Spectroscopy as a tool to detect multinuclear Cu(II)-triethanolamine complexes in aqueous solution

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Supplementary Information

A speciation curve representing the expected prevalence of monomeric versus dimeric species based on literature stability constants

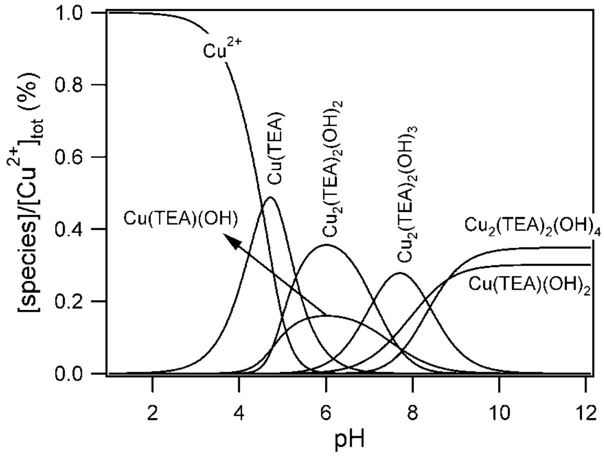


Figure S1. Speciation simulation for an aqueous solution containing [$CuSO_4$] = 0.058 mol/L and [TEA] = 0.295 mol/L, based on the model shown in Table S2.

Table S1. Cumulative stability constants for Cu^{2+}- complexes defined as $(Cu)_p(TEA)_q(OAc)_r(NH_3)_sH_t \rightleftarrows$ pCu + qTEA + rOAc + sNH_3 + tH used in HYSS2006[1] for modelling the speciation of the different samples. Charges were omitted for simplicity. The log β value for the species followed by (s) is the solubility product of the related precipitate 1-4.

Species	Log β_{pqrst}	Stoichiometry				
		Cu	TEA	OAc	NH_3	H
Cu(TEA)	3.85	1	1	0	0	0
Cu(TEA)(OH)	-1.74	1	1	0	0	-1
$Cu(TEA)(OH)_2$	-9.21	1	1	0	0	-2
TEAH	7.81	0	1	0	0	1
$Cu(OH)_2$	-15.2	1	0	0	0	-2
$Cu(OH)_2$ (s)	9.1	1	0	0	0	-2
	dimeric TEA complexes					
$Cu_2(TEA)_2(OH)_2$	-1.1	2	2	0	0	-2
$Cu_2(TEA)_2(OH)_3$	-8.2	2	2	0	0	-3
$Cu_2(TEA)_2(OH)_4$	-16.6	2	2	0	0	-4

References

[1] L. Alderighi, P. Gans, A. Ienco, D. Peters, A. Sabatini, A. Vacca, *Coordination Chemistry Reviews* **1999**, *184*, 311-318.

Measurement of T_1 and T_2 relaxation constants.

Relaxation time constants of the TEA proton resonances were measured on two samples using the standard inversion recovery delay and CPMG sequences in the Bruker library. All measurements were performed at 20°C on a Bruker Avance II 500.13 MHz spectrometer equiped with a ^{1}H-^{13}C-^{31}P TXI probehead. For the inversion recovery experiment, the interscan delay was set to 2 s and the recovery delay was varied from 4 µs to 1 s, sampled over 16 data points. For the CPMG experiment, the interscan delay was 2.5 s and a spin echo duration of 1 ms was used. The number of spin echoes varied from 0 to 400 for the sample at pH 1.69 and from 2 to 16 for the sample at pH 9.57, in both cases sampled over 8 data points. Data fitting was performed using the relaxation module within TopSpin 3.2.

Sample composition :

Sample 1 : 0.055 $mol.L^{-1}$ $CuSO_4$, Cu/TEA = 1:5.25, pH = 1.7
Sample 2 : 0.055 $mol.L^{-1}$ $CuSO_4$, Cu/TEA = 1:5.25, pH = 9.6

