Supporting Information

Surfactant Effects on the Synthesis of Oxide Nanoparticles using Deep Eutectic Solvents

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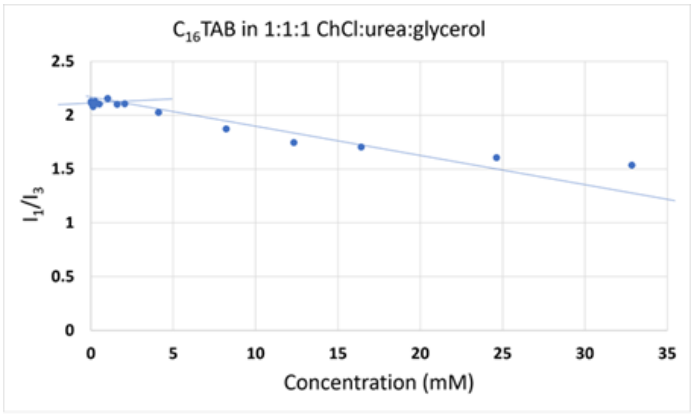
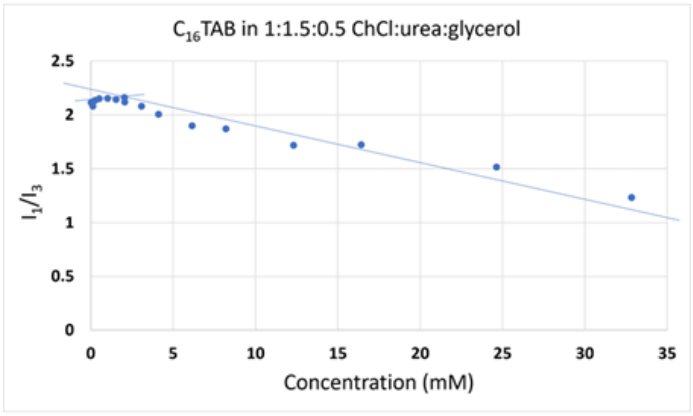
S1 CMC measurement for CTAB in DES using Pyrene Fluorescence



(a)



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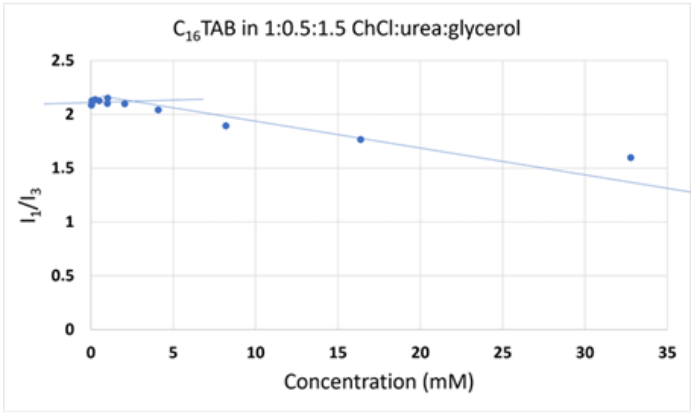

(c)

Figure S1: I_1/I_3 data from pyrene fluorescence measurements on solutions of CTAB at different concentration in 1:1:1 DES (a), 1:1.5:0.5 DES (b) and 1:0.5:1.5 DES (c).

