Liquid Nanostructure of Choline Lysinate with Water and a Model Lignin Residue

Supplementary Information
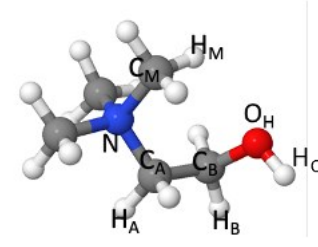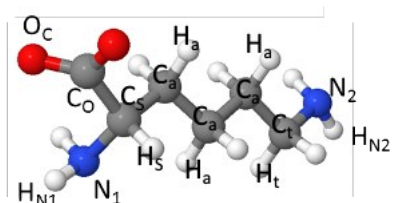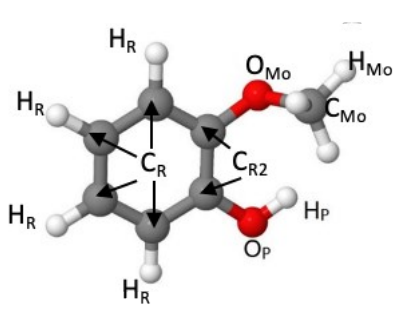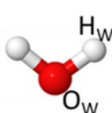
Haihui Joy Jiang,[a] Shurui Miao,[a] Silvia Imberti,[1b] Blake A. Simmons,[c] Rob Atkin,[d] Gregory G. Warr[2a]

a) School of Chemistry and Sydney Nano Institute, The University of Sydney, NSW 2006, Australia
b) STFC, ISIS Neutron and Muon Source, Rutherford Appleton Laboratory, Didcot OX11 0QX, United Kingdom
c) Joint BioEnergy Institute, Lawrence Berkeley National Laboratory, Berkeley CA 94720
d) School of Molecular Sciences, The University of Western Australia, WA 6009, Australia

---

[1] Current address: Global Journals Development, ACS International Ltd., Oxford OX2 0QS, United Kingdom
[2] author for correspondence. E-mail: gregory.warr@sydney.edu.au

Table S1 Initial Lennard-Jones parameters for EPSR modeling.[1,2] Note that simplified labels were used in the main text.

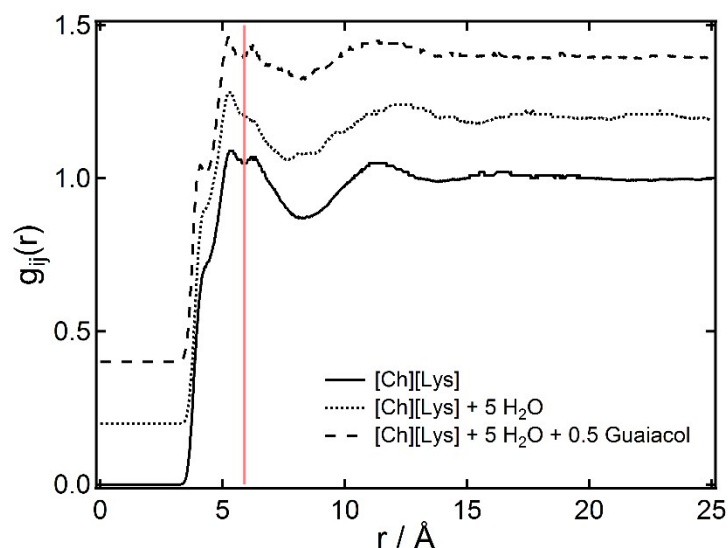| Atom	ε (kJ mol^{-1})	σ (Å)	q (e)	element	labelled structure
Cholinium (Ch⁺)					
C_B	0.276	3.500	0.232	C	
C_A	0.276	3.500	-0.111	C	
N	0.712	3.250	0.164	N	
H_B	0.126	0.250	0.040	H	
H_A	0.126	2.500	0.125	H	
H_M	0.126	2.500	0.193	H	
C_M	0.276	3.500	-0.385	C	
O_H	0.712	3.070	-0.655	O	
H_O	0.000	0.000	0.454	H	
Lysinate (Lys⁻)					
C_t	0.800	3.700	0.150	C	
C_a	0.800	3.700	-0.099	C	
H_t	0.126	2.500	0.050	H	
N_1	0.170	3.300	-1.193	N	
N_2	0.170	3.300	-1.193	N	
C_s	0.066	3.500	0.636	C	
C_O	0.105	3.750	0.809	C	
O_C	0.210	2.960	-0.877	O	
H_a	0.126	2.500	0.050	H	
H_s	0.030	2.500	-0.068	H	
H_{N1}	0.015	2.000	0.382	H	
H_{N2}	0.015	2.000	0.375	H	
guaiacol					
C_R	0.293	3.550	-0.115	C	
C_{R2}	0.293	3.550	0.135	C	
H_R	0.126	2.520	0.115	H	
H_{Mo}	0.065	1.800	0.005	H	
O_{Mo}	0.711	3.000	-0.385	O	
O_P	0.711	3.070	-0.585	O	
H_P	0.000	0.000	0.435	H	
C_{Mo}	0.711	3.800	0.250	C	
water					
O_W	0.650	3.166	-0.848	O	
H_W	0.000	0.000	0.424	H	

Figure S1. Intermolecular pair-correlation functions between C_a carbons of the lysinate anion (see Table S1) in the three systems studied, offset for clarity, a vertical cut off is shown in red at 5.9 Å.

