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Mechanism of Cellulose Dissolution in the Ionic Liquid 1-n-Butyl-3-Methylimidazolium Chloride: A ^{13}C and $^{35/37}Cl$ NMR Relaxation Study on Model Systems

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Supporting Information

Calculation of Interaction Stoichiometries From $^{35/37}Cl$ Linewidth Data

As discussed in the text, the $^{35/37}Cl$ linewidth data can be employed to investigate the interaction stoichiometry between the chloride ions and the OH groups of the sugar solutes. In the case of a rapid exchange process (*vide infra*), the following relationship is valid:[14,15]

$$\lambda_{obs} = \lambda_{free} \cdot \chi_{Cl^-_{free}} + \lambda_{bound} \cdot \chi_{Cl^-_{bound}} \; ; \chi_{Cl^-_{free}} + \chi_{Cl^-_{bound}} = 1$$

where $\chi_{Cl^-_{free}}$ and $\chi_{Cl^-_{bound}}$ are the molar fractions of free and interacting (i.e., bound) chloride ions, and the remaining quantities are defined in the text. The chloride ion molar fractions can be computed from the moles of free and bound chloride species, which can in turn be expressed as a function of the chloride-to-carbohydrate interaction stoichiometry (*N*), the molecular weights of the sugar and the IL (MW_{carb} and MW_{IL}), and the wt% concentration of carbohydrate solute if 100 g of solution is used for the calculations:

$$\chi_{Cl^-_{free}} = \frac{\text{moles of } Cl^-_{free}}{\text{moles of } Cl^-_{total}} = \frac{\dfrac{100 - [carb]_{\%}}{MW_{IL}} - N \cdot \dfrac{[carb]_{\%}}{MW_{carb}}}{\dfrac{100 - [carb]_{\%}}{MW_{IL}}} = 1 - N \cdot \frac{[carb]_{\%} \cdot MW_{IL}}{MW_{carb} \cdot (100 - [carb]_{\%})}$$

$$\chi_{Cl^-_{bound}} = \frac{\text{moles of } Cl^-_{bound}}{\text{moles of } Cl^-_{total}} = \frac{N \cdot \dfrac{[carb]_{\%}}{MW_{carb}}}{\dfrac{100 - [carb]_{\%}}{MW_{IL}}} = N \cdot \frac{[carb]_{\%} \cdot MW_{IL}}{MW_{carb} \cdot (100 - [carb]_{\%})}$$

Substitution of these values into the original relationship yields:

$$\lambda_{obs} = \lambda_{free} \cdot \left(1 - N \cdot \frac{[\text{carb}]_{\%} \cdot \text{MW}_{\text{IL}}}{\text{MW}_{\text{carb}} \cdot (100 - [\text{carb}]_{\%})}\right) + \lambda_{bound} \cdot N \cdot \frac{[\text{carb}]_{\%} \cdot \text{MW}_{\text{IL}}}{\text{MW}_{\text{carb}} \cdot (100 - [\text{carb}]_{\%})}$$

which can be rearranged to obtain the equation presented in the text:

$$\lambda_{obs} = \lambda_{free} + (\lambda_{bound} - \lambda_{free}) \cdot N \cdot \frac{[\text{carb}]_{\%} \cdot \text{MW}_{\text{IL}}}{\text{MW}_{\text{carb}} \cdot (100 - [\text{carb}]_{\%})}$$

The two unknown parameters in the above relationship are N and λ_{bound}, which were estimated by non-linear fitting to the $^{35/37}$Cl linewidth versus sugar concentration data presented in **Tables S2** and **S3** using Mathematica 5.0 (Wolfram Research, Inc., Champaign, IL). Fits against ^{35}Cl data yields N estimates of 7.8 and 4.9 and λ_{bound} values of 9119.5 and 6867.6 Hz for cellobiose and glucose, respectively. If the calculations are repeated using ^{37}Cl linewidth data, N values of 7.6 and 4.8 and λ_{bound} values of 6601.3 and 4424.8 Hz are obtained for cellobiose and glucose, respectively. In order to corroborate these results, solutions of 19.7 wt% cellobiose and 17.1 wt% glucose in [C_4mim]Cl, which correspond to the theoretical saturation concentrations computed from N values of 8 and 5 for each sugar were prepared, and their $^{35/37}$Cl linewidths were measured at 90 ºC. λ values of 9205.7 ± 208.9 Hz (^{35}Cl) and 6491.4 ± 180.2 Hz (^{37}Cl) for the 19.7 wt% cellobiose solution, and 6934.0 ± 91.8 Hz (^{35}Cl) and 4528.5 ± 152.1 Hz (^{37}Cl) for the 17.1 wt% glucose solution were determined experimentally. These results agree remarkably well with the non-linear fit estimates presented above, and serve to further validate the interaction stoichiometry calculations described in the text.

