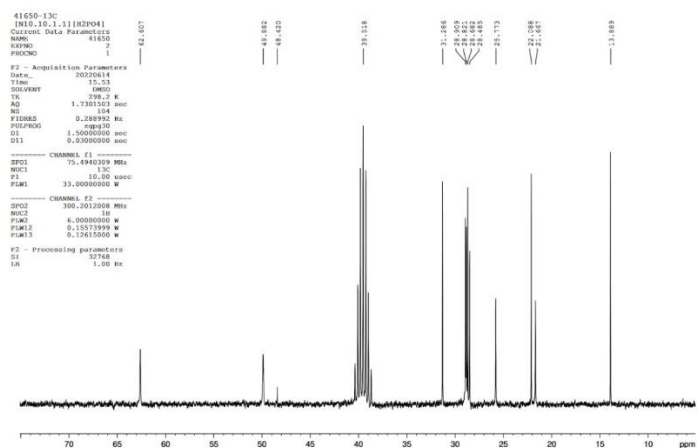
NMR spectra were recorded on the spectrometer 300 MHz in the presence of tetramethylsilane

Figure S3. NMR of didecyldimethylammonium dihydrogen phosphate, [N_{10,10,1,1}][H₂PO₄]: a) ¹H NMR; b) ¹³C NMR, c) ³¹P NMR

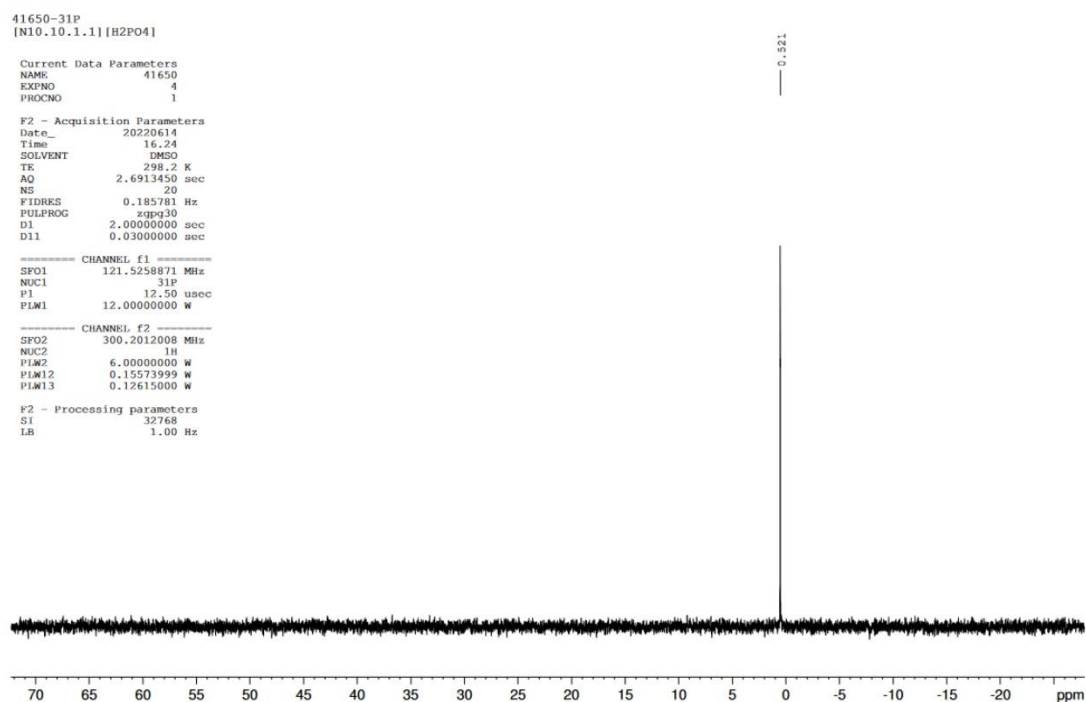
- a) ¹H NMR (300 MHz, DMSO-d₆), δ : 0.85 (t, 6H, 2 \times CH₃CH₂, J = 6.8 Hz), 1.18-1.35 (m, 28H, 14 \times CH₂), 1.56-1.69 (m, 4H, 2 \times CH₂CH₂[N⁺]), 3.03 (s, 6H, 2 \times CH₃[N⁺]), 3.25-3.31 (m, 4H, 2 \times CH₂[N⁺]), 3.75 (s, 2H, H₂PO₄⁻) ppm.