S2 TEM images from Iron and Zinc nanoparticles post and pre calcination

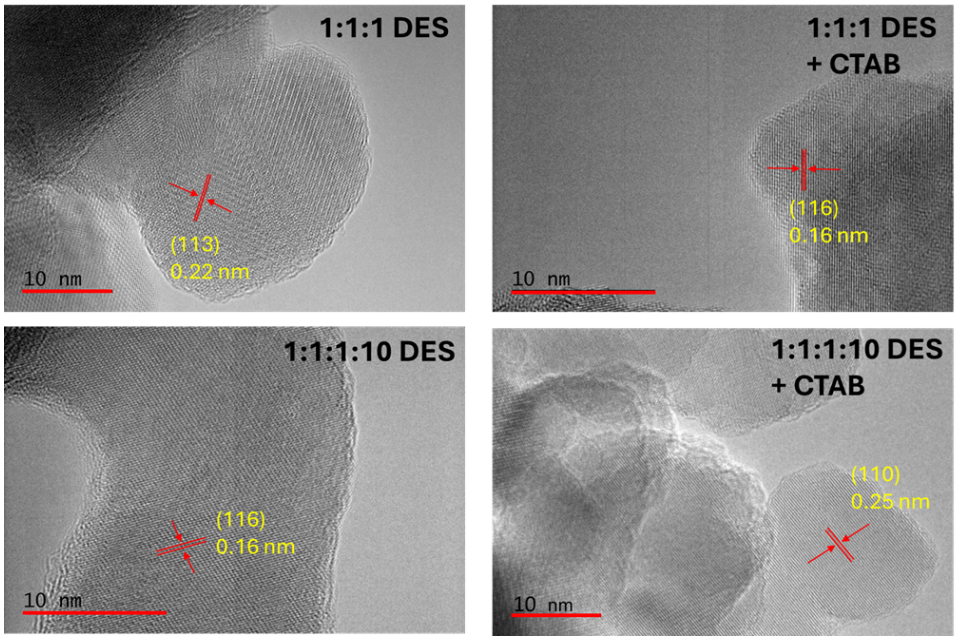

Figure S2: TEM images of iron oxide particles post-calcination from the solvothermal synthesis in 1:1:1 DES and 1:1:1:10 DES, with and without added CTAB, with a scale bar of 10 nm as shown. The red arrows indicate crystal planes of the rhombohedral α-Fe_2O_3 structure, with d-spacings in yellow, confirming the structure identified by PXRD.

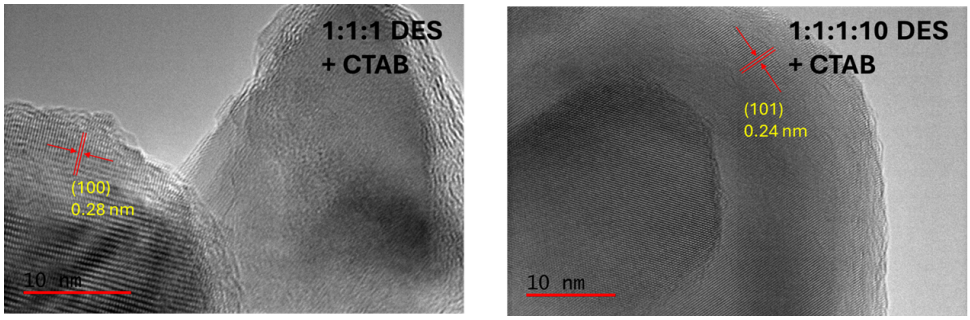

Figure S3: TEM images of zinc oxide particles post-calcination from the solvothermal synthesis in 1:1:1 DES and 1:1:1:10 DES with added CTAB, with a scale bar of 10 nm as shown. The red arrows indicate crystal planes of the hexagonal wurtzite ZnO structure, with d-spacings in yellow, confirming the structure identified by PXRD.

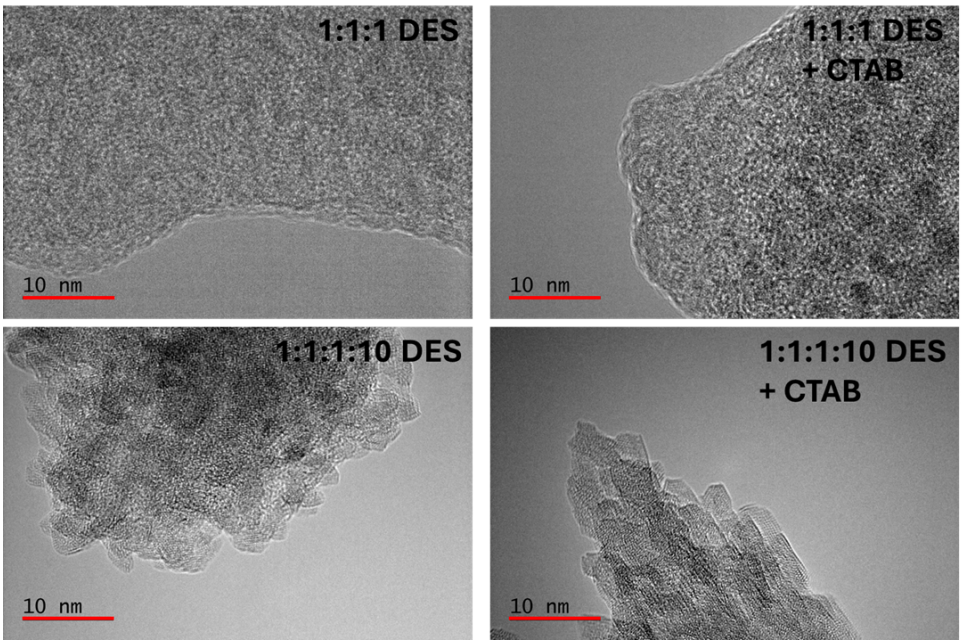

Figure S4: TEM images of iron nanoparticles before calcination from the solvothermal synthesis in 1:1:1 DES and 1:1:1:10 DES, with and without added CTAB with a scale bar of 10 nm as shown.