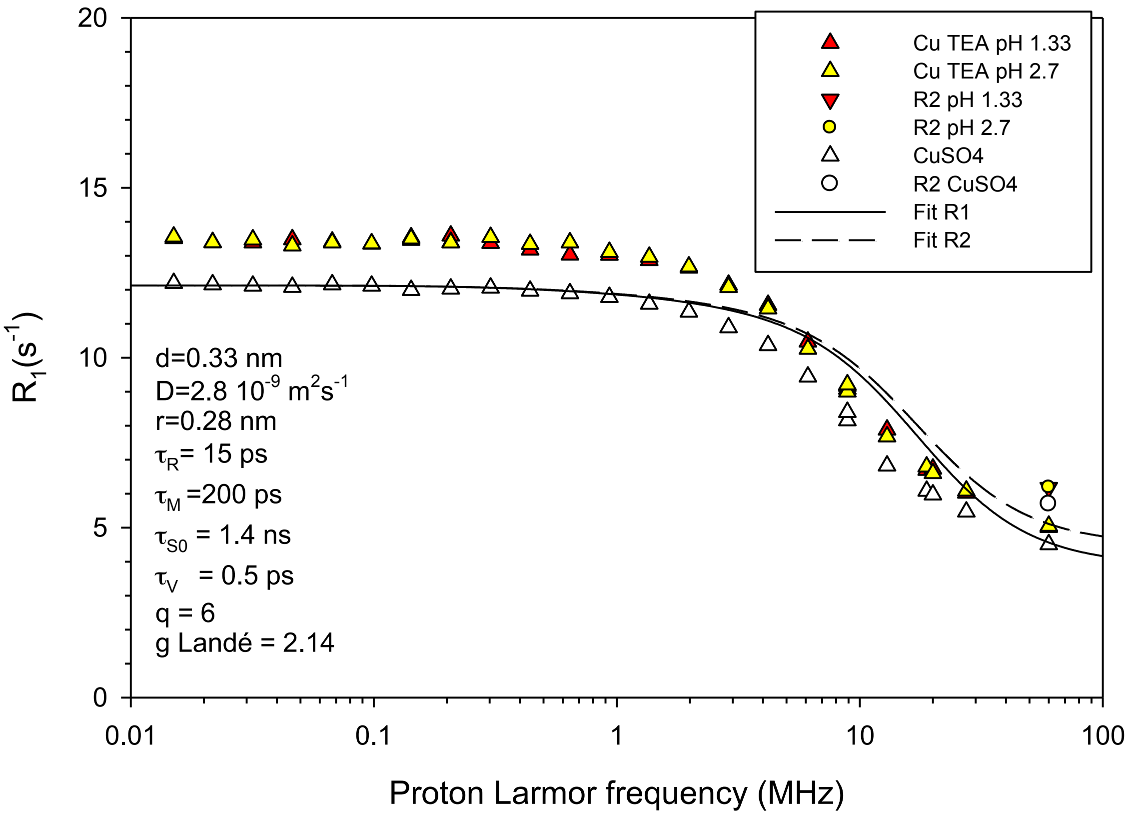
Table S2. Relaxation time constants of the TEA resonances at different pH values.

pH	T_1 (CH_2^a) / ms	T_1 (CH_2^b) / ms	T_2 ($CH_2^{a)}$) / ms	T_2 (CH_2^b) / ms
1.69	161.9	151.0	124.1	122.8
9.57	7.0	8.6	4.4	4.3

