# NMR and Raman Spectroscopy Monitoring of Proton/Deuteron Exchange in Aqueous Solutions of Ionic Liquids Forming Hydrogen Bond: A Role of Anions, Self-Aggregation, and Mesophase Formation

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ABSTRACT: The H/D exchange process in the imidazolium-based room temperature ionic liquids (RTILs) 1-decyl-3-methyl-imidazolium bromide- and chloride ($[C_{10}mim][Br]$ and $[C_{10}mim][Cl]$) in D_2O solutions of various concentrations was studied applying ^1H, ^{13}C NMR, and Raman spectroscopy. The time dependencies of integral intensities in NMR spectra indicate that the H/D exchange in $[C_{10}mim][Br]$ at very high dilution (10^{-4} mole fraction of RTIL) runs only slightly faster than in $[C_{10}mim][Cl]$. The kinetics of this process drastically changes above critical aggregation concentration (CAC). The time required to reach the apparent reaction saturation regime in the solutions of 0.01 mole fraction of RTIL was less 10 h for $[C_{10}mim][Br]$, whereas no such features were seen for $[C_{10}mim][Cl]$ even tens of days after the sample was prepared. The H/D exchange was not observed in the liquid crystalline gel mesophase. The role of anions, self-aggregation (micellization), and mesophase formation has been discussed. Crucial influence of Br^- and Cl^- anions on the H/D exchange rates above CAC could be related to the short-range ordering and molecular microdynamics, in particular that of water molecules. The concept of the conformational changes coupled with the H/D exchange in imidazolium-based ionic liquids with longer hydrocarbon chains can be rejected in the light of ^{13}C NMR experiment. The revealed changes in ^{13}C NMR spectra are caused by the secondary (^{13}C) isotope effects not being the signal shifts due to the conformational *trans–gauche* transition.
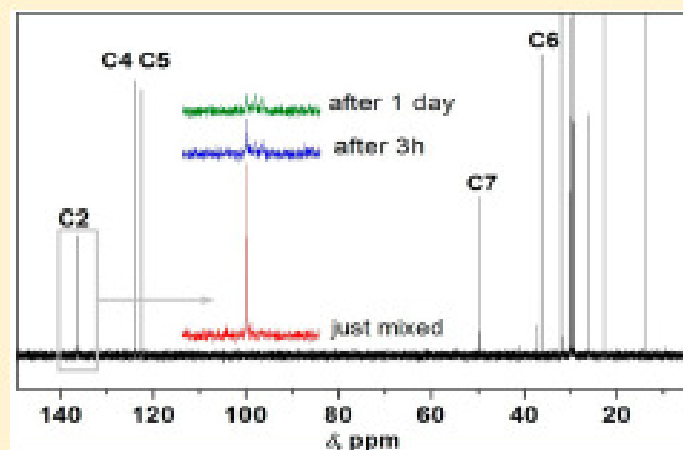
Motivations and Problem

➢ Ionic liquids (Ils) including various artificial sensors of new generation, electrochemistry, fuel cells and batteries, (bio-) catalysis.

➢ Not completely understood PROCESS……

➢ The (H/D) exchange for possible pathways of reaction and its kinetics that shows valuable information on the picture of H-bond in Ils.

➢ H/D exchange process depend on phase behavior

The purposes of present work were

(i) To study the anion, self-aggregation, and mesophase effects on the H/D exchange below and above CAC

(ii) To check the possibility of conformational changes induced by the H/D exchange having longer alkyl chains

What is CAC?