- b) ^{13}C NMR (75.5 MHz, DMSO- d_6), δ : 13.89 ($2 \times \text{CH}_3\text{CH}_2$), 21.67 ($2 \times \text{CH}_2$), 22.09 ($2 \times \text{CH}_2$), 25.77 ($2 \times \text{CH}_2$), 28.48 ($2 \times \text{CH}_2$), 28.68 ($2 \times \text{CH}_2$), 28.82 ($2 \times \text{CH}_2$), 28.91 ($2 \times \text{CH}_2$), 31.29 ($2 \times \text{CH}_2$), 49.88 ($2 \times \text{CH}_3[\text{N}^+]$), 62.61 ($2 \times \text{CH}_2[\text{N}^+]$) ppm.

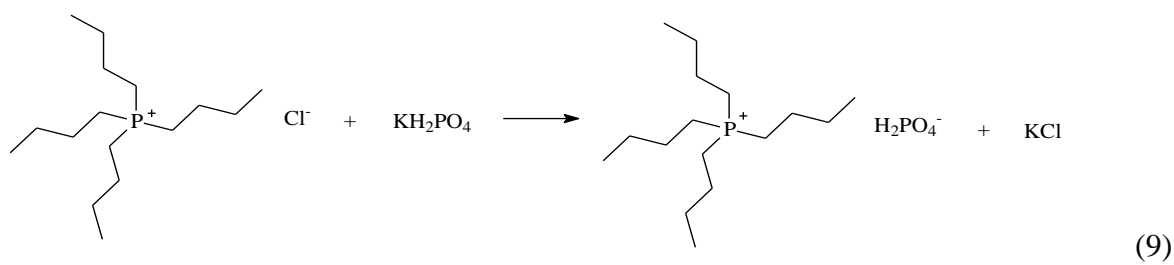


c) ^{31}P NMR (121.5 MHz, DMSO- d_6), δ : 0.52 (H_2PO_4^-) ppm.



