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Ionic liquid surfactants as multitasking micellar catalysts for epoxidations in water

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Supporting Information

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1. Synthesis Procedures

Synthesis of imidazolium bromides

The 1-alkyl-3-methylimidazolium bromides were synthesised by equimolar addition of 1-Methylimidazole (Sigma-Aldrich) to the corresponding 1-bromoalkane (Sigma-Aldrich) on a scale of 30 g. The solution was stirred for 24 h at 50 °C followed by evaporation of impurities for 16 h at 60 °C and 10^{-3} mbar.

Synthesis of surface-active imidazolium tungstates

The imidazolium tungstates were synthesised according to our literature reported procedure[S1] via an anion exchange procedure from the corresponding imidazolium bromides. 20.0 mmol (2.0 equiv.) [RMIM]Br (R = butyl, octyl, decyl, dodecyl) were dissolved in 800 mL deionised water and subsequently rinsed over 120 g freshly regenerated Amberlite 402 (OH). The basic fractions of the eluted [RMIM]OH were collected and 10.5 mmol (1.05 equiv.) H_2WO_4 (purchased from VWR) were added. The dispersion was stirred for 1 h until a pH of 7 was reached. Then the excess tungstic acid was removed by filtration and the water evaporated under reduced pressure. The resulting solid was further dried overnight at 10^{-6} mbar and 80 °C using a turbomolecular pump. The resulting colorless solids were obtained in very good yields (>95%, >9.5 mmol) and further on stored under an argon atmosphere due to the high hygroscopy.

1-Butyl-3-methylimidazolium tungstate $[BMIM]_2[WO_4]$

$C_{16}H_{30}N_4O_4W$: MW = 526.28 g/mol.

^{1}H-NMR* (400 MHz, D_2O, 298 K) δ [ppm]: 0.85 (t, J = 7.4 Hz, 3H), 1.24 (h, J = 7.3 Hz, J = 7.4 Hz, 2H), 1.77 (p, J = 7.1 Hz, J = 7.3 Hz, 2H), 3.82 (s, 3H), 4.12 (t, J = 7.1 Hz, 2H), 7.35 (d, J = 2.0 Hz, 1H), 7.40 (d, J = 2.0 Hz, 1H).

^{13}C-NMR (101 MHz, D_2O, 29 8K) δ [ppm]: 12.59, 18.72, 31.22, 35.55, 49.22, 122.13, 123.40, 135.59.

Elemental analysis calcd. (%) for $C_{16}H_{30}N_4O_4W \cdot H_2O$: C 35.31, H 5.93, N 10.29, O 14.70, W 33.78; found: C 34.60, H 5.75, N 10.01.

1-Octyl-3-methylimidazolium tungstate $[OMIM]_2[WO_4]$

$C_{24}H_{46}N_4O_4W$: MW = 638.50 g/mol.

^{1}H-NMR* (400 MHz, D_2O, 298K) δ [ppm]: 1.09 – 1.26 (m, 3H), 1.78 (p, J = 7.2 Hz, 2H), 3.85 (s, 3H), 4.14 (t, J = 7.2 Hz, 2H), 7.41 (s, 1H), 7.43 (s, 1H).

^{13}C-NMR (101 MHz, D_2O, 298K) δ [ppm]: 13.59, 22.20, 25.61, 28.55, 29.44, 31.30, 35.72, 49.51, 122.11, 123.64, 135.65.

Elemental analysis calcd. (%) for $C_{24}H_{46}N_4O_4W$: C 45.15, H 7.26, N 8.77, O 10.02, W 28.79; found: C 44.65, H 7.95, N 8.64.

1-Decyl-3-methylimidazolium tungstate $[DeMIM]_2[WO_4]$

$C_{28}H_{54}N_4O_4W$: MW = 694.40 g/mol.

^{1}H-NMR* (400 MHz, D_2O, 298 K) δ [ppm]: 0.75 (t, J = 6.6 Hz, 3H), 1.01 – 1.29 (m, 14H), 1.79 (t, J = 7.2 Hz, 2H), 3.86 (s, 2H), 4.15 (t, J = 7.2 Hz, 2H), 7.41 (d, J = 2.0 Hz, 1H), 7.45 (d, J = 2.0 Hz, 1H).

^{13}C-NMR (101 MHz, D_2O, 298 K) δ [ppm]: 13.66, 22.37, 25.79, 28.66, 28.99, 29.09, 29.21, 29.58, 31.61, 35.77, 49.51, 122.07, 123.73, 135.75.

Elemental analysis calcd. (%) for $C_{28}H_{54}N_4O_4W$: C 48.42, H 7.84, N 8.07, O 9.21, W 26.47; found: C 48.40, H 8.38, N 8.14.

1-Dodecyl-3-methylimidazolium tungstate $[DoMIM]_2[WO_4]$

$C_{32}H_{62}N_4O_4W$: MW = 750.71 g/mol.

^{1}H-NMR* (400 MHz, D_2O, 298 K) δ [ppm]: 0.85 (t, J = 6.7 Hz, 3H), 1.15 – 1.44 (m, 18H), 1.89 (t, J = 7.2 Hz, 2H), 3.97 (s, 3H), 4.26 (t, J = 7.3 Hz, 2H), 7.51 (d, J = 2.0 Hz, 1H), 7.59 (d, J = 2.0 Hz, 1H).