the **critical micelle concentration** (**CMC**) is defined as the concentration of surfactants above which micelles form and all additional surfactants added to the system go to micelles
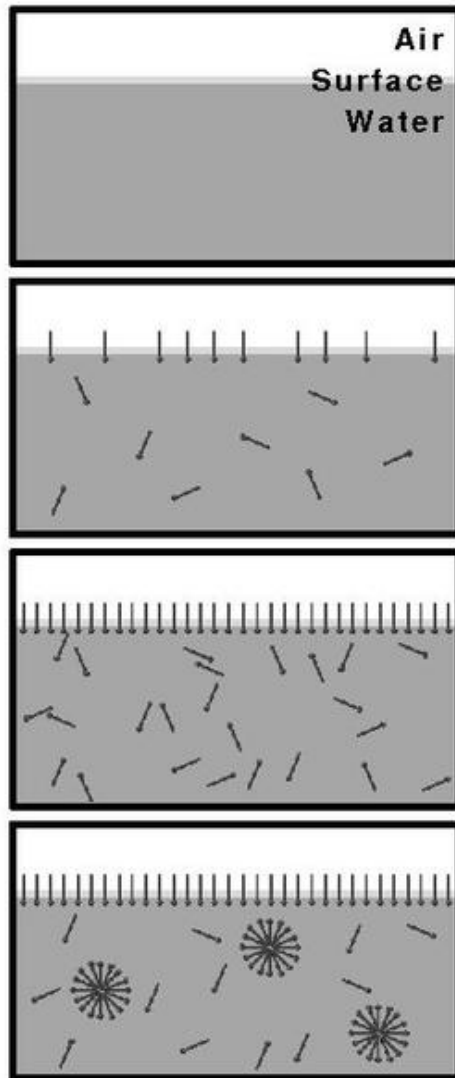
Increasing concentration of surfactant in water slowly forming a layer on the surface and eventually forming micelles at or above the CMC
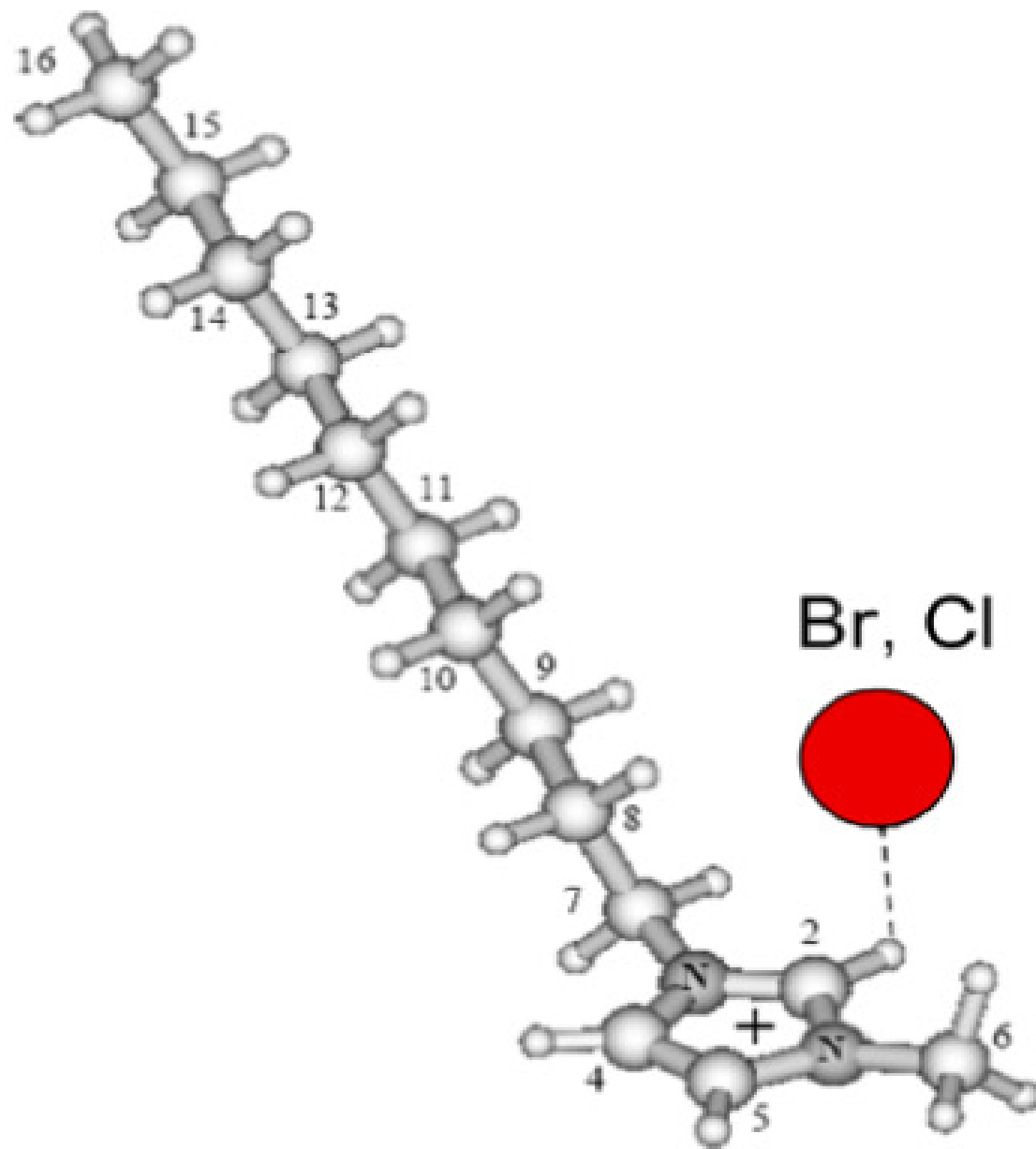
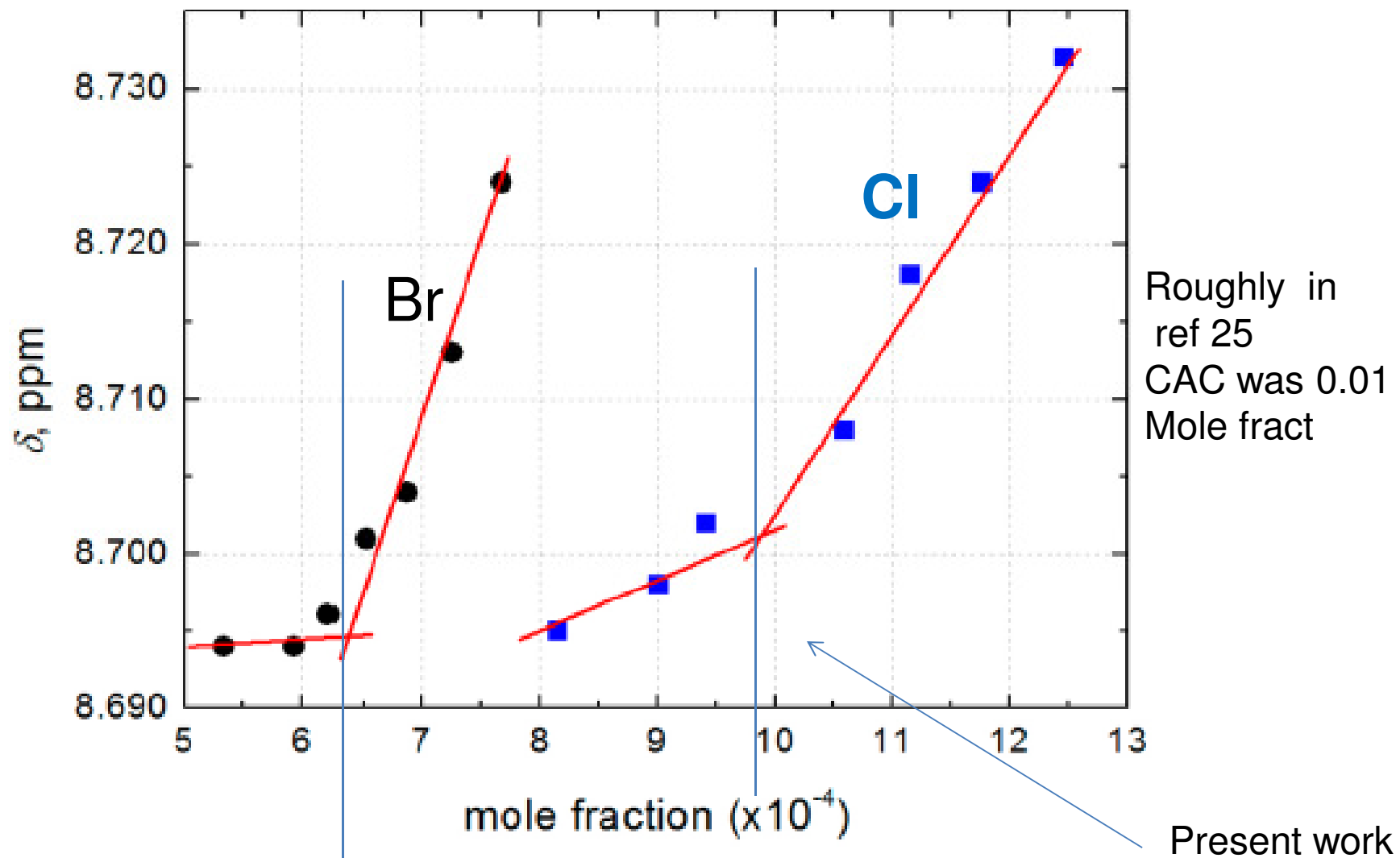Figure 1. Molecular structure and carbon numbering of $[C_{10}mim][X]$, X = Br, Cl.

Figure 2. Determination of critical aggregation concentration (CAC) of $[C_{10}mim][X]$, X = Br (black circles), Cl (blue squares) using dependencies of chemical shift of C(2)−H···X⁻ proton on concentration in H_2O.

