

Electronic Supplementary Information

**Synthesis of glucaminium-based ionic liquids and their application
in the removal of boron from water**

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Experimental

Materials:

N-methyl-D-glucamine, boric acid, 1-bromodecane, chromotropic acid, ethylenediaminetetraacetic acid and sodium perchlorate was obtained from Sigma-aldrich, St.louis, MO, USA. Hydrochloric acid, methanol, isopropanol, sodium carbonate, ammonium acetate, disodium phosphate, ethyl acetate and toluene were purchased from Fisher Scientific, (Fair lawn, NJ). Pyridine and 4-dimethylaminopyridine (DMAP) was obtained from Acros, (Morris Plains, NJ, USA). N-octyltrimethyl ammonium chloride was purchased from TCI America, (Portland, OR). Potassium tris-(pentafluoroethyl)trifluorophosphate was obtained from Merck KGaA, (Darmstadt, Germany).

Synthesis of N-decyl-N-methyl-D-glucamine (1):

N-decyl-N-methyl-D-glucamine **1** was synthesized by combining two moles of N-methyl-D-glucamine with one mole of 1-bromodecane and 0.5 mole of sodium carbonate in 150 mL of methanol and stirred at 50-55 °C for 48 hours. To this reaction mixture, 250 mL methanol was added and the temperature increased to 50-55 °C and kept for 45 minutes. Methanol was completely removed under reduced pressure and the product suspended in 300 mL of DI water to remove unreacted N-methyl-D-glucamine. To this, 150 mL of ethyl acetate was added. The solid product was filtered using vacuum filtration and dried at room temperature. The product was recrystallized using ethanol and dried under vacuum for 24 hours at 70 °C. The melting point for compound **1** was found to be 85 °C. The yield was 88.6 %.

¹H-NMR (d₆-DMSO, 600 MHz): 0.8 ppm (*t*, 3H, *J* = 6.8, -CH₃), 1.2 ppm (*m*, 14H, -CH₂), 1.3 ppm (*t*, 2H, *J* = 6.4, -CH₂), 2.1 ppm (*s*, 3H, -CH₃), 2.3 ppm (*d*, 2H, *J* = 2.4, -CH₂OH), 4.3 ppm (*t*, 2H, *J* = 5.2, -NCH₂), 4.4 ppm (*d*, 2H, *J* = 5.6, -NCH₂), 2.4, 3.4, 3.5, 3.6 ppm (*m*, 1H, -CHOH), 4.6 ppm (*s*, 1H, -OH).

¹³C-NMR (d₆-DMSO, 400 MHz): 14.0 ppm (-CH₃), 22.1 ppm (-CH₂), 26.6, 26.9, 28.7, 29.0, 29.0, 29.1, 31.3 ppm (-CH₂), 42.5 ppm (N-CH₃), 58.0, 60.2 ppm (N-CH₂), 63.5 ppm (-CH₂OH), 70.3, 70.4, 71.4, 72.0 ppm (-CHOH).

Synthesis of N,N-didecyl-N-methyl-D-glucaminium bromide (2):

Synthesis of N,N-didecyl-N-methyl-D-glucaminium bromide **2** included reaction of one mole of N-decyl-N-methyl-D-glucamine **1** with one mole of 1-bromodecane in isopropanol for 72 hours at 70 °C. Isopropanol was completely removed under reduced pressure to obtain the final product. The product was dried under vacuum at 70 °C for 24 hours. The yield was 83.4 %.

¹H-NMR (d₆-DMSO, 600 MHz): 0.8 ppm (*t*, 6H, *J* = 6.8, -CH₃), 1.2 ppm (*m*, 29H, -CH₂), 1.6 ppm (*t*, 2H, *J* = 6.8, -CH₂), 2.9 ppm (*s*, 3H, -CH₃), 3.4 ppm (*m*, 2H, -NCH₂), 3.4, 3.5, 3.6, 3.9 ppm (*m*, 1H, -CHOH), 5.3 ppm (*d*, 1H, *J* = 4.8, -NCH₂), 4.8 ppm (*d*, 1H, *J* = 6.0, -NCH₂), 2.4, 3.6, 3.7, 4.1 ppm (*s*, 1H, -OH), 4.6 ppm (*d*, 2H, *J* = 5.2, -CH₂OH).

¹³C-NMR (d₆-DMSO, 400 MHz): 13.9 ppm (-CH₃), 21.4, 22.1 ppm (-CH₂), 25.4, 25.8, 26.2, 28.5, 28.7, 28.8, 28.9, 31.3 ppm (-CH₂), 48.5 ppm (N-CH₃), 58.0, 60.2 ppm (N-CH₂), 63.5 ppm (-CH₂OH), 70.3, 70.4, 71.4, 72.0 ppm (-CHOH).

Experimental result for elemental analysis: C 57.31%, H 10.79%, N 2.89%

Theoretical values for elemental analysis: C 58.26%, H 10.50%, N 2.52%

Synthesis of N-decyl-N-methyl-D-glucaminium chloride (3):

N-decyl-N-methyl-D-glucaminium chloride **3** was synthesized by reacting one mole of N-decyl-N-methyl-D-glucamine **1** with 1.1 mole of 12.1 M hydrochloric acid in water for 12 hours at room temperature. Water was completely removed under vacuum and the product was dried under vacuum at 70 °C for 24 hours. The percent yield was 98.9 %.

¹H-NMR (d₆-DMSO, 600 MHz): 0.8 ppm (*t*, 3H, *J* = 3.6, -CH₃), 1.2 ppm (*m*, 14H, -CH₂), 1.6 ppm (*m*, 2H, -CH₂), 2.7 ppm (*d*, 3H, *J* = 18.4, -CH₃), 2.9 ppm (*m*, 2H, -NCH₂), 3.0 ppm (*m*, 2H, -NCH₂), 3.4 ppm (*m*, 1H, -CHOH), 3.5 ppm (*d*, 1H, *J* = 7.2, -CHOH), 4.8 ppm (*d*, 1H, *J* = 11.6, -CHOH), 3.9 ppm (*m*, 1H, -CHOH), 3.4, 3.6, 4.4, 5.4 ppm (*s*, 1H, -OH), 4.6 ppm (*d*, 2H, *J* = 17.6, -CH₂OH), 9.1 ppm (*s*, 1H, -NH).