As stated earlier, the above derivations hold true only for rapid exchange processes. In order to establish that this is indeed the case for the systems studied, the ratio between the ^{35}Cl and ^{37}Cl linewidths, $\lambda_{^{35}\text{Cl}} / \lambda_{^{37}\text{Cl}}$, was determined in all cases. It can be shown that in a rapid exchange regime this ratio is equal to the square of the ratio between the ^{35}Cl and ^{37}Cl quadrupole moments, $Q_{^{35}\text{Cl}}$ and $Q_{^{37}\text{Cl}}$:[15]

$$\frac{\lambda_{^{35}\text{Cl}}}{\lambda_{^{37}\text{Cl}}} \approx \left(\frac{Q_{^{35}\text{Cl}}}{Q_{^{37}\text{Cl}}}\right)^2 \approx 1.6$$

Ratios between 1.6 and 1.0 indicate medium exchange, and values equal to 1.0 correspond to slow exchange processes. As shown in **Tables S1**-**S4**, the experimental $\lambda_{^{35}Cl}$ / $\lambda_{^{37}Cl}$ ratios are higher than 1.4 for all the systems considered in the study, and show that the interactions between the $[C_4mim]Cl$ chloride ions and the solutes are in a medium to rapid exchange regime when compared to the timescale of the NMR measurements.

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Table S1. Relaxation data for the ^{13}C and $^{35/37}Cl$ nuclei in neat [C_4mim]Cl as a function of temperature.

Temperature (ºC)	Relative viscosity[(a)]	T_1[(b)]									
		C-2	C-4	C-5	C-1'	C-2'	C-3'	C-4'	C-1"	^{35}Cl	^{37}Cl
40	28.2	0.443	0.409	0.424	0.305	0.293	0.416	1.271	1.734	136.5 ± 3.2	209.2 ± 3.8
50	11.1	0.322	0.298	0.299	0.256	0.300	0.455	1.414	1.281	159.7 ± 7.2	236.1 ± 3.6
60	5.36	0.257	0.239	0.235	0.225	0.321	0.520	1.572	1.038	211.5 ± 3.6	347.9 ± 3.7
70	2.78	0.237	0.225	0.224	0.219	0.359	0.616	1.807	0.894	307.2 ± 6.6	526.3 ± 5.0
80	1.63	0.256	0.246	0.243	0.240	0.441	0.775	2.253	0.932	498.8 ± 12.8	809.7 ± 3.4
90	1.00	0.287	0.275	0.270	0.276	0.522	0.945	2.547	1.026	717.7 ± 19.7	1187.0 ± 7.3

Temperature (ºC)	Relative viscosity	T_2										$\lambda_{^{35}Cl} / \lambda_{^{37}Cl}$
		C-2	C-4	C-5	C-1'	C-2'	C-3'	C-4'	C-1"	^{35}Cl	^{37}Cl	
40	28.2	0.028	0.030	0.025	0.030	0.068	0.119	0.412	0.145	45.5 ± 0.7	64.1 ± 0.8	1.41 ± 0.04
50	11.1	0.053	0.058	0.053	0.057	0.121	0.205	0.600	0.269	63.1 ± 1.6	87.1 ± 1.5	1.38 ± 0.06
60	5.36	0.089	0.093	0.088	0.089	0.194	0.317	0.970	0.405	97.5 ± 2.0	145.7 ± 0.8	1.49 ± 0.04
70	2.78	0.128	0.133	0.125	0.133	0.241	0.449	1.133	0.514	156.5 ± 2.0	249.5 ± 3.5	1.60 ± 0.04
80	1.63	0.170	0.175	0.174	0.173	0.320	0.668	1.398	0.664	258.8 ± 0.4	392.2 ± 2.4	1.52 ± 0.01
90	1.00	0.209	0.219	0.219	0.216	0.399	0.832	1.505	0.762	382.4 ± 7.6	597.2 ± 6.9	1.56 ± 0.05

a) Relative to the viscosity of neat [C_4mim]Cl measured at 90 ºC (60.9 ± 0.5 cP).

b) T_1 and T_2 relaxation times are in seconds and microseconds for ^{13}C and $^{35/37}Cl$ nuclei, respectively.