➢ Next couple of samples of 0.01 mole fraction of RTIL in D2O was prepared

➢ 0.01 M, both systems are close to the midpoint between the onsets of aggregation and the gel mesopase formation.

➢ [C10mim][Br]/H2O and [C10mim][Cl]/H2O solutions convert at higher content of water from a viscous liquid to the anisotropic gel.

➢ This gel was found to be stable over the range of ~5–40% w/w of water (i.e., 0.08 - 0.53 mole fraction of RTIL).

➢ In order to check the influence of this mesophase on the H/D exchange rate another two samples of 0.4 mole fraction of RTIL in D2O were prepared and investigated.

6×10^{-4}

0.01

0.4

MESOPHASE

Table 1. Literature and Present Work Data on Critical Aggregation Concentration (CAC) of $[C_{10}mim][X]$, X = Br, Cl in H_2O and D_2O at 298 K

$[C_{10}mim][Br]$			$[C_{10}mim][Cl]$		
CAC, M	solvent and method	ref	CAC, M	solvent and method	ref
0.030–0.032	D_2O, NMR	29	0.055	H_2O, interfacial tension	27
0.029	H_2O, surface tension	32	0.045	H_2O, fluorescence	27
0.033	H_2O, conductivity	32	0.055	H_2O, NMR	27
0.04	H_2O, potentiometry	33	0.054	H_2O, surface tension	30
			0.060	H_2O, conductivity	30
CAC values recalculated to mole fraction: $(5.3 - 7.2) \times 10^{-4}$			CAC values recalculated to mole fraction: $(8 - 10) \times 10^{-4}$		
6.4×10^{-4} mole fraction	H_2O, NMR	present work	9.9×10^{-4} mole fraction	H_2O, NMR	present work

Our group data

Table 1. Parameters Obtained from Fitting of Surface Tension against Surfactant Concentration Data Using Eq 4 for Aqueous Solutions of $[C_{12}mim][Cl]$ and $[C_{12}mim][I]$ [a]

surfactant	CMC (mM)	γ_{CMC} (mN/m)	$\Gamma_{m,L}$ ($\mu mol/m^2$)	K_L (m^3/mol)	Γ_{max} ($\mu mol/m^2$)[b]	A_{min} (Å^2)
$[C_{12}mim][Cl]$	18.2 ± 1.0	38.4	4.0 ± 0.7	0.24 ± 0.08	3.3 ± 0.3	51 ± 5
$[C_{12}mim][I]$	4.2 ± 0.2	31.5	6.8 ± 1.7	0.56 ± 0.20	4.8 ± 0.5	35 ± 4
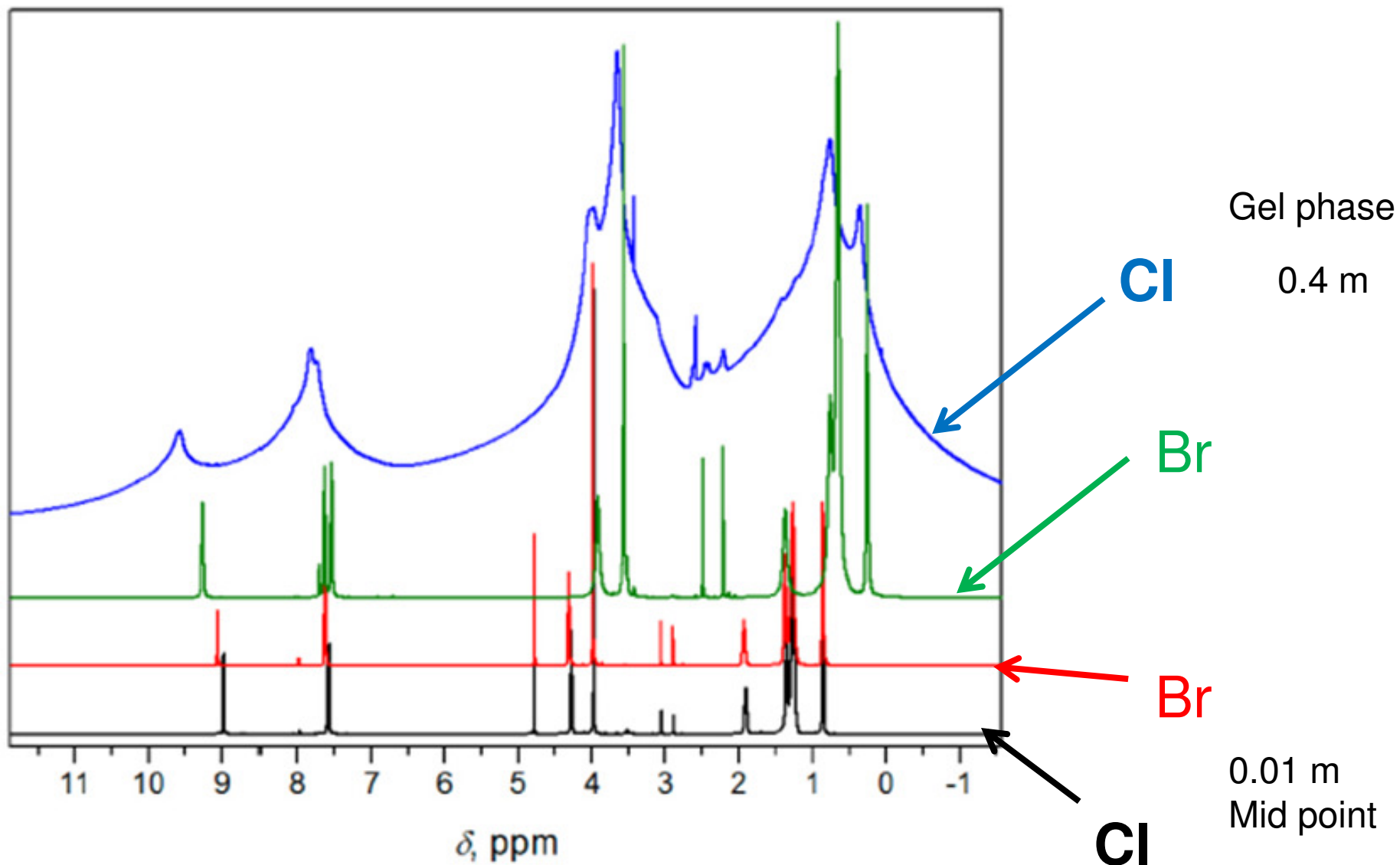
**Figure 3.** ^{1}H NMR spectra of $[C_{10}mim][X]$ in D_2O solutions: close to the midpoint between the onset of aggregation and the gel formation (0.01 mole fraction of RTIL), X = Cl (black) and X = Br (red); in the gel phase (0.4 mole fraction of RTIL), X = Br (green) and X = Cl (blue); all at T = 298 K. The spectra below CAC are not shown because they inessential differ from those at 0.01 mole fraction of RTIL.