¹³C-NMR (d₆-DMSO, 400 MHz): 14.0 ppm (-CH₃), 22.2, 23.6, 26.2, 28.7, 28.8, 29.0, 29.0, 31.4 ppm (-CH₂), 40.6 ppm (N-CH₃), 55.9, 57.9 ppm (N-CH₂), 63.5 ppm (-CH₂OH), 67.6, 70.4, 71.2 ppm (-CHOH).

Experimental result for elemental analysis: C 54.67%, H 10.59%, N 3.99%

Theoretical values for elemental analysis: C 54.90%, H 10.30%, N 3.77%

Synthesis of peracetylated N-decyl-N-methyl-D-glucaminium chloride (4):

One mole of N-decyl-N-methyl-D-glucaminium chloride **3** was dissolved in 10 mL of pyridine followed by the addition of eight moles of acetic anhydride. A catalytic amount of DMAP was added. The reaction was stirred for 12 hours at room temperature. Pyridine was completely removed by co-distillation with toluene. The resulting solid was dissolved in water and the product isolated using ethyl acetate. Ethyl acetate was completely removed under reduced pressure and the product was dried under vacuum for 24 hours at 70 °C. The yield was found to be 89.9 %.

¹H-NMR (d₆-DMSO, 600 MHz): 0.8 ppm (*t*, 3H, *J* = 6.6, -CH₃), 1.2 ppm (*m*, 14H, -CH₂), 1.6 ppm (*m*, 2H, -CH₂), 1.9 ppm (*s*, 6H, -COCH₃), 2.0 ppm (*s*, 9H, -COCH₃), 3.3 ppm (*s*, 3H, -CH₃), 4.0, 4.3 ppm (*m*, 1H, -NCH₂), 5.3 ppm (*d*, 2H, *J* = 5.4, -NCH₂), 3.3, 5.0 ppm (*m*, 1H, -CHOCO), 10.4 ppm (*s*, 1H, -NH).

¹³C-NMR (d₆-DMSO, 400 MHz): 13.9 ppm (-CH₃), 21.4, 20.4, 20.5, 20.5 (-COCH₃), 22.6, 25.4, 26.1, 28.5, 28.7, 28.8, 28.9, 31.3 ppm (-CH₂), 40.9 ppm (N-CH₃), 54.3, 56.9 ppm (N-CH₂), 61.2 ppm (-CH₂OCOCH₃), 68.5 (-CHOCOCH₃), 169.4, 169.6, 170.0, 171.9 ppm (-C=O).

Experimental result for elemental analysis: C 57.78%, H 8.72%, N 2.59%

Theoretical values for elemental analysis: C 55.71%, H 8.31%, N 2.41%

¹¹B NMR Experiments:

The ¹¹B NMR experiments were performed at room temperature (19 ± 1 °C) on a Varian VXR 400 MHz NMR spectrometer with a 5 mm broadband probe at a resonance frequency of 128.0 MHz. All measurements were performed in a 5 mm quartz tube obtained from Wilmad, (Vineland, NJ). Stock solutions of 0.1 M IL and 0.1 M boric acid were prepared in DI water. All buffer solutions were prepared in deionized water. The sample for ¹¹B NMR was prepared by taking different volumes of stock solutions where D₂O was present 10-30 % of the total sample volume. The sample pH was adjusted by using different buffer solutions. The parameters for ¹¹B NMR were as follows:

The flip angle: 75 °

Pulse repetition time: 0.06 Sec

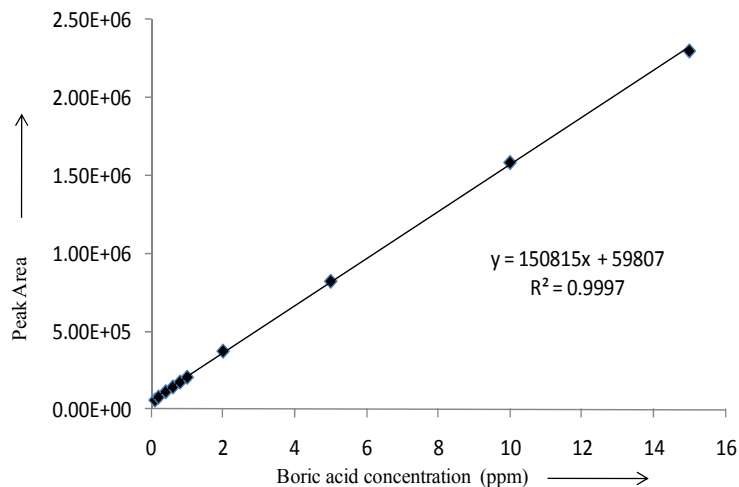
The spectral width: 27.0 KHz

Number of scans received: 8064

Sample preparation and Calibration curve for HPLC method:

All measurements were performed on Simadzu LC20-AT HPLC instrument. A TSK gel anion exchange column IC-Anion-PW (5.0 cm X 4.6 mm (ID)) was obtained from Tosoh Bioscience (Montgomeryville, PA, USA). 5.0 mL of aqueous phase was placed in a polypropylene tube. In this, 0.25 mL of solution A (0.016 M chromotropic acid and 0.1 M EDTA) and 0.25 mL of solution B (2.0 M octyltrimethylammonium chloride and 1.0 M sodium acetate) were added. The mixture was stirred well and kept in the dark for 2.5 hours. 10 µL aqueous phase was injected using a mobile phase consisting of 0.2 M sodium perchlorate and 0.001 M sodium acetate was used. The anionic complex peak was observed at 350 nm. The retention time for chromotropic acid and the anionic complex was 1 min and 3 min, respectively. The calibration curve was generated as shown below where the concentration of boric acid was varied from 0.1 to 15 ppm.