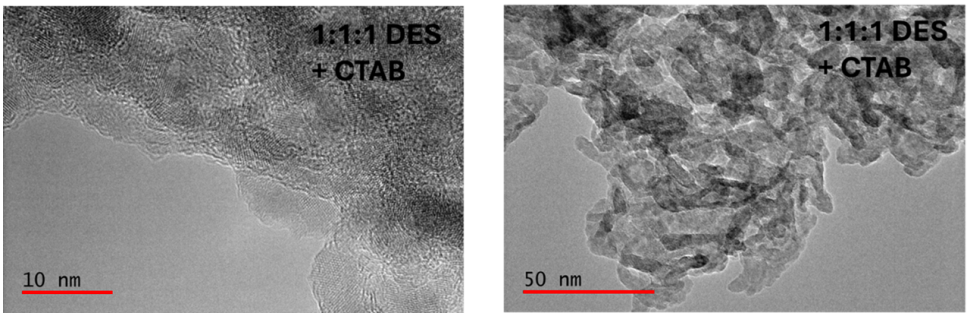

Figure S5: TEM images of zinc nanoparticles before calcination from the solvothermal synthesis in 1:1:1 DES with added CTAB with a scale bar of 10 nm (left) and 50 nm (right) as shown.

S3 SAXS and SANS data from the samples

The neutron scattering length density (SLD; ρ) of any component in a system is calculated using the equation:

$$\rho = \frac{\sum_i^n b_{c_i}}{\overline{V}}$$

where b_{c_i} is the bound coherent scattering length of atom i in a molecule and $\overline{V}$ is the volume containing all the n atoms. The volumes, neutron scattering lengths and calculated SLD values for various individual components in the system is given in Table S1. The SLD values for each DES at different contrasts calculated using the neutron scattering lengths of individual DES components and their mole fractions in each DES are given in Table S2.

Table S1: Volumes, neutron scattering lengths ($\sum b_{c_i}$) and calculated SLD of constituents of the system. The neutron scattering length of each constituent was calculated as the sum of the neutron scattering lengths of the constituting atoms

Chemical	Formula	Volume Å^3	$\sum b_{c_i}$ fm	SLD $\times 10^{-06}$ Å^{-2}
ChCl	$C_5H_{14}NOCl$	202	5.6	0.29
d-ChCl	$C_5H_5D_9NOCl$	202	99.3	5.16
Urea	$CO(NH_2)_2$	76	16.2	0.61
d-Urea	$CO(ND_2)_2$	76	57.9	7.48
Glycerol	$HOCH_2CH(OH)CH_2OH$	121	7.4	2.15
d-Glycerol	$DOCD_2CD(OD)CD_2OD$	121	90.7	7.66
C_nTA^+ head-group[a]	$N(CH_3)_3^+$	135	-4.3	-0.3
d-C_nTA^+ head-group[a]	$N(CD_3)_3^+$	135	89.3	7.12
Hexadecyl alkyl tail	$C_{16}H_{33}$	508.4	-20.79	-0.41
d-Hexadecyl alkyl tail	$C_{16}D_{33}$	508.4	333.15	6.55

(a) The bromide will dissociate in solution and therefore the head group for the micelle is likely to comprise C_nTA^+.

Table S2: Calculated SLD values for DES investigated in this study. SLDs were obtained by considering the neutron scattering lengths of individual DES components and their mole fractions in each DES.