Figure 4. Monitoring of H/D exchange in ^{13}C NMR spectra of $[C_{10}mim][Br]$ in D_2O solution (0.01 mole fraction of RTIL) at $T = 298$ K.
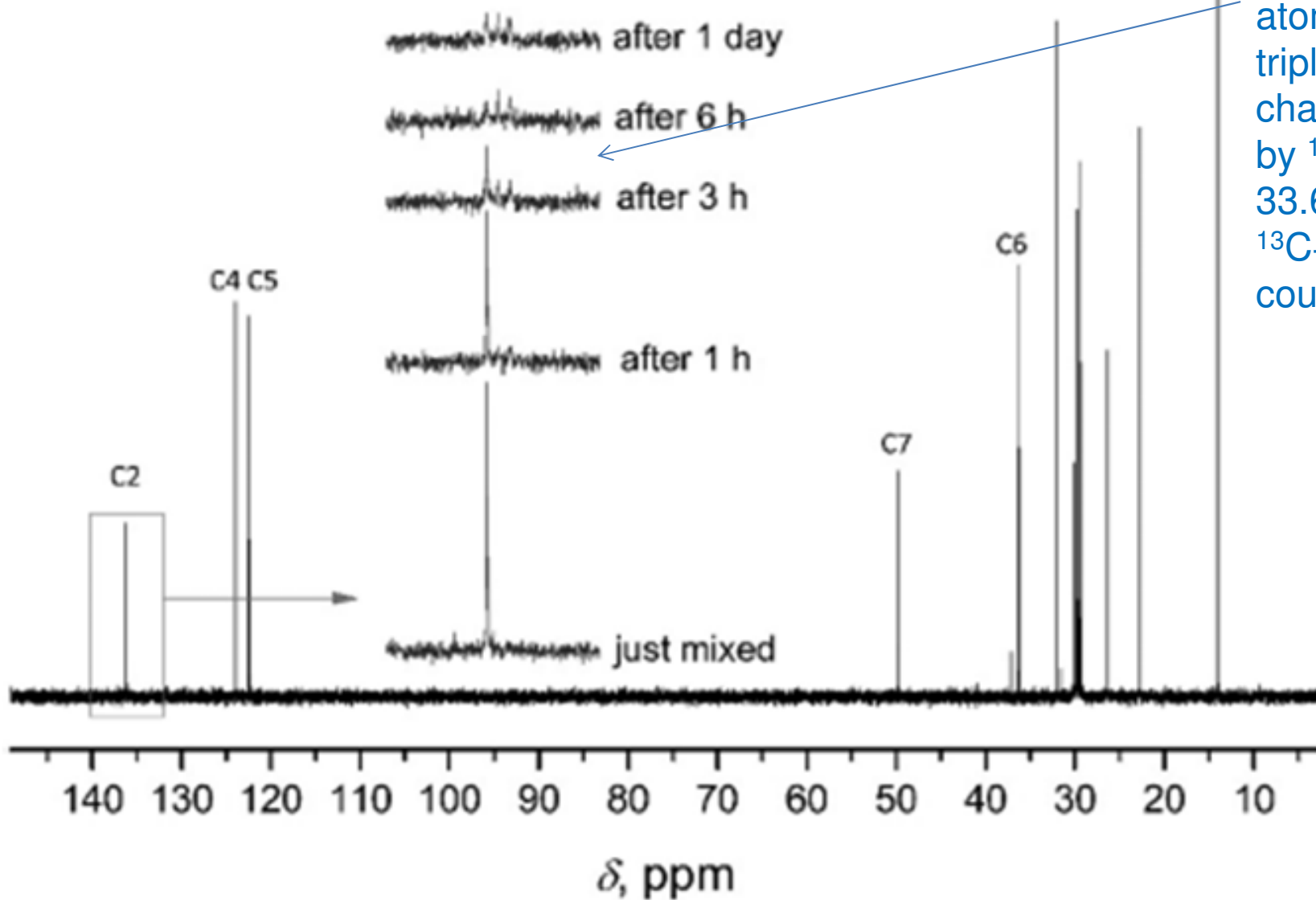
C(2) carbon atom splits into triplet characterized by $^1J(^{13}C-^2H) = 33.6$ Hz due to $^{13}C-^2H$ spin coupling.

after 1 day

after 6 h

after 3 h

C6

C4 C5

after 1 h

C7

C2

just mixed

δ, ppm
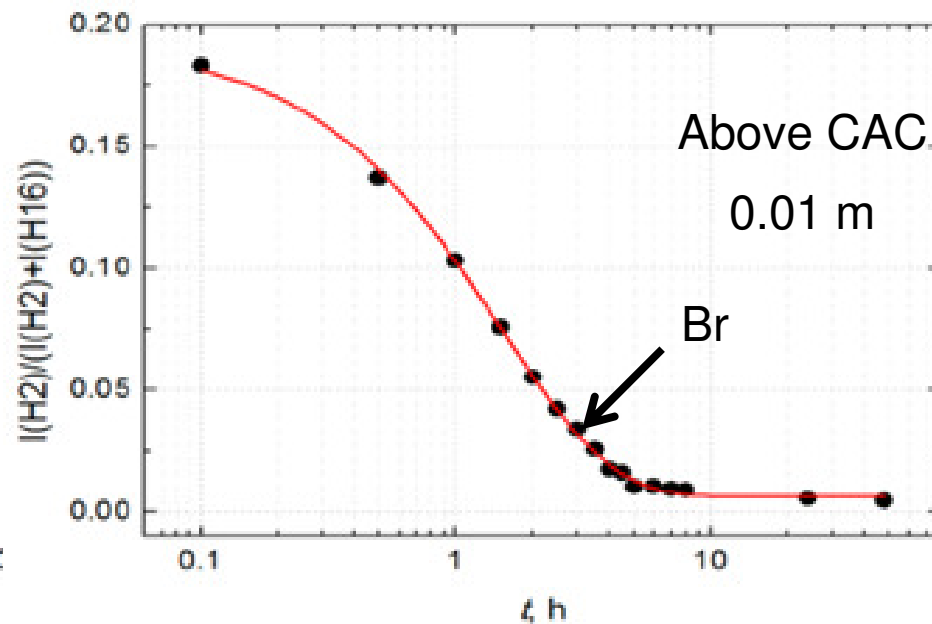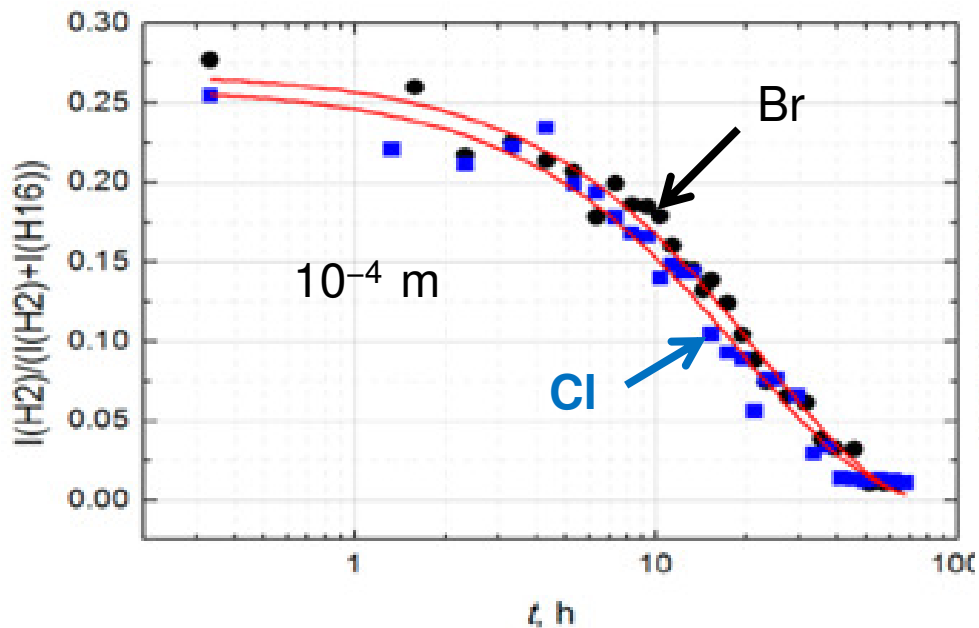
The kinetics of this process drastically changes above CAC