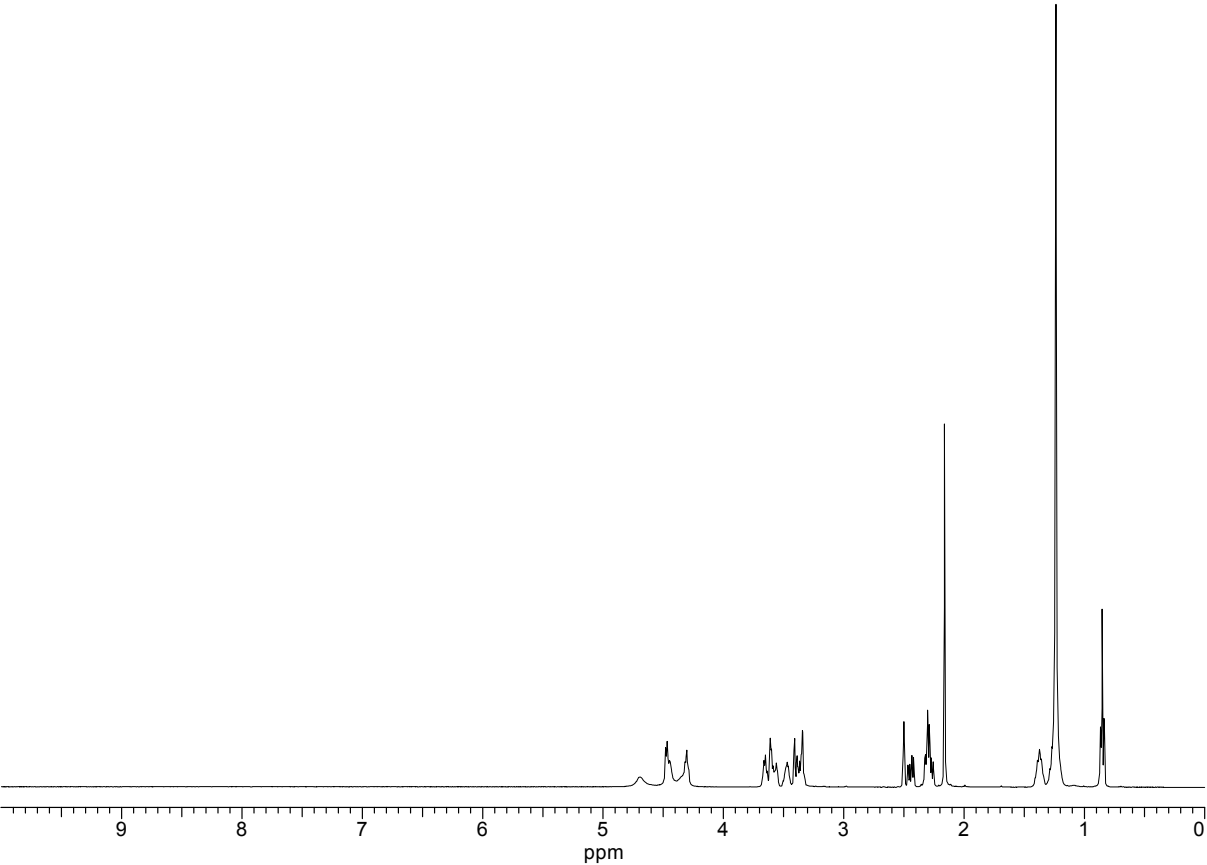
Boric acid Concentration (ppm)	Average Peak Area (N=6)	%Relative Standard Deviation
0.1	62834	2.1
0.2	82550	1.8
0.4	116635	1.2
0.6	146955	1.0
0.8	179120	0.9
1	209938	0.7
2	377247	0.5
5	825288	0.9
10	1587486	0.9
15	2303627	0.9



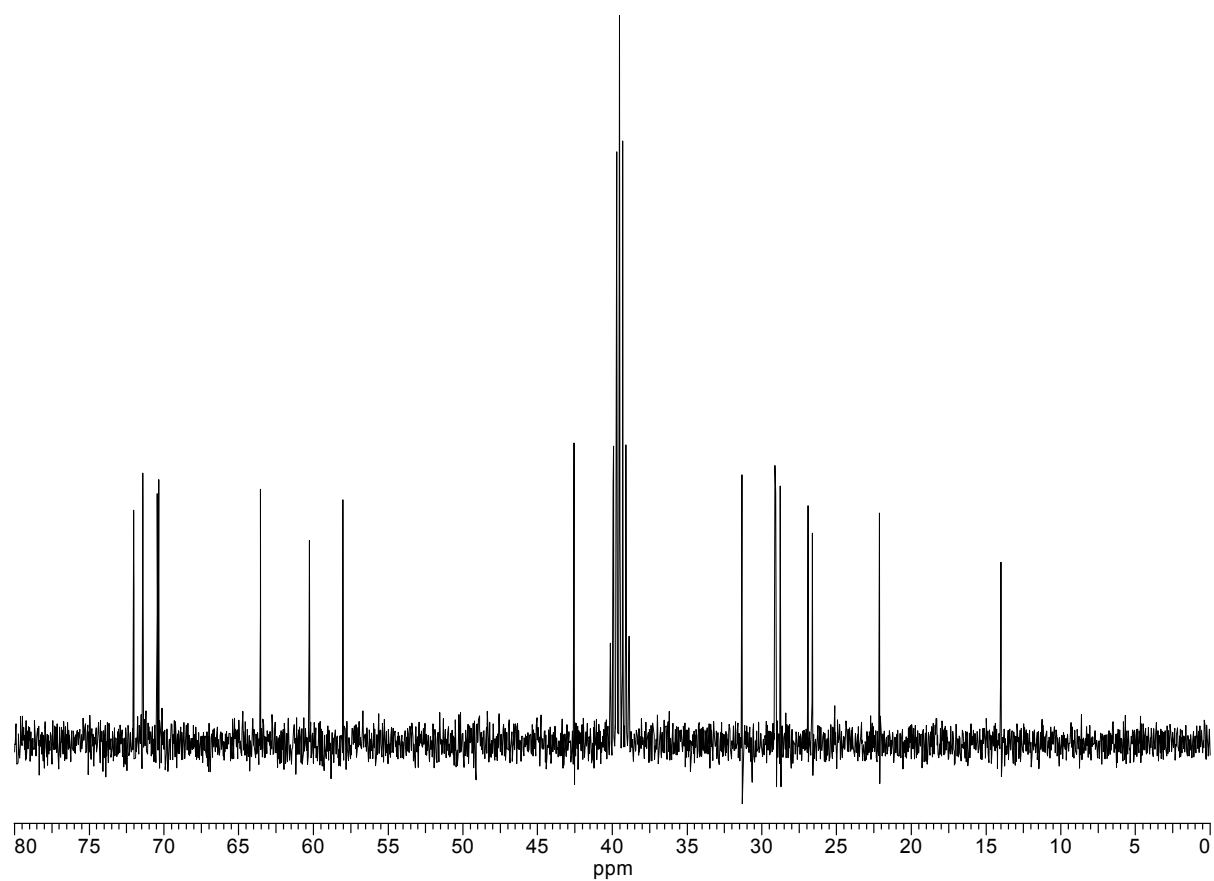
Scheme 2: *In-situ* dispersive liquid-liquid microextraction:

IL is dissolved in deionized water as shown in Scheme 2(a). An aqueous solution of boric acid is then added to this IL solution as shown in Scheme 2(b). The resulting solution is vortexed followed by the addition of an aqueous solution of metathesis salt potassium tris-(pentafluoroethyl)trifluorophosphate (KFAP). A cloudy solution immediately appears (Scheme 2(c)). This will be followed by the vortexing and centrifugation of the sample. As shown in Scheme 2(d), two separate layers can be observed where the top and bottom layer correspond to the aqueous and IL layers, respectively. Here, 0.05 g (9.78×10^{-5} moles) of IL was dissolved in 9.0 mL of a 10 ppm boric acid solution in a polypropylene tube. The solution was vortexed for 1 min. A cloudy solution was observed upon addition of 1.0 mL of 9.78×10^{-5} M potassium tris-(pentafluoroethyl)trifluorophosphate (KFAP) solution. The solution was vortexed for 1 min and centrifuged for 10 to 30 minutes. Two separate layers namely aqueous and IL layer were observed.

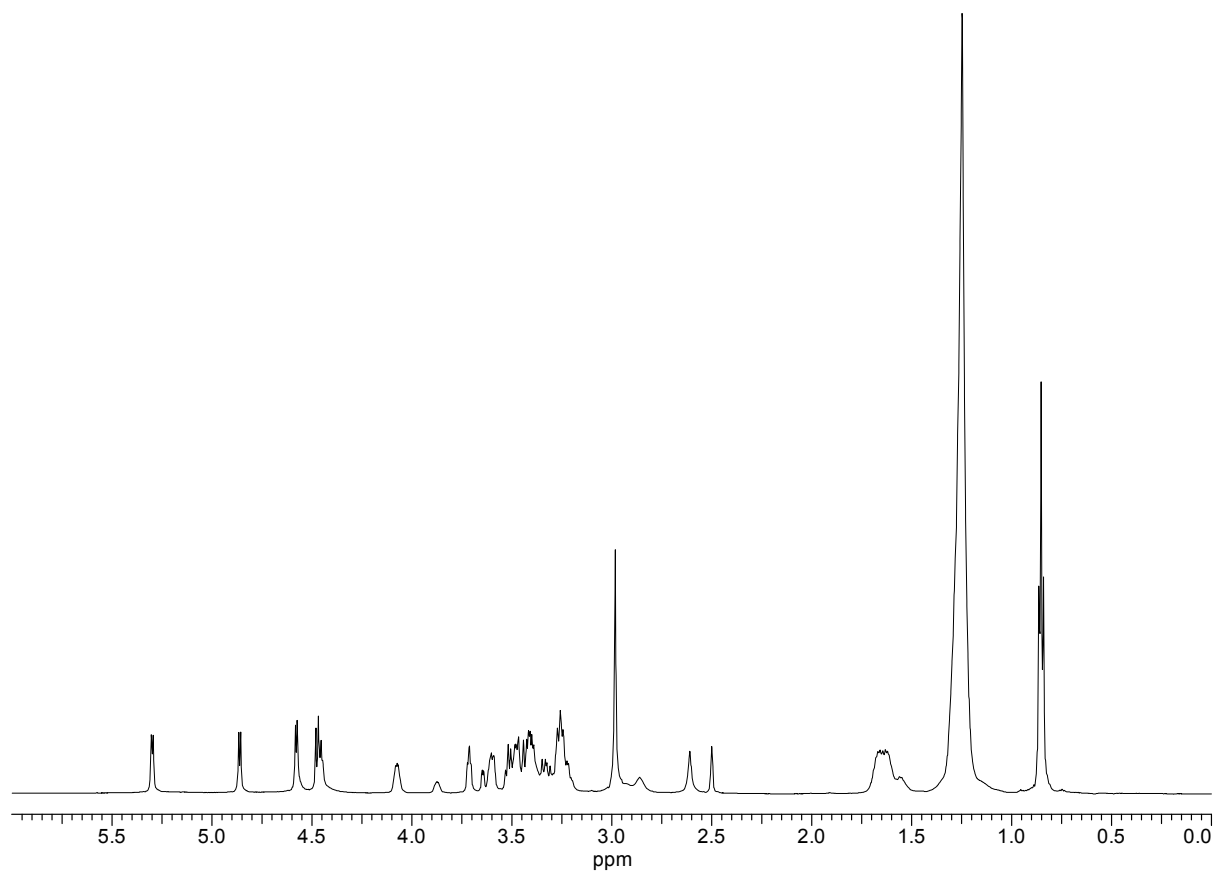
¹H NMR of N-decyl-N-methyl-D-glucamine (**1**):