The non-polar tetramethylene group of lysinate is expected to be the major constituent of the apolar network within the amphiphilic nanostructure of [Ch][Lys] systems. Figure S1 shows the intermolecular pair-correlation function between C_a side-chain carbons of lysinate (Table S1), neglecting the carbons adjacent to both α and ε amine groups. The behaviour is similar in all three systems, with no pronounced correlations at any specific distances, indicating an absence of short-range order. Nevertheless, all three share three common features: i) a small but noticeable shoulder at short range (~ 4.4 Å); ii) a split in the first major peak at 5.9 Å for [Ch][Lys] and [Ch][Lys] + H_2O + guaiacol systems; iii) the first major minimum > 7.9 Å. Cluster analysis was compared using each of these features, as shown in Figure S2. Using a 4.4 Å nearest-neighbour cut-off yields only random associations of finite clusters containing up to ~30 molecules in pure [Ch][Lys] before falling below the percolation line. Addition of water reduces the maximum cluster size to <10, and subsequent addition of guaiacol has little further effect. On the other hand, the pronounced minimum near 7.9 Å returns a single, box-spanning (i.e. continuous) cluster for every simulation frame across all three systems. This is unsurprising, considering that this cut-off is >10% of the box dimension.

Figure S2 shows that, using an intermediate nearest-neighbour cut-off value defined by the second feature at 5.9 Å (also shown in the main text as Figure 4B) reveals a transition between a predominantly continuous apolar domain structure and overall bicontinuous liquid nanostructure in [Ch][Lys] and [Ch][Lys] + H_2O, and the formation of finite clusters upon addition of guaiacol.
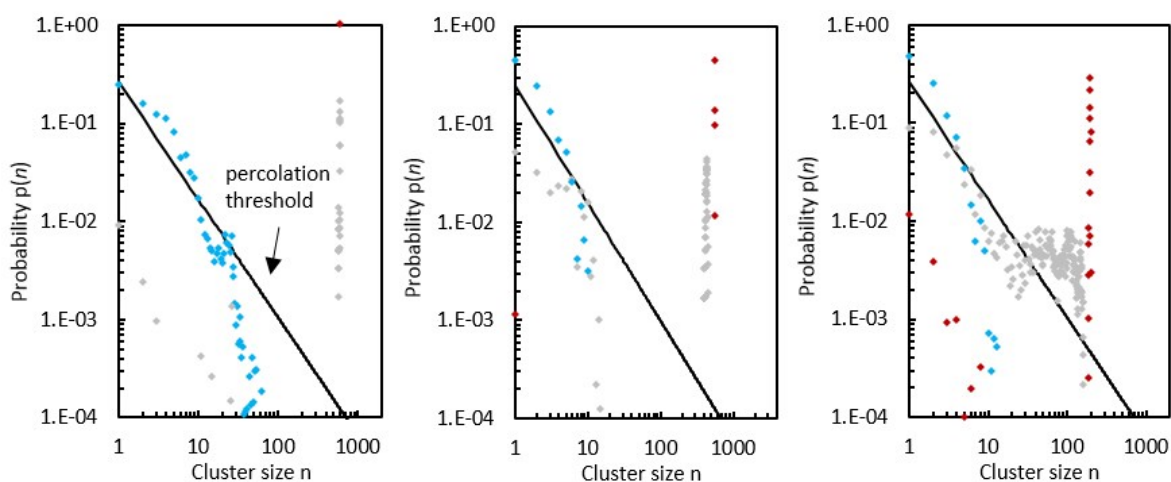
Figure S2. Apolar network based on different features (i.e. different cut-off lengths) in $C_a - C_a$ intermolecular pair-correlation functions (Figure S1). From left to right the three panels correspond to [Ch][Lys], [Ch][Lys] + 5 H_2O and [Ch][Lys] + 5 H_2O + 0.5 guaiacol systems, the different cut-off lengths are colour coded with 4.4 Å, 5.9 Å and 7.6 Å.
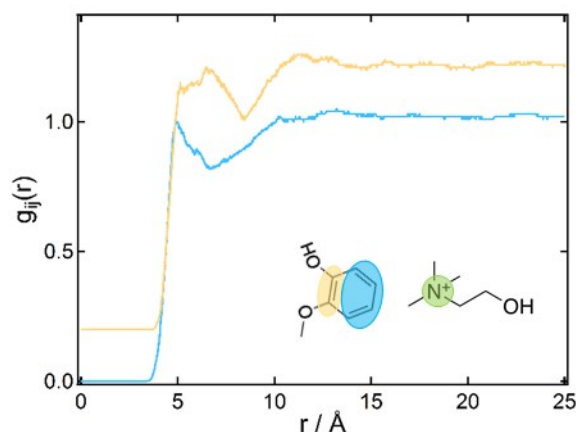