Our group results

The ^{1}H NMR signal corresponding to the C(2)–H proton disappears completely in 0.01 mole fraction solution in D_2O after 20 h
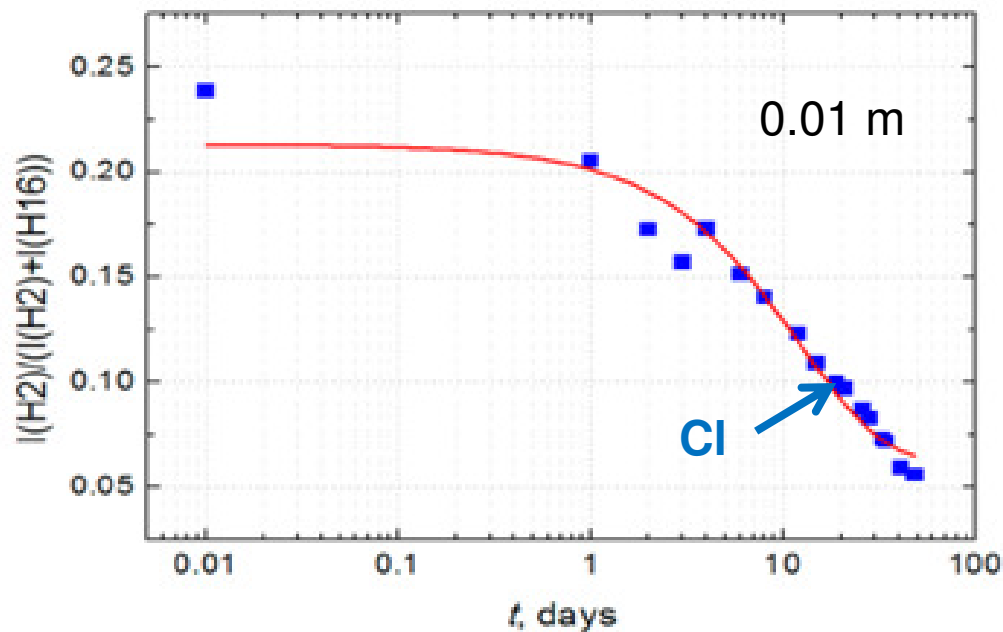
Fig. 5. Kinetics of the H/D exchange reaction

No changes in the intensity of ^{1}H NMR signal of C(2)–H proton were noticed for the gel samples (0.4 mole fraction of RTIL) during 48 days of observation from the sample preparation. Thus, this reaction does not run in the gel phase.

Table 2. Chemical Shifts of Carbon Nuclei and Secondary (^{13}C) Isotope Effects $\delta_H - \delta_D$ (in ppm) in $[C_{10}mim][X]$, X = Br, Cl in D_2O Solution at 298 K

| carbon no. | $[C_{10}mim][Cl]$ | | | $[C_{10}mim][Br]$ | | |
	H^a	D^a	$\delta_H - \delta_D$	H	D	$\delta_H - \delta_D$
C(2)	136.23	135.98	0.25	136.28	136.04	0.24
C(4)	122.34	122.30	0.04	122.46	122.41	0.05
C(5)	124.03	123.98	0.04	124.01	123.97	0.04
C(6)	36.11	36.08	0.03	36.27	36.24	0.03
C(7)	49.72	49.69	0.03	49.78	49.76	0.02

^{a}The label 'H' refers to the species with a proton in C(2)–H···X$^-$ bonding, while 'D' refers to that with a deuteron.

BR

Black- 10
Red- 20
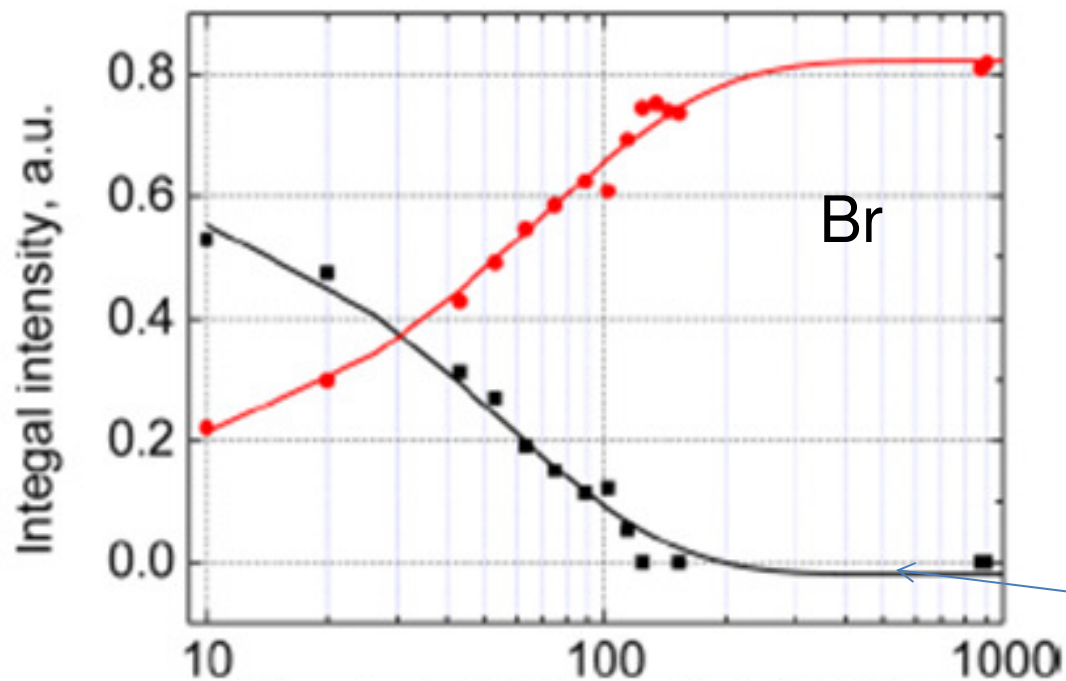Blue- 50
Green- 900 min