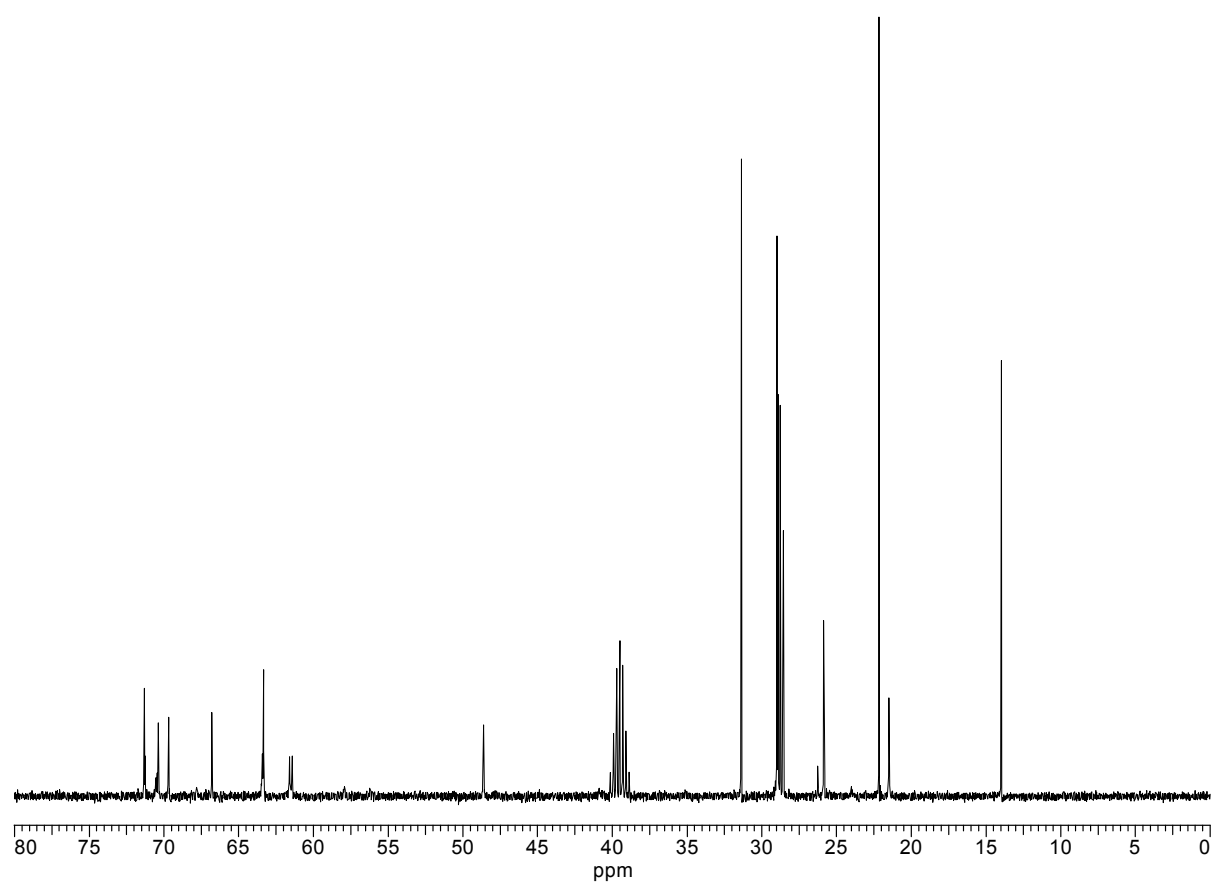
^{13}C NMR of N-decyl-N-methyl-D-glucamine (**1**):



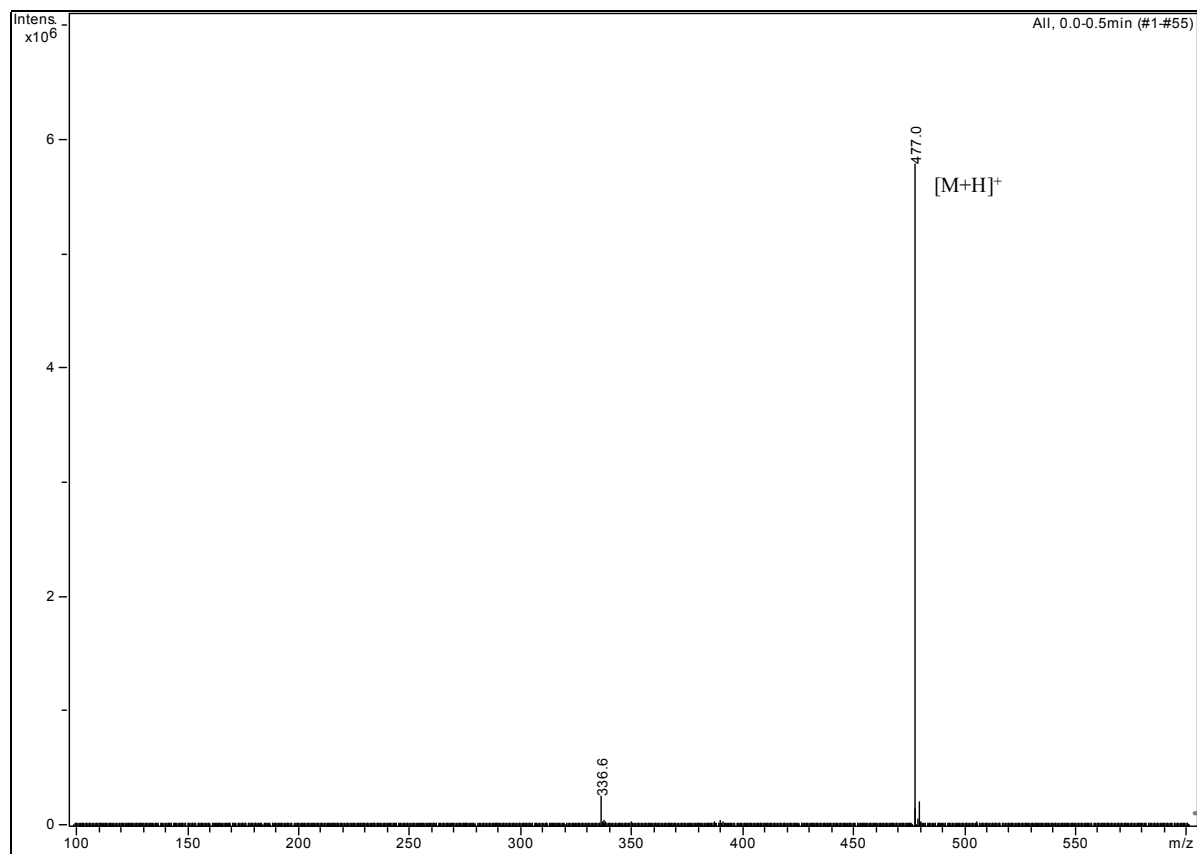
^1H NMR for N,N-didecyl-N-methyl-D-glucaminium bromide (**2**):