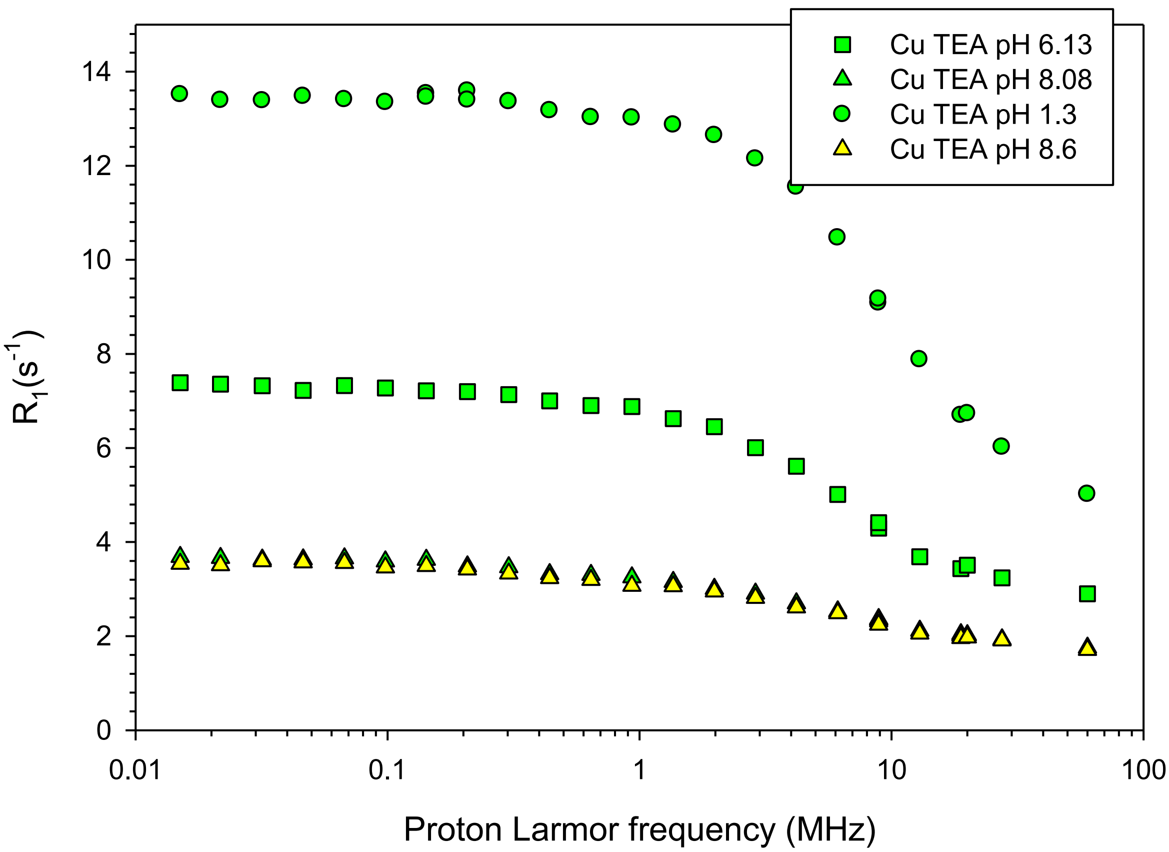
$N(CH_2^aCH_2^bOH)_3$

NMRD R_1 curves, R_2 values at 60 MHz, and fitted curves.

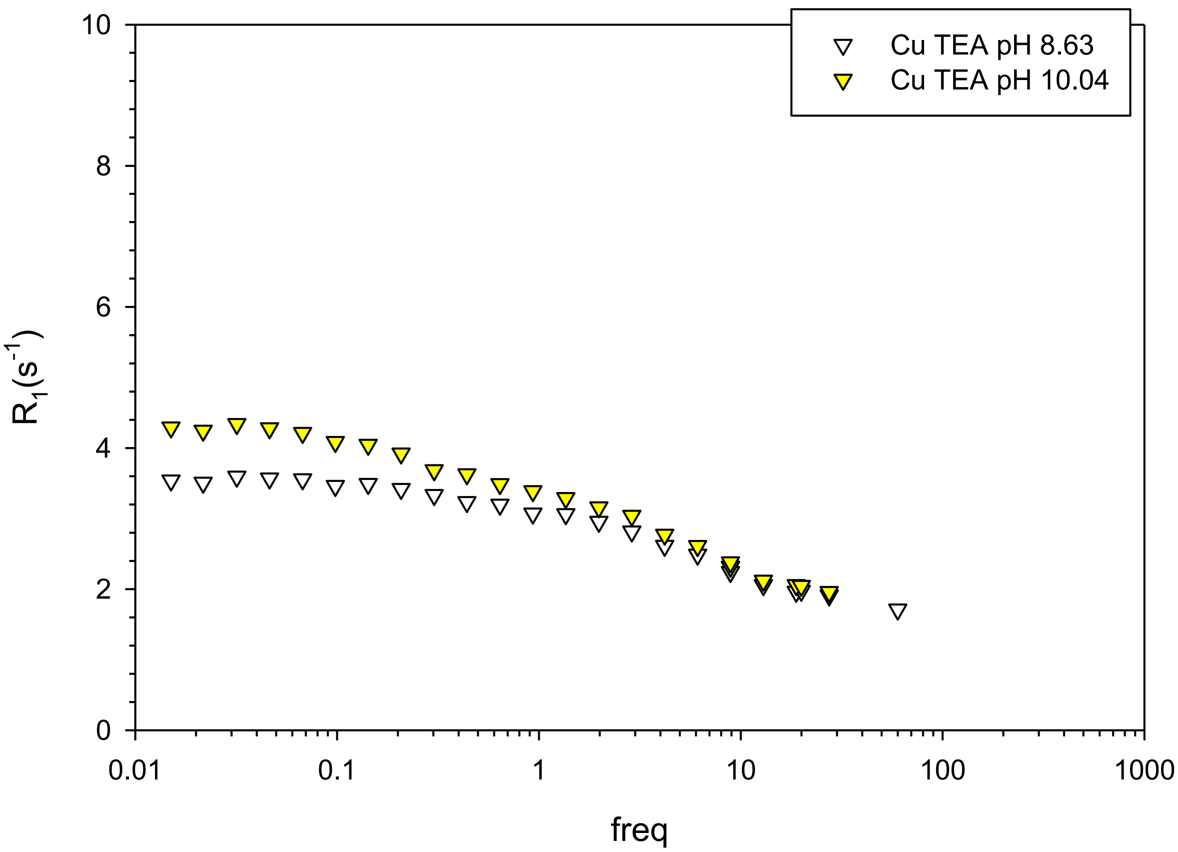
R_1 curves of a $CuSO_4$ reference solution and of Cu-TEA samples at pH 1.3 and 2.7. Additional R_2 values at 60 MHz. Fitted R_1 curve of the $CuSO_4$ reference and predicted R_2 curve.