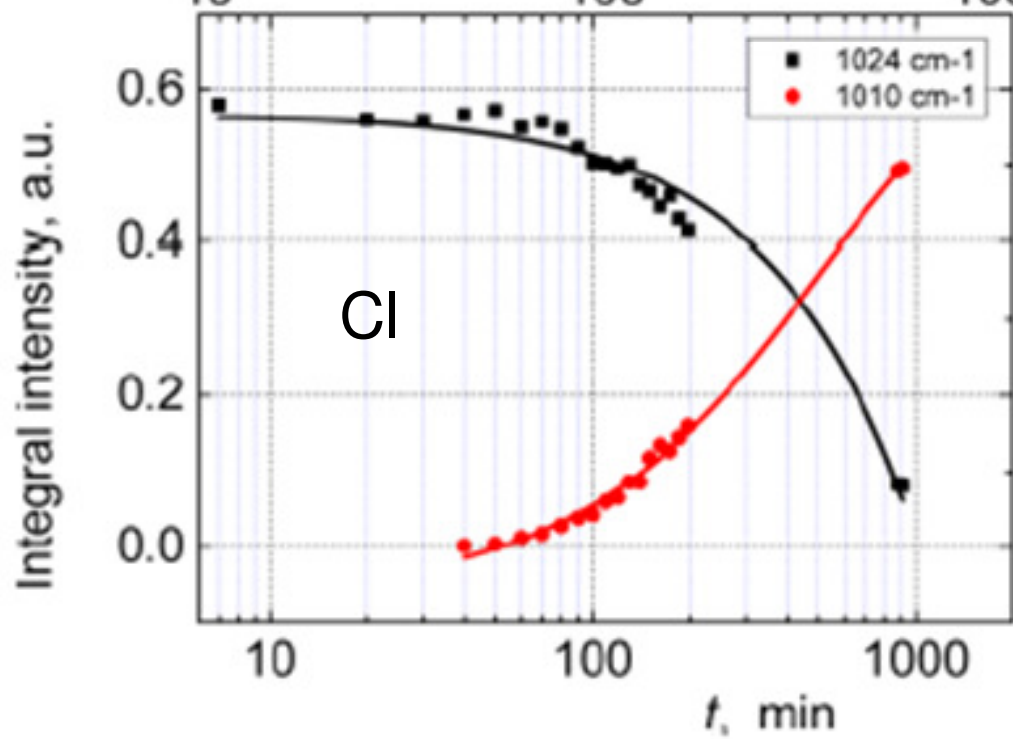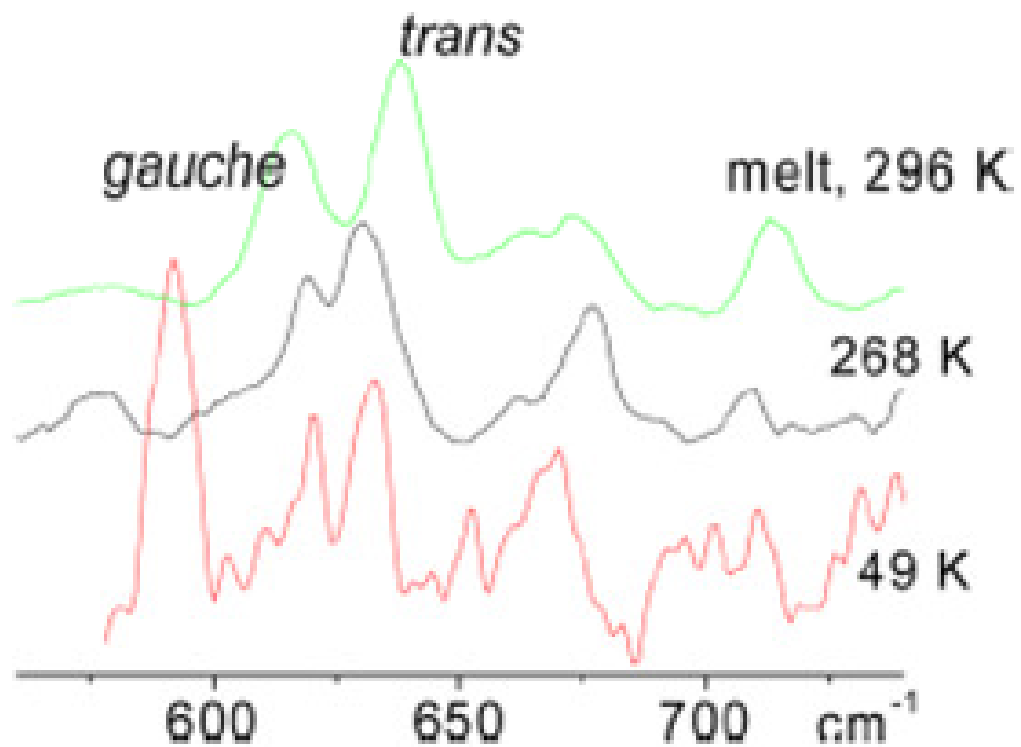Cl