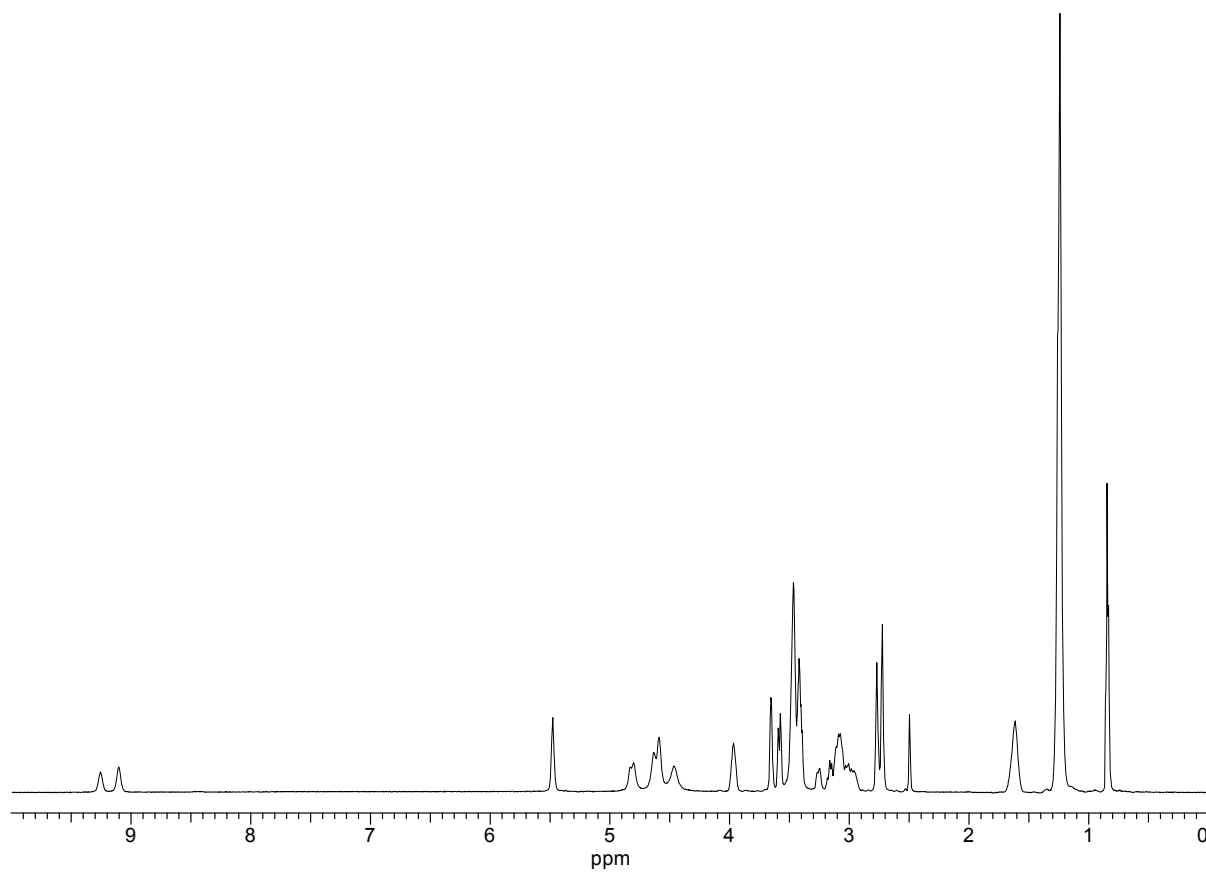
^{13}C NMR for N,N-didecyl-N-methyl-D-glucaminium bromide (**2**):



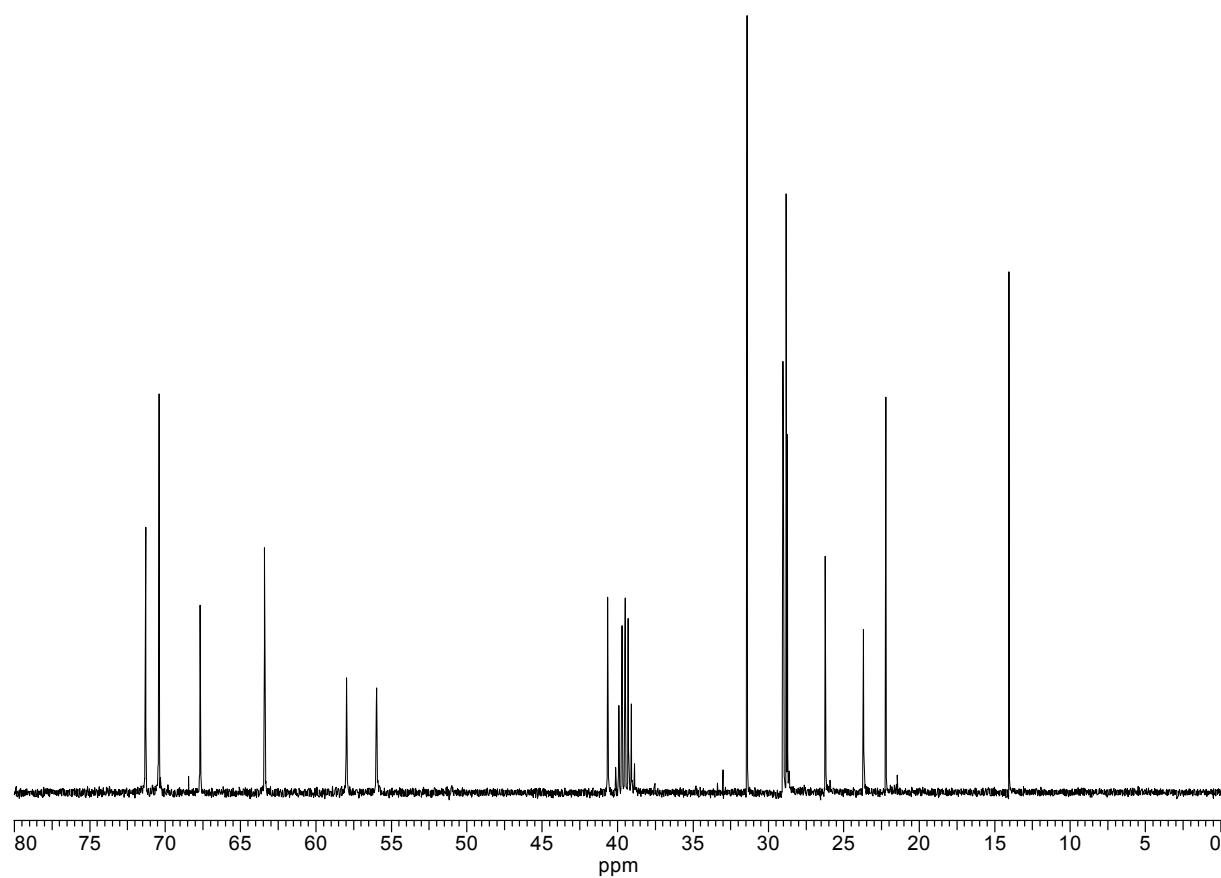
ESI mass spectrum of N,N-didecyl-N-methyl-D-glucaminium bromide (**2**):