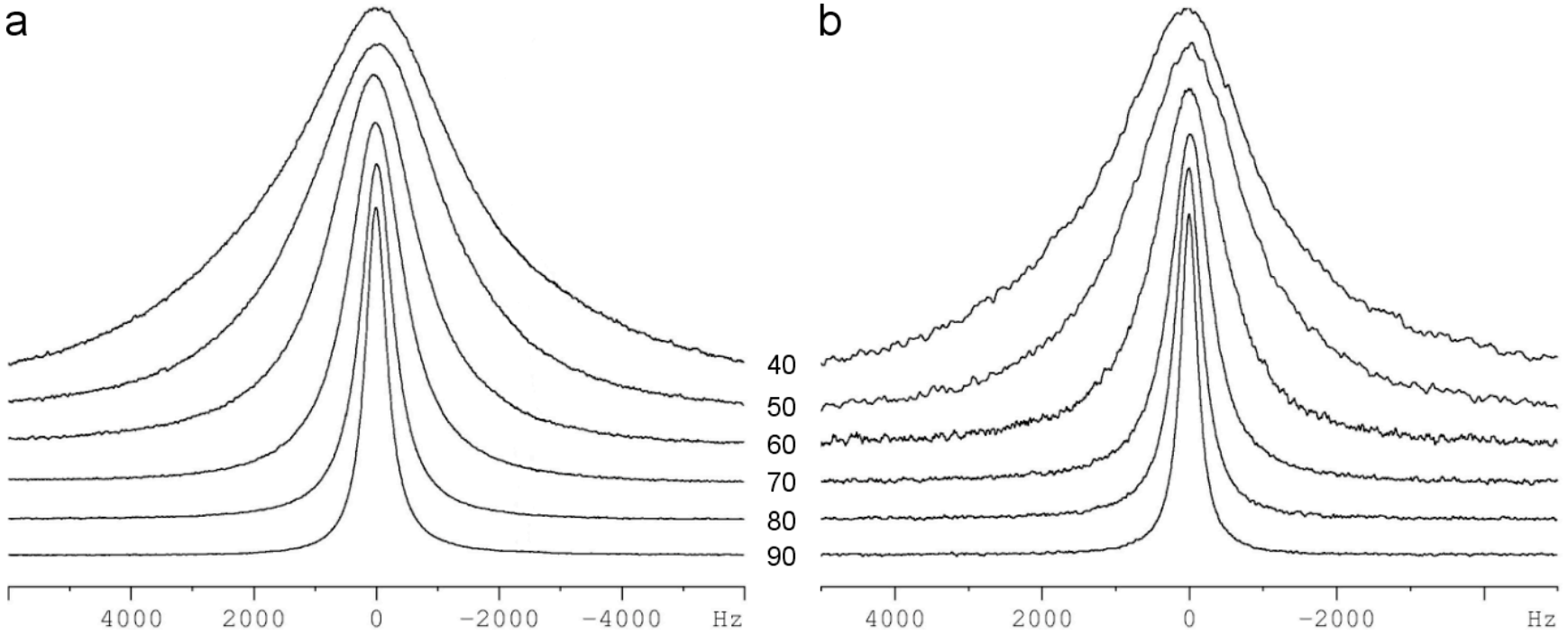

Figure S1. ^{35}Cl (**a**) and ^{37}Cl (**b**) spectra of neat [C_4mim]Cl as a function of temperature (ºC).

Table S2. Relaxation data for the ^{13}C and $^{35/37}Cl$ nuclei in $[C_4mim]Cl$ as a function of cellobiose concentration measured at 90 ºC.