Black- 10
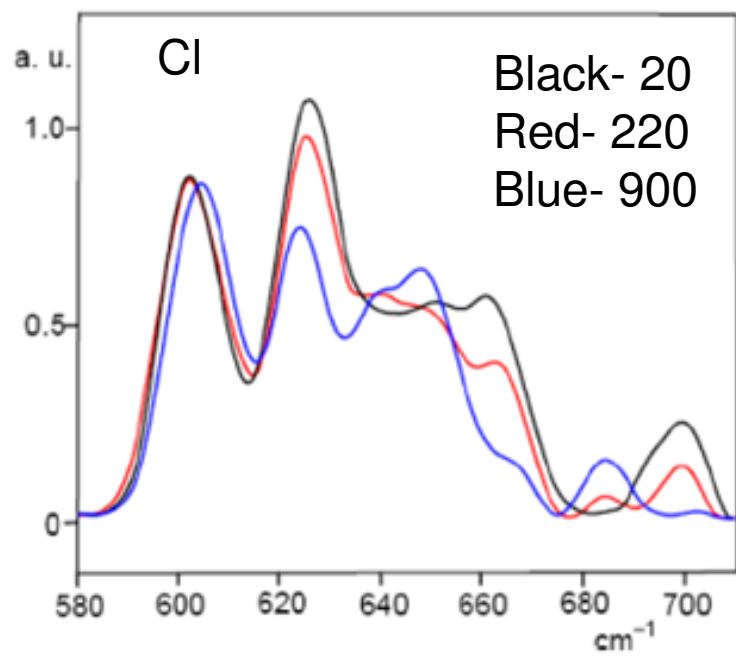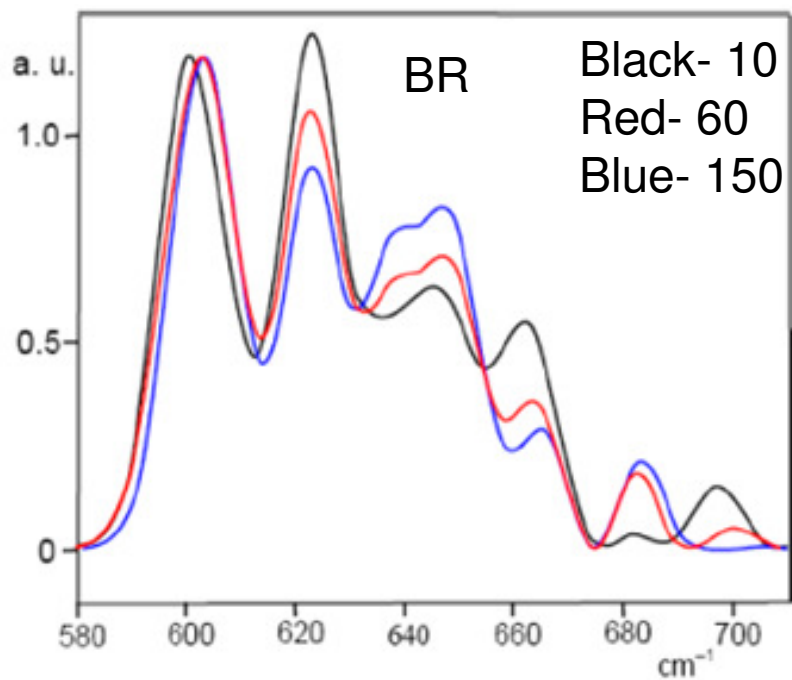Red- 200
Blue- 900
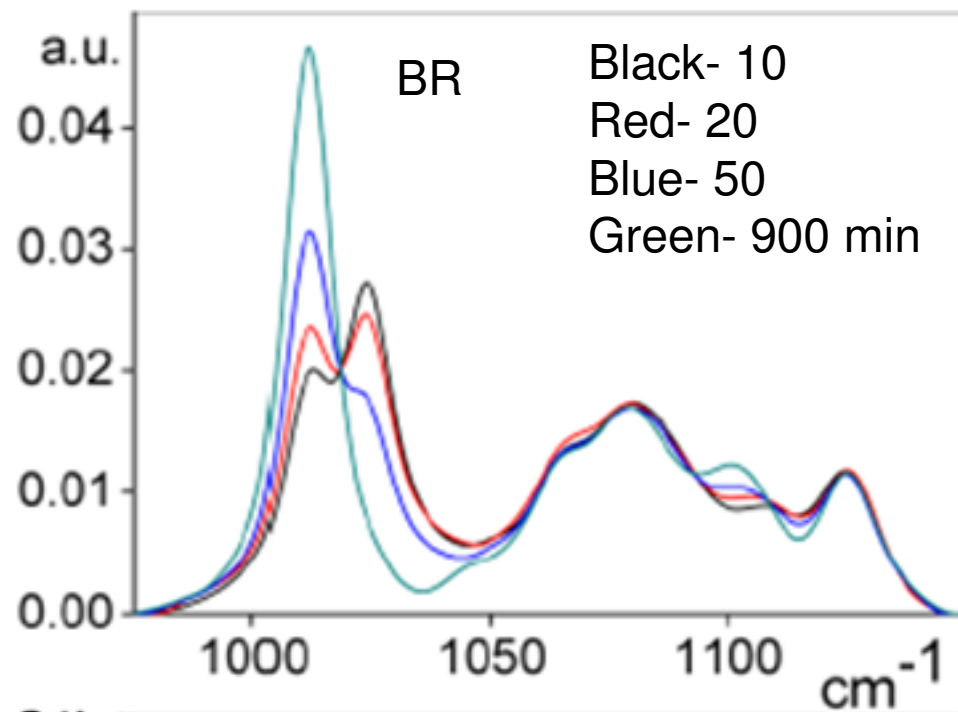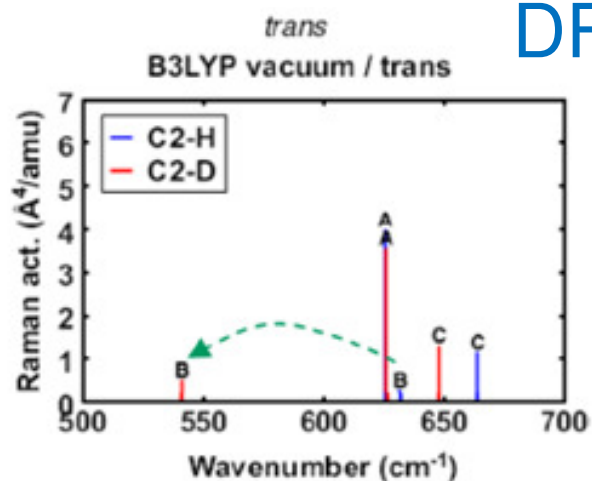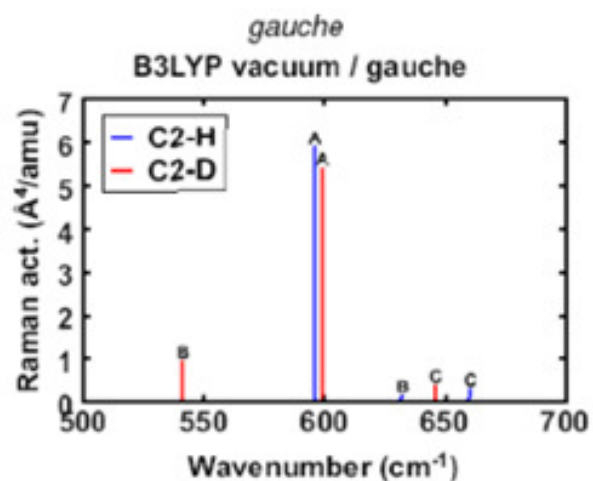
Raman spectra