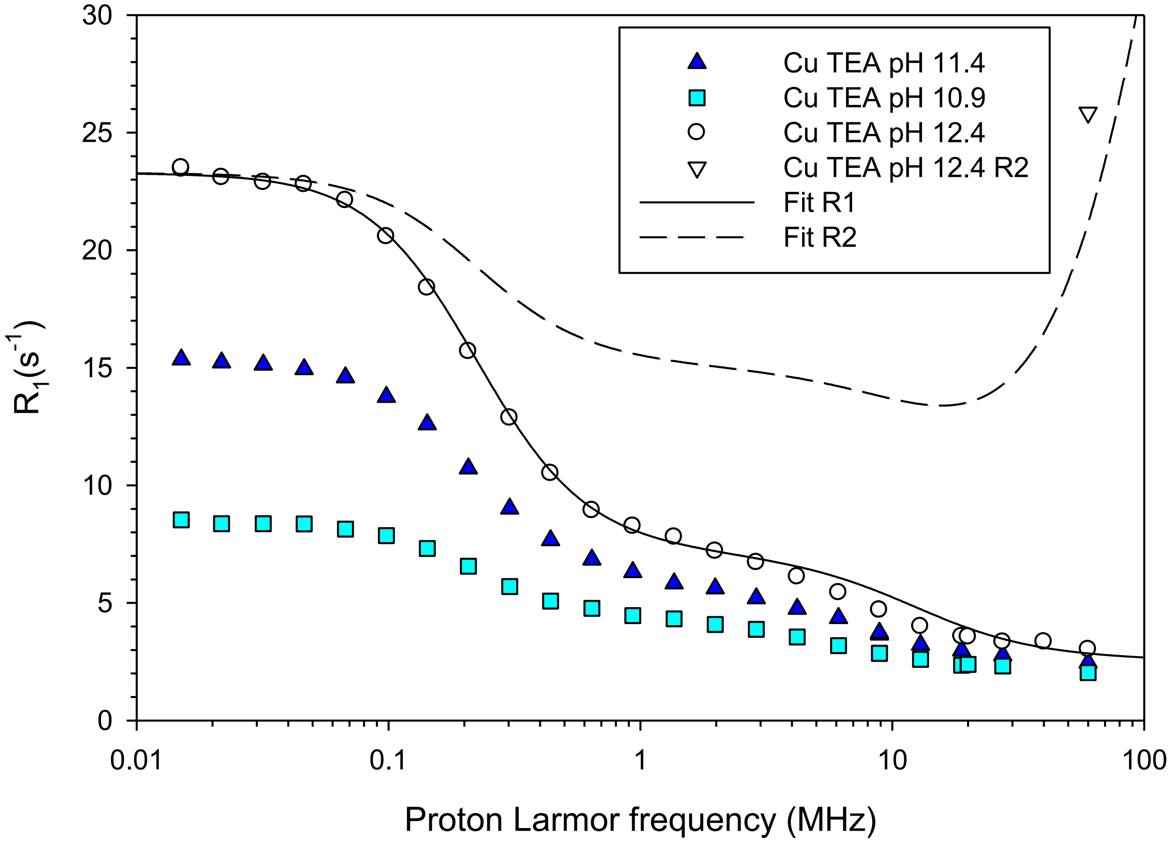
R_1 curves of Cu-TEA samples at pH 1.3, 6.1, 8.1 and 8.6.



R_1 curves of Cu-TEA samples at pH 8.6 and 10.0.



R_1 curves of Cu-TEA samples at pH 11.4, 10.9, and 12.4. Additional R_2 value measured at 60 MHz for pH 12.4. Fitted R_1 curve at pH 12.4 and predicted R_2 curve.



d=0.33 nm

D=2.8 10^{-9} m^2s^{-1}

r=0.28 nm

τ_R=20 ps

τ_M=10 ns

τ_{S0}=1.22 10^{-9} s

τ_V=3 ps

A/h=1.43 10^6 rads^{-1}

Q=2.

g Landé=2.14