[Cellobiose] (wt%)	Relative viscosity[(a)]	T_1[(b)]									
		C-2	C-4	C-5	C-1'	C-2'	C-3'	C-4'	C-1"	^{35}Cl	^{37}Cl
0.0	1.00	0.287	0.275	0.270	0.276	0.522	0.945	2.547	1.026	717.7 ± 19.7	1187.0 ± 7.3
2.5	1.18	0.281	0.269	0.264	0.270	0.509	0.907	2.487	0.990	278.9 ± 4.7	411.2 ± 3.5
5.0	1.32	0.276	0.261	0.259	0.263	0.507	0.880	2.356	0.985	166.0 ± 1.7	247.5 ± 4.6
7.5	1.59	0.273	0.259	0.255	0.262	0.484	0.873	2.554	1.002	133.8 ± 8.2	172.8 ± 5.2
10.0	1.85	0.265	0.250	0.245	0.252	0.449	0.793	2.385	0.966	81.9 ± 2.3	128.4 ± 4.8

[Cellobiose] (wt%)	Relative viscosity	T_2										$\lambda_{^{35}Cl} / \lambda_{^{37}Cl}$
		C-2	C-4	C-5	C-1'	C-2'	C-3'	C-4'	C-1"	^{35}Cl	^{37}Cl	
0.0	1.00	0.209	0.219	0.219	0.216	0.399	0.832	1.505	0.762	382.4 ± 7.6	597.2 ± 6.9	1.56 ± 0.05
2.5	1.18	0.203	0.210	0.211	0.203	0.405	0.760	1.509	0.765	127.3 ± 3.5	173.7 ± 3.1	1.37 ± 0.06
5.0	1.32	0.194	0.202	0.199	0.196	0.382	0.758	1.583	0.711	70.4 ± 2.6	103.3 ± 1.6	1.47 ± 0.08
7.5	1.59	0.173	0.189	0.186	0.178	0.340	0.712	1.501	0.679	50.4 ± 1.2	70.0 ± 2.6	1.39 ± 0.09
10.0	1.85	0.166	0.178	0.172	0.165	0.319	0.669	1.503	0.640	36.9 ± 1.1	53.6 ± 2.3	1.45 ± 0.11

a) Relative to the viscosity of neat $[C_4mim]Cl$ measured at 90 ºC (60.9 ± 0.5 cP).

b) T_1 and T_2 relaxation times are in seconds and microseconds for ^{13}C and $^{35/37}Cl$ nuclei, respectively.