⬇

0.01 m

⬇

Anomalous conformation
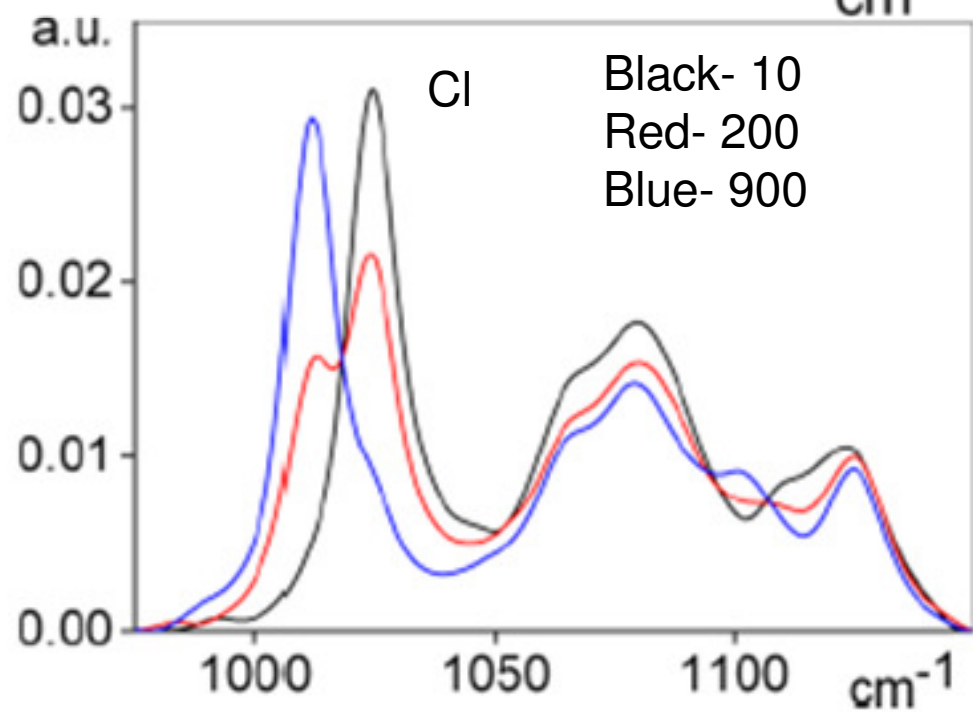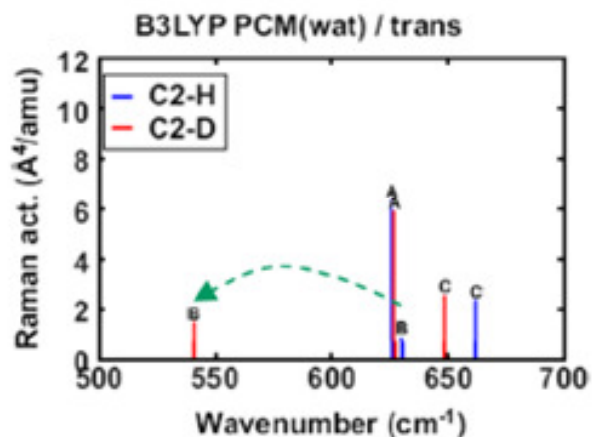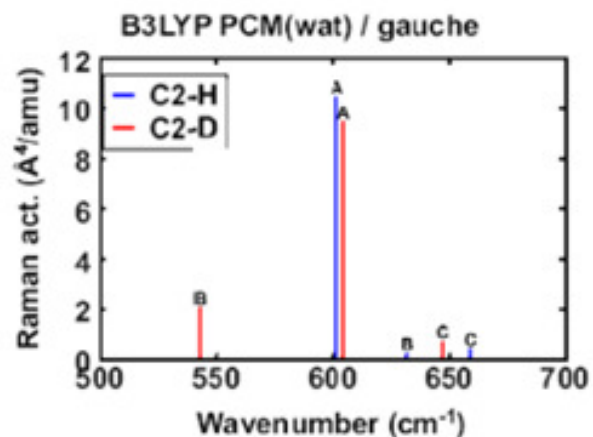
Kinetics of H/D exchange

Supporting of NMR

Saturation regime

Raman spectra

DFT Calculated results

gauche

B3LYP vacuum / gauche

B3LYP PCM(wat) / gauche

B3LYP H_2O+PCM(wat) / gauche

trans

B3LYP vacuum / trans

B3LYP PCM(wat) / trans

B3LYP H_2O+PCM(wat) / trans
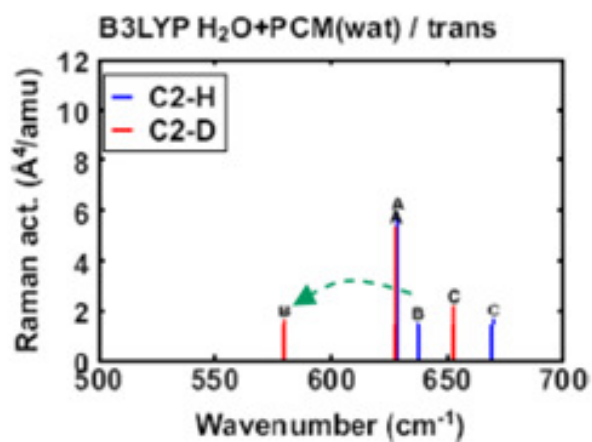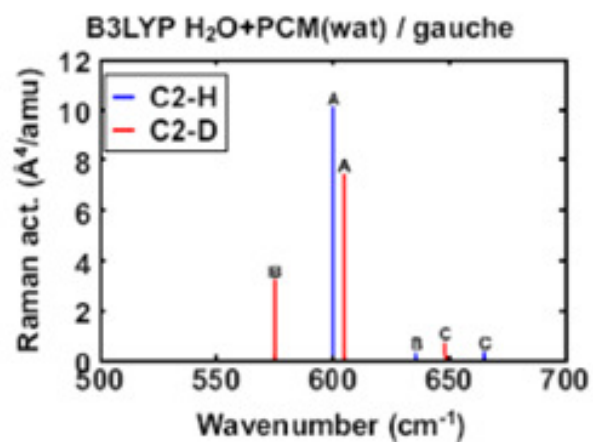
In vacuo

PCM

Water+PCM

Conclusions

The H/ D exchange process, depending on the anions, can be very significantly damped or stimulated above CAC

This reaction does not run in the liquid crystalline gel phase

No observation of conformation changes

The revealed changes in ^{13}C NMR spectra are caused by the secondary isotope effects on chemical shifts not being the signal shifts due to the conformational trans–gauche transition.