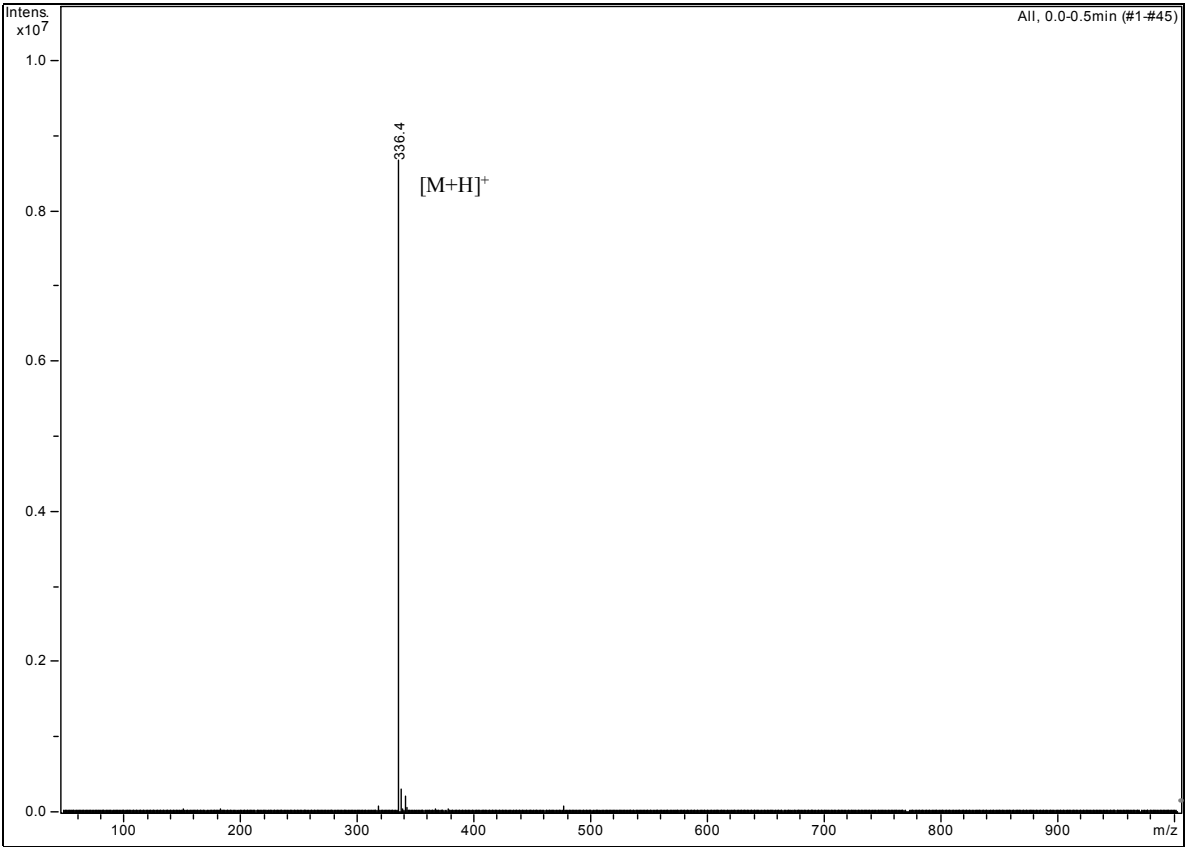
^1H NMR for N-decyl-N-methyl-D-glucaminium chloride (**3**):