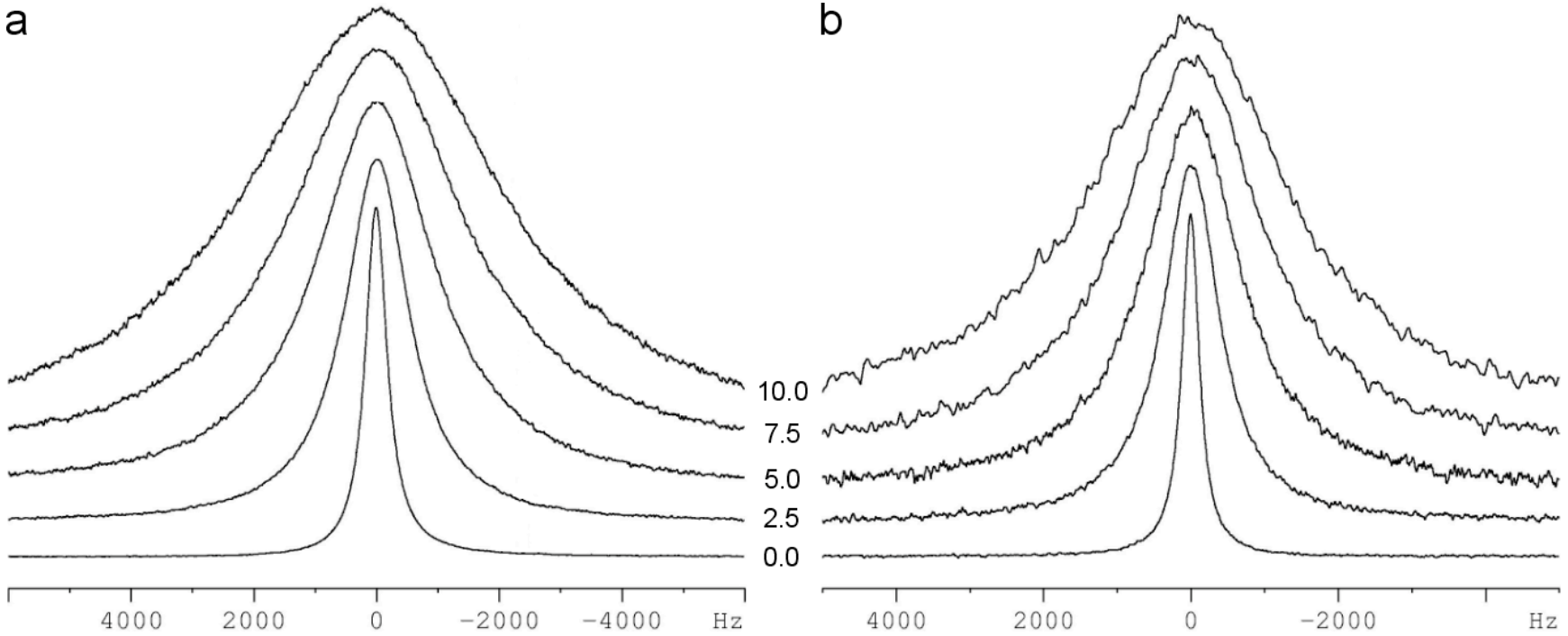

Figure S2. ^{35}Cl (**a**) and ^{37}Cl (**b**) spectra of [C_4mim]Cl as a function of cellobiose wt% concentration recorded at 90 ºC.

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Table S3. Relaxation data for the ^{13}C and $^{35/37}Cl$ nuclei in $[C_4mim]Cl$ as a function of glucose concentration measured at 90 ºC.

[Glucose] (wt%)	Relative viscosity[(a)]	T_1[(b)]									
		C-2	C-4	C-5	C-1'	C-2'	C-3'	C-4'	C-1"	^{35}Cl	^{37}Cl
0.0	1.00	0.287	0.275	0.270	0.276	0.522	0.945	2.547	1.026	717.7 ± 19.7	1187.0 ± 7.3
2.5	1.08	0.282	0.273	0.264	0.270	0.509	0.914	2.534	1.043	269.0 ± 3.4	429.2 ± 4.2
5.0	1.16	0.283	0.273	0.267	0.276	0.504	0.919	2.435	1.021	162.2 ± 1.6	279.5 ± 2.7
7.5	1.27	0.280	0.267	0.259	0.266	0.500	0.881	2.442	1.003	116.3 ± 1.0	180.6 ± 3.2
10.0	1.35	0.288	0.265	0.263	0.269	0.483	0.876	2.356	1.060	89.6 ± 0.9	134.1 ± 3.1

[Glucose] (wt%)	Relative viscosity	T_2										$\lambda_{^{35}Cl} / \lambda_{^{37}Cl}$
		C-2	C-4	C-5	C-1'	C-2'	C-3'	C-4'	C-1"	^{35}Cl	^{37}Cl	
0.0	1.00	0.209	0.219	0.219	0.216	0.399	0.832	1.505	0.762	382.4 ± 7.6	597.2 ± 6.9	1.56 ± 0.05
2.5	1.08	0.201	0.217	0.212	0.213	0.411	0.832	1.451	0.771	133.1 ± 2.4	205.3 ± 5.5	1.54 ± 0.07
5.0	1.16	0.196	0.213	0.205	0.201	0.372	0.823	1.419	0.742	78.0 ± 1.1	127.5 ± 0.7	1.64 ± 0.03
7.5	1.27	0.188	0.202	0.200	0.202	0.379	0.773	1.429	0.727	54.5 ± 0.9	86.5 ± 1.1	1.59 ± 0.05
10.0	1.35	0.185	0.199	0.195	0.195	0.372	0.735	1.438	0.736	42.3 ± 0.5	66.3 ± 0.5	1.57 ± 0.03

a) Relative to the viscosity of neat $[C_4mim]Cl$ measured at 90 ºC (60.9 ± 0.5 cP).

b) T_1 and T_2 relaxation times are in seconds and microseconds for ^{13}C and $^{35/37}Cl$ nuclei, respectively.