1.4. The synthesis of tetrabutylphosphonium dihydrogen phosphate [$\text{P}_{4,4,4,4}$][H_2PO_4]

($\text{C}_{16}\text{H}_{38}\text{O}_4\text{P}_2$), $M = 356.48 \text{ g/mol}$

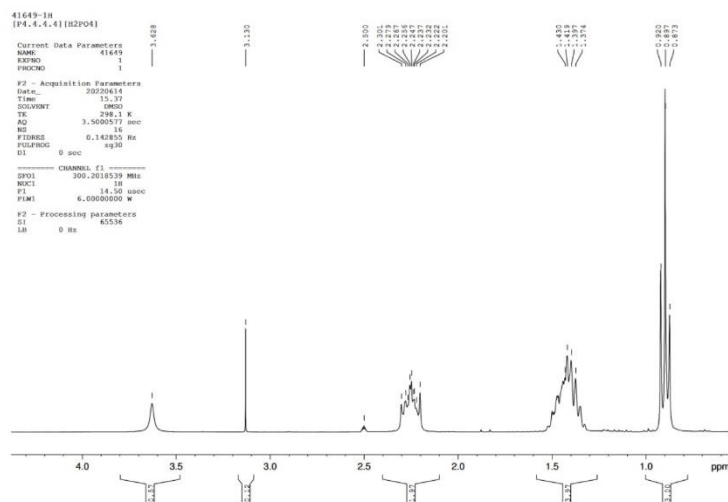


In 250 cm³ reaction flask a solution of tetrabutylphosphonium chloride (58.98 g, 0.2 mol) in deionized water (60 cm³) was placed and heated to the temperature $T = 333$ K. A solution of potassium dihydrogen phosphate (27.22 g, 0.2 mol) in deionized water (80 cm³) was heated to the temperature $T = 333$ K and slowly added to the solution of tetrabutylphosphonium chloride. After addition of the solution of KH₂PO₄, turbidity appeared and two phases separated. The contents of the flask were stirred at the temperature $T = 343$ K for 8 h. The reaction mixture was cooled to the temperature $T = 303$ K and two phases were separated. The slightly colored upper phase containing the IL was concentrated by the distillation of water under reduced pressure and the residue was dried at the temperature $T = 333$ K for 10 h (1.3 hPa). 80 cm³ of methanol was added to the residue, mixed and frozen to the temperature $T = 253$ K and left at this temperature for 15 h. The precipitated KCl was collected by the filtration and the filtrate was concentrated by the distillation of methanol under the reduced pressure. The IL was dried under the pressure 1.3 hPa for 10 h (333 K). 55.6 g (0.156 mol) of tetrabutylphosphonium dihydrogen phosphate was obtained. Yield 78%.

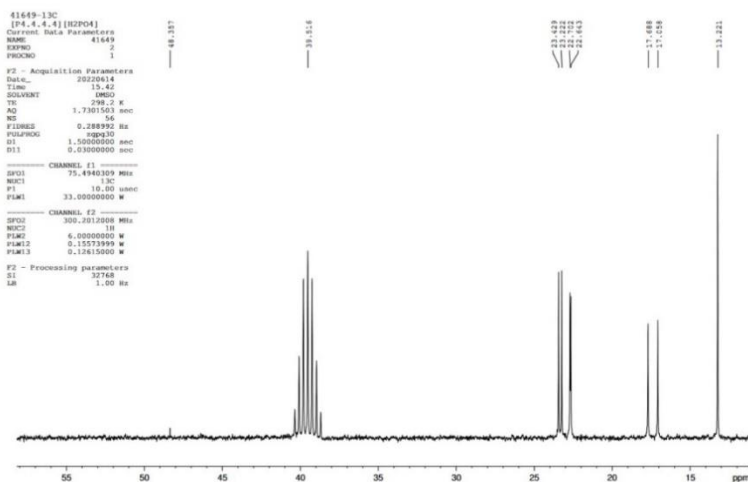
NMR spectra were recorded on the spectrometer 300 MHz in the presence of tetramethylsilane

Figure S4. NMR of tetrabutylphosphonium dihydrogen phosphate [P_{4,4,4,4}][H₂PO₄]: a) ¹H NMR; b) ¹³C NMR, c) ³¹P NMR

¹H NMR (300 MHz, DMSO-d₆), δ : 0.90 (t, 12H, 4 \times CH₃, J = 7.0 Hz), 1.32-1.51 (m, 16H, 8 \times CH₂), 2.20-2.30 (m, 8H, 4 \times CH₂[P⁺]), 3.63 (s, 2H, H₂PO₄⁻) ppm.



- a) ^{13}C NMR (75.5 MHz, DMSO- d_6), δ : 13.22 ($4 \times \text{CH}_3$), 17.06 ($2 \times \text{CH}_2$), 17.69 ($2 \times \text{CH}_2$), 22.64 ($2 \times \text{CH}_2$), 22.70 ($2 \times \text{CH}_2$), 23.22 ($2 \times \text{CH}_2$), 23.43 ($2 \times \text{CH}_2$) ppm.



- b) ^{31}P NMR (121.5 MHz, DMSO- d_6), δ : 33.71 ($(\text{CH}_2)_4[\text{P}^+]$) ppm.