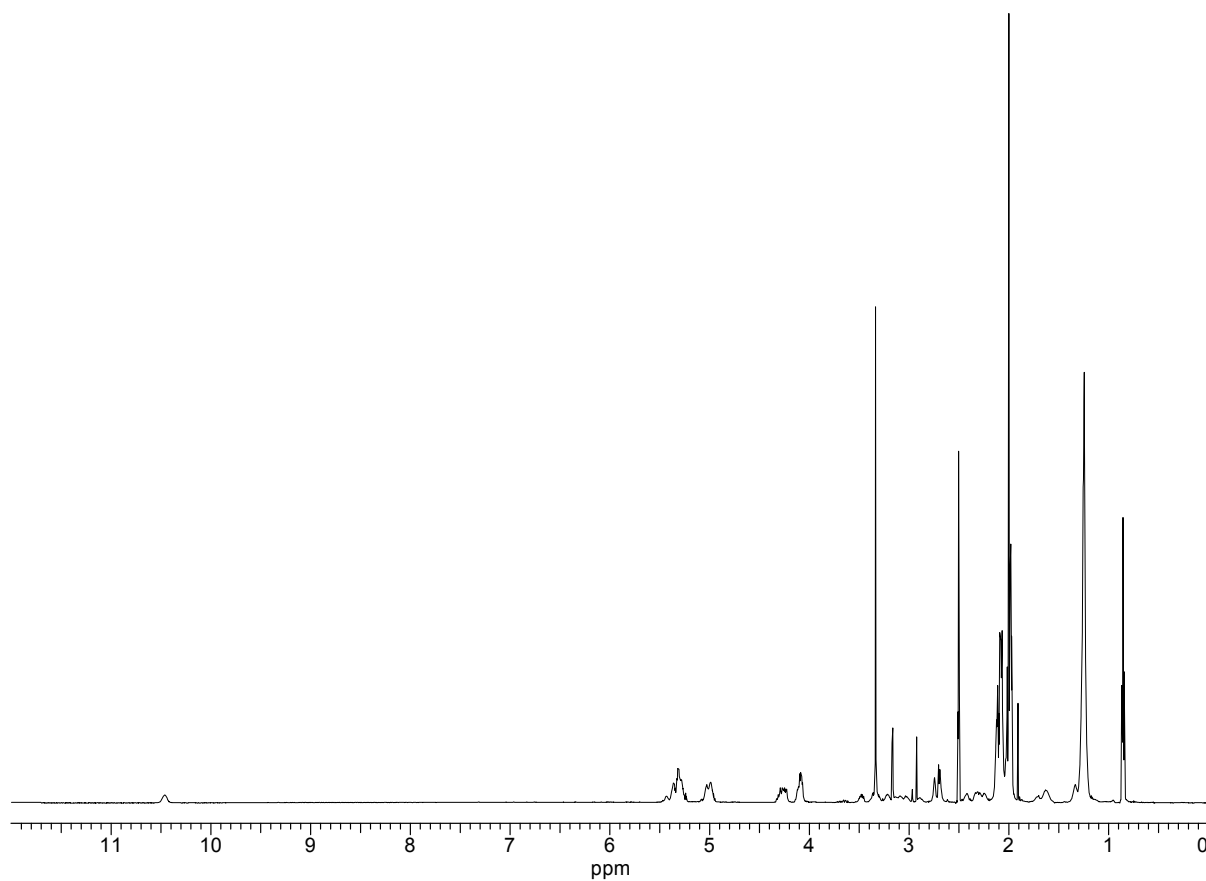
^{13}C NMR for N-decyl-N-methyl-D-glucaminium chloride (**3**):



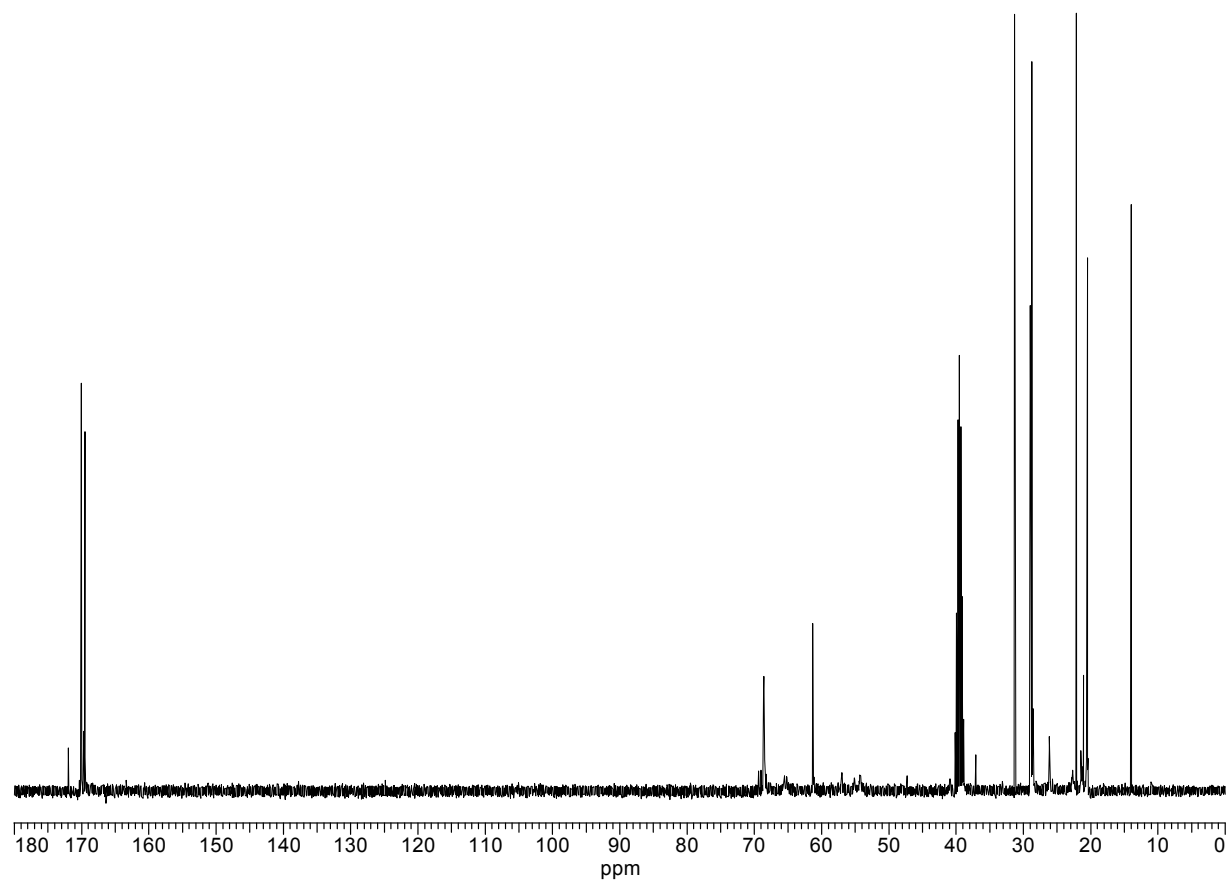
ESI mass spectrum for N-decyl-N-methyl-D-glucaminium chloride (**3**):



^1H NMR for peracetylated N-decyl-N-methyl-D-glucaminium chloride (**4**):



^{13}C NMR for peracetylated N-decyl-N-methyl-D-glucaminium chloride (**4**):



ESI mass spectrum for peracetylated N-decyl-N-methyl-D-glucaminium chloride (**4**):