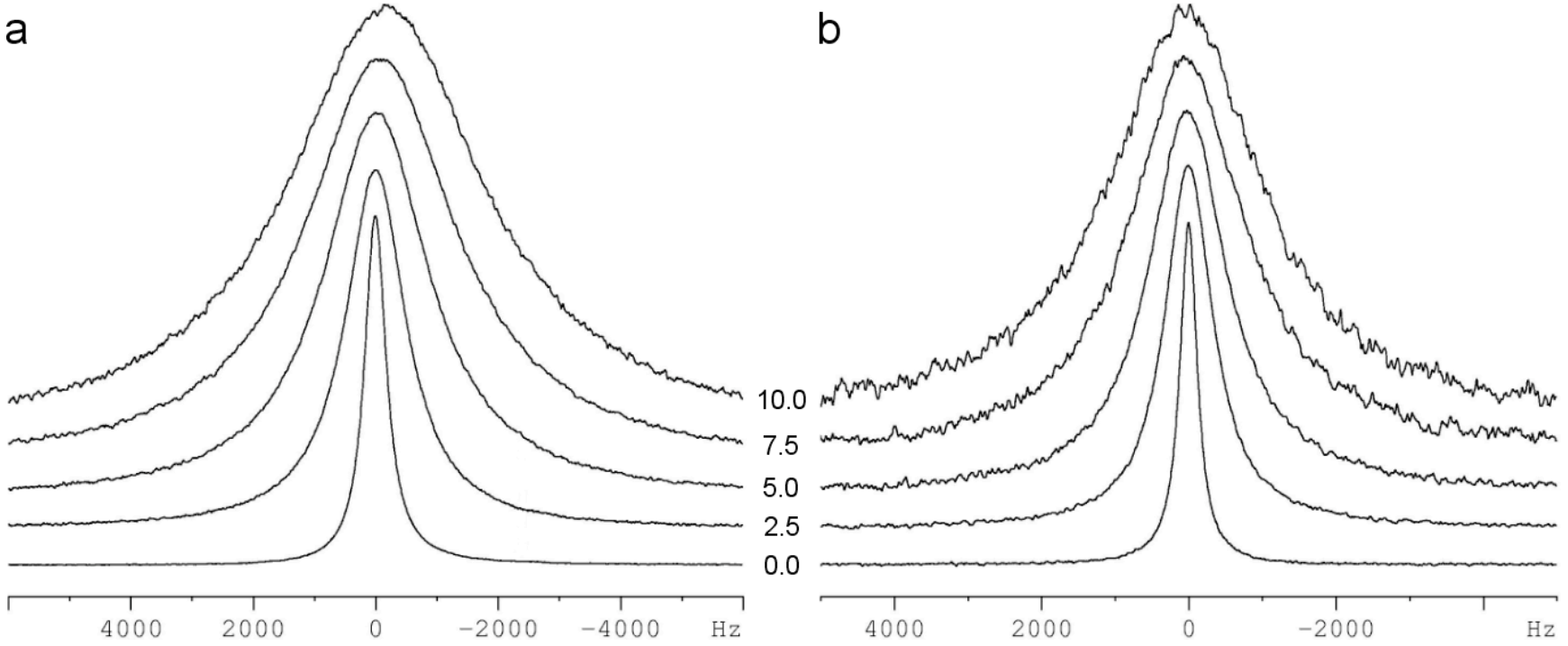

Figure S3. ^{35}Cl (**a**) and ^{37}Cl (**b**) spectra of [C_4mim]Cl as a function of glucose wt% concentration recorded at 90 ºC.

Table S4. Relaxation data for the ^{13}C and $^{35/37}Cl$ nuclei in $[C_4mim]Cl$ as a function of $Glcp(Ac)_5$ concentration measured at 90 ºC.

$[Glcp(Ac)_5]$ (wt%)	Relative viscosity[(a)]	T_1[(b)]									
		C-2	C-4	C-5	C-1'	C-2'	C-3'	C-4'	C-1"	^{35}Cl	^{37}Cl
0.0	1.00	0.287	0.275	0.270	0.276	0.522	0.945	2.547	1.026	717.7 ± 19.7	1187.0 ± 7.3
2.5	0.94	0.302	0.287	0.281	0.287	0.541	0.994	2.624	1.075	665.4 ± 19.8	1164.4 ± 2.5
5.0	0.92	0.295	0.285	0.276	0.283	0.536	0.979	2.663	1.075	625.3 ± 15.8	1073.8 ± 3.1