Composition	Contrast	Abbreviation	SLD ($\times 10^{-6}$ Å^{-2})
1ChCl:1U:1Gly	H:H:H	1:1:1 h-DES	0.74
1ChCl:1.5U:0.5Gly	H:H:H	1:1.5:0.5 h-DES	0.92
1ChCl:0.5U:1.5Gly	H:H:H	1:0.5:1.5 h-DES	0.6
1ChCl:1U:1Gly	D:D:D	1:1:1 d-DES	6.37
1ChCl:1.5U:0.5Gly	D:D:D	1:1.5:0.5 d-DES	6.32
1ChCl:0.5U:1.5Gly	D:D:D	1:0.5:1.5 d-DES	6.41
1ChCl:1U:1Gly:10W	H:H:H:H	1:1:1:10 h-DES	0.18
1ChCl:1.5U:0.5Gly:10W	H:H:H:H	1:1.5:0.5:10 h-DES	0.25
1ChCl:0.5U:1.5Gly:10W	H:H:H:H	1:0.5:1.5:10 h-DES	0.11
1ChCl:1U:1Gly:10W	D:D:D:D	1:1:1:10 d-DES	6.29
1ChCl:1.5U:0.5Gly:10W	D:D:D:D	1:1.5:0.5:10 d-DES	6.26
1ChCl:0.5U:1.5Gly:10W	D:D:D:D	1:0.5:1.5:10 d-DES	6.32

Table S3: Cylindrical fit parameter for the SANS data from solutions of CTAB in DES and Zn^{2+} + CTAB in DES shown in Figure 2 in the manuscript and SAXS from the phase separated region of Zn^{2+} + CTAB in 1:1.5:0.5 DES shown in Figure S6. The fit parameters from Atri et. al. [1] using an ellipsoidal form factor are given for comparison.

	This study			Atri et. al. [1]		
	Radius (Å)	Length (Å)	ϕ ($\times 10^{-2}$)	Radius (Å)	Length (Å)	ϕ ($\times 10^{-2}$)
1:1.5:0.5 DES						
+ CTAB	21.2 ± 2.2	134 ± 12	6.1 ± 0.2	21.7 ± 0.1	156 ± 5	5.2 ± 0.2
+ CTAB + Zn^{2+}	21.9 ± 1.8	67.2 ± 3.5	0.72 ± 0.03			
1:1.5:0.5 DES						
+ CTAB + Zn^{2+}						
dense phase (SAXS)	14.7 ± 1.1	85 ± 5	20 ± 1			
1:0.5:1.5 DES						
+ CTAB	19.9 ± 1.6	65.6 ± 3.1	5.8 ± 0.2	20.5 ± 0.7	74 ± 2	5.4 ± 0.4
+ CTAB + Zn^{2+}	20.7 ± 1.8	509 ± 25	3.1 ± 0.2			

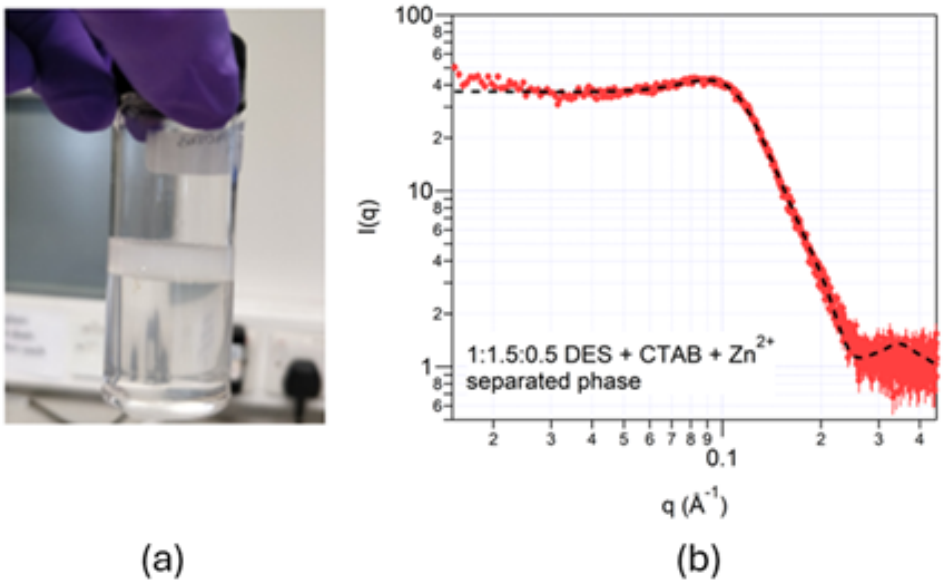

Figure S6: (a) Photograph showing phase separation observed upon the addition of Zn^{2+} in 1:1.5:0.5 DES with CTAB and allowing the mixture to stand at 70 °C for 2 days, (b) SAXS data from the phase separated region from the solution of Zn^{2+} in 1:1.5:0.5 DES with CTAB.The data was fitted to a cylindrical form factor (dashed black line)

Table S4: Ellipsoidal fit parameter, Polar radius (R_{polar}) and Equatorial radius (R_{eq}) and volume fraction of the micelles (ϕ), from co-fitting of the SANS data at two contrasts for solutions of CTAB in unhydrated and hydrated DES ((h-CTAB in d-DES and d-CTAB in h-DES) shown in Figure S7.