Figure S3. Intermolecular pair-correlation functions between choline ammonium and the guaiacol aromatic carbons. The blue line denotes $N - C_R$ sites and the yellow $N - C_{R2}$ sites (see Table S1), offset for clarity.

Our previous study of choline phenylalaninate revealed a significant cation-π interaction between the cholinium cation and the aromatic sidechain of the anion.[3] This prompted us to investigate the role of the cation in solubilising aromatic solutes such as guaiacol, as shown in Figure S3. However, unlike choline phenylalaninate, the pair-correlation function between the cation charge centre and carbon sites of the aromatic group in the [Ch][Lys] + H_2O + guaiacol system did not show any strong short-range correlation. This indicates cation-π interactions are absent in our systems.

Previous work has identified the oxygen-oxygen pair-correlation function is useful for diagnosing the presence of bulk water structures.[4] The intense primary peak near 2.8 Å is due to intermolecular hydrogen bond, and the small secondary peak near 4.5 Å is a signature to the next nearest neighbour correlation, present when water molecules are close packed in near-tetrahedral arrangements. Figure S4

shows that bulk water structures are present in both [Ch][Lys] plus water systems. Without guaiacol, the oxygen-oxygen radial distribution function is in excellent agreement with pure water, however, after guaiacol addition, both the primary and the secondary correlation peaks have been intensified. This is consistent with the cluster analysis where evidence for the formation of discrete water pockets upon addition of guaiacol is observed. Consequently, when strong, short-range correlations are normalised to the volume fraction of water, it is expected that these correlation peaks will have elevated intensity. Overall, bulk water structures are present in both [Ch][Lys] systems with 1:5 (mol:mol, IL:water) water addition, which is also evidenced in the oxygen-oxygen coordination number shown in Table S2.
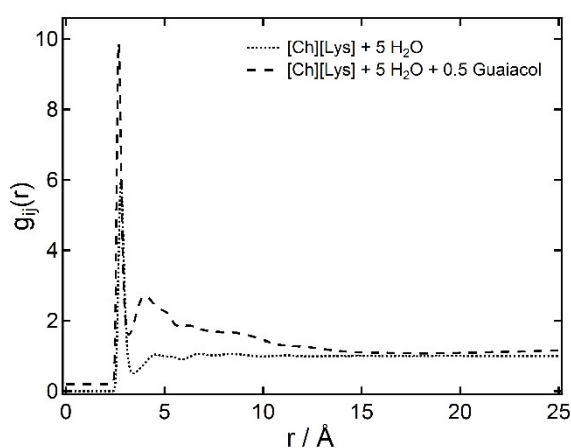

Figure S4. Intermolecular pair-correlation functions between oxygen of water molecules, offset for clarity.

Table S2. Coordination number of waters around water molecules, calculated through a cut-off distance of 3.4 Å between water oxygens.

	Coord. No.	std
[Ch][Lys] + 5 H_2O	2.0	1.0
[Ch][Lys] + 5 H_2O + 0.5 guaiacol	2.4	1.3

References

1.   Jorgensen, W. L.; Laird, E. R.; Nguyen, T. B.; Tirado-Rives, J., Monte Carlo simulations of pure liquid substituted benzenes with OPLS potential functions. *Journal of Computational Chemistry* **1993,** *14* (2), 206-215.
2.   Sambasivarao, S. V.; Acevedo, O., Development of OPLS-AA Force Field Parameters for 68 Unique Ionic Liquids. *Journal of Chemical Theory and Computation* **2009,** *5* (4), 1038-1050.
3.   Miao, S.; Wood, J.; Jiang, H. J.; Imberti, S.; Atkin, R.; Warr, G., Unusual origin of choline phenylalaninate ionic liquid nanostructure. *J. Mol. Liq.* **2020,** *319*, 114327.
4.   Soper, A. K., The Radial Distribution Functions of Water as Derived from Radiation Total Scattering Experiments: Is There Anything We Can Say for Sure? **2013,** *2013*.