^{13}C-NMR (101 MHz, D_2O, 298K) δ [ppm]: 13.78, 22.57, 26.12, 29.09, 29.39, 29.52, 29.71 (2C), 29.75, 29.85, 31.90, 35.89, 49.49, 122.01, 123.87, 135.89.

Elemental analysis calcd. (%) for $C_{32}H_{62}N_4O_4W \cdot H_2O$: C 50.00, H 8.39, N 7.29, O 10.41, W 23.91; found: C 50.07, H 8.61, N 7.29.

*C2 proton is not visible due to a fast H/D exchange in D_2O.

Synthesis of phosphonates

p-Fluorophenylphosphonate (B1)[S2]

8.3 g diethyl-p-fluorophenylphosphonate (**A1**) (35.8 mmol, synthesised analogous to a literature procedure[S3]) was suspended in 50 mL conc. HCl and stirred under reflux for 8 h. Afterwards, the solution was washed with dichloromethane (2 × 50 mL) and the aqueous phase concentrated in vacuo and diluted with 3 x 10 mL H_2O, resulting in 4.29 g (24.4 mmol) p-fluorophenylphosphonate (**B1**) in 68 % yield.

^{1}H-NMR (400 MHz, D_2O, 298 K) δ [ppm]: 7.08 (m, 2H), 7.62 (m, 2H).

^{13}C-NMR (101 MHz, D_2O, 298 K) δ [ppm]: 115.70 (dd, J = 21.6, 16.1 Hz), 126.86 (d, J = 185.7 Hz), 133.07 (t, J = 10.6 Hz), 164.78 (d, J = 251.5 Hz).

^{19}F-NMR (376 MHz, D_2O, 298 K) δ [ppm]: −107.8 (s).

^{31}P-NMR (162 MHz, D_2O, 298 K) δ [ppm]: 15.9 (s).

p-Tolylphosphonate (B2)[S2]

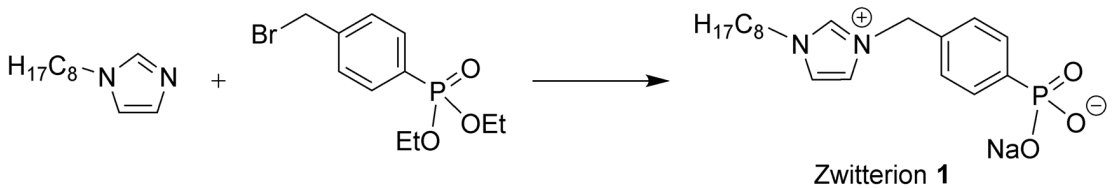
1.5 g diethyl-p-tolylphosphonate (**A2**) (6.57 mmol, synthesised according to a literature procedure[S3]) was suspended in 10 mL conc. HCl and stirred under reflux for 8 h. Afterwards, the solution was washed with dichloromethane (2 × 10 mL) and the aqueous phase was concentrated in vacuo and diluted with 3 x 2 mL H_2O, resulting in 950 mg (5.52 mmol) p-tolylphosphonate (**B2**) in 84% yield.

^{1}H-NMR (400 MHz, D_2O, 298 K) δ [ppm]: 2.26 (s, 1H), 7.24 (dd, J = 8.0 Hz, J = 3.7 Hz, 1H), 7.54 (dd, J = 13.2 Hz, J = 8.1 Hz, 1H).

^{13}C-NMR (101 MHz, D_2O, 298 K) δ [ppm]: 20.58 (s), 127.85 (d, J = 184.3 Hz), 129.19 (d, J = 15.1 Hz), 130.44 (d, J = 10.7 Hz), 142.95 (s).

^{31}P-NMR (162 MHz, D_2O, 298 K) δ [ppm]: 17.0 (s).

Synthesis of zwitterion 1



Zwitterion **1**

1.54 mL 1-octylimidazole (1.40 g, 7.75 mmol, 1.0 equiv.) and 2.38 g diethyl-4-bromomethyl-phenylphosphonate (7.75 mmol, 1.0 equiv.; synthesised according to a literature procedure[S3])

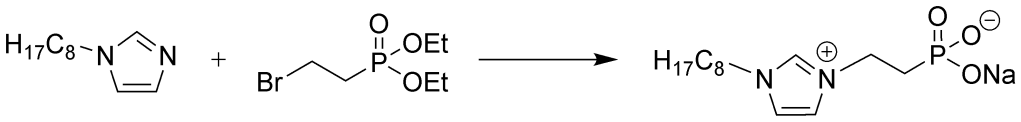
were slowly heated to 100 °C from 0 °C within 2 h and then all volatiles removed under reduced pressure at 100 °C for 4 h. Afterwards, 10 mL 48% aq. HBr was added and stirred for 4 h under reflux. After cooling to room temperature, HBr is evaporated and the residue dissolved in 20 mL water. The solution is neutralised with aq. Na_2CO_3. The