	Unhydrated DES			Hydrated DES		
ChCl:U:Gly	R_{polar} (Å)	R_{eq} (Å)	ϕ ($\times 10^{-2}$)	R_{polar} (Å)	R_{eq} (Å)	ϕ ($\times 10^{-2}$)
1:1.5:0.5	137.8 ± 0.3	21.8 ± 0.1	5.2 ± 0.2	118.7 ± 0.6	21.4 ± 0.1	5.1 ± 0.1
1:1:1	118.9 ± 0.3	20.7 ± 0.1	5.5 ± 0.1	90.1 ± 0.5	20.9 ± 0.1	5.1 ± 0.1
1:0.5:1.5	75.5 ± 0.4	19.8 ± 0.1	5.6 ± 0.1	76.6 ± 0.5	20.7 ± 0.1	5.2 ± 0.1

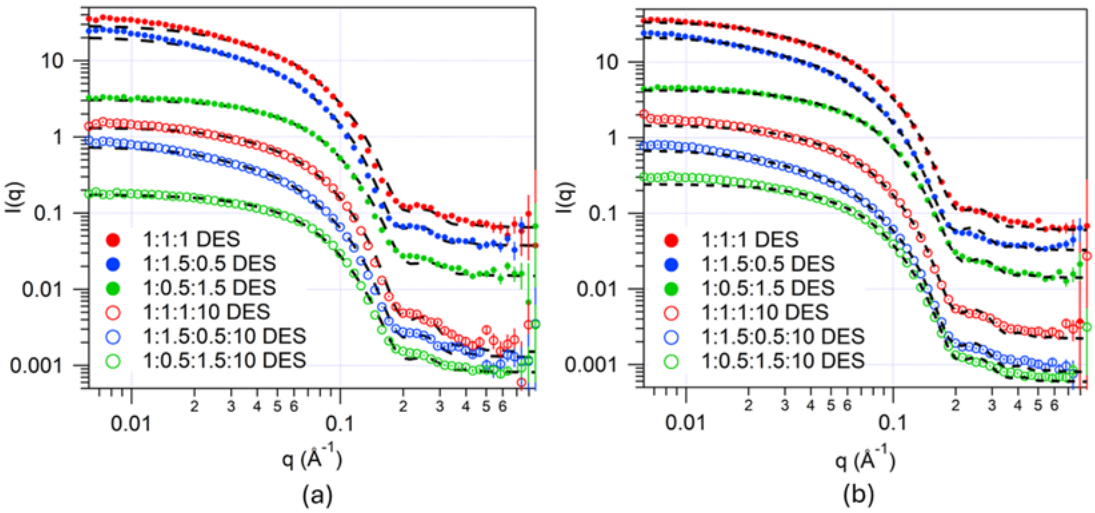

Figure S7: SANS data from CTAB in unhydrated DES: 1:1:1 DES (red solid circles), 1:1.5:0.5 DES (blue solid circles), 1:0.5:1.5 DES (green solid circles), and hydrated DES: 1:1:1:10 DES (red hollow circles), 1:1.5:0.5:10 DES (blue hollow circles) and 1:0.5:1.5 DES (green hollow circles). (a) d-CTAB in h-DES. (b) h-CTAB in d-DES. The two SANS datasets for each DES was co-fitted to uniform ellipsoidal models shown by the black dashed lines. The data is offset along the y-axis for clarity.