$[Glcp(Ac)_5]$ (wt%)	Relative viscosity	T_2										$\lambda_{^{35}Cl} / \lambda_{^{37}Cl}$
		C-2	C-4	C-5	C-1'	C-2'	C-3'	C-4'	C-1"	^{35}Cl	^{37}Cl	
0.0	1.00	0.209	0.219	0.219	0.216	0.399	0.832	1.505	0.762	382.4 ± 7.6	597.2 ± 6.9	1.56 ± 0.05
2.5	0.94	0.220	0.232	0.223	0.222	0.414	0.874	1.434	0.842	360.4 ± 8.3	589.5 ± 9.5	1.64 ± 0.07
5.0	0.92	0.202	0.220	0.209	0.211	0.410	0.760	1.415	0.716	323.7 ± 0.2	533.8 ± 7.2	1.65 ± 0.02

a) Relative to the viscosity of neat $[C_4mim]Cl$ measured at 90 ºC (60.9 ± 0.5 cP).

b) T_1 and T_2 relaxation times are in seconds and microseconds for ^{13}C and $^{35/37}Cl$ nuclei, respectively.

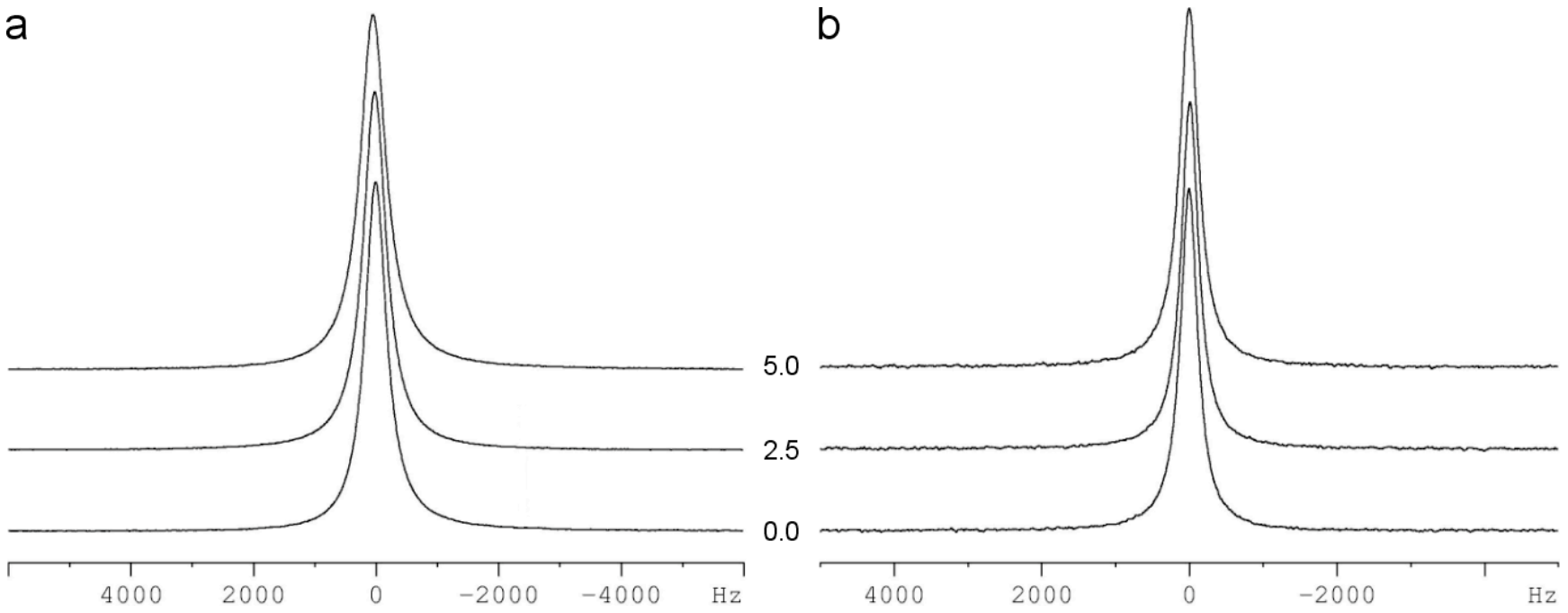

Figure S4. ^{35}Cl (**a**) and ^{37}Cl (**b**) spectra of $[C_4mim]Cl$ as a function of $Glcp(Ac)_5$ wt% concentration recorded at 90 ºC.