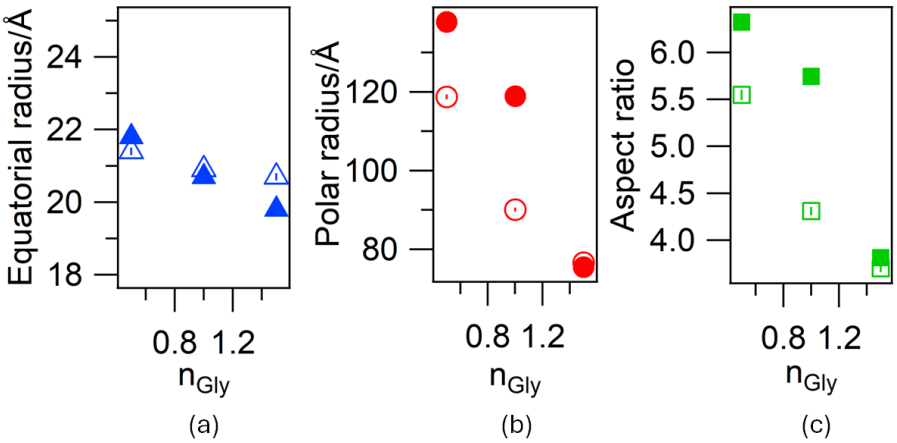

Figure S8: Structural parameters of surfactant micelles at different solvent compositions obtained through the uniform ellipsoidal fits to SANS data from CTAB in unhydrated DES (solid circles) and hydrated DES (hollow circles) shown in Figure S7 and fit parameters summarised in Table S4. (a) Equatorial radius, (b) Polar radius, and (c) Aspect Ratio (Polar ratio/Equatorial ratio). The data is plotted against (n_{Gly} which is the ratio of glycerol to ChCl in the solvent; 0.5 for 1:1.5:0.5 DES, 1 for 1:1:1 DES and 1.5 for 1:1.5:0.5 DES)

S4 N_2 sorption results and analysis

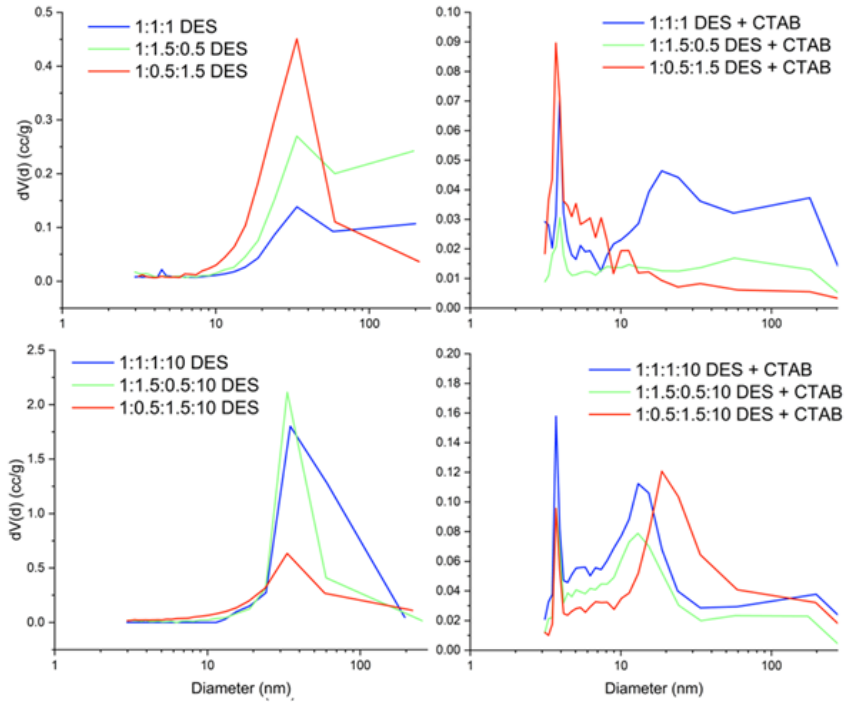

Figure S9: Pore size distribution calculated using BJH analysis from the N_2 adsorption isotherms of the FeOx samples from the solvothermal synthesis in ChCl:U:Gly DES and DES with added water, with and without added CTAB: ChCl:U:Gly DES without CTAB, ChCl:U:Gly DES with 5 wt% CTAB, ChCl:U:Gly:Water DES without CTAB, and ChCl:U:Gly:Water DES with 5 wt% CTAB.

References

[1] Ria S. Atri, Adrian Sanchez-Fernandez, Oliver S. Hammond, Iva Manasi, James Doutch, James P. Tellam, and Karen J. Edler. Morphology modulation of ionic surfactant micelles in ternary deep eutectic solvents. *J. Phys. Chem. B*, 124(28):6004–6014, 2020. PMID: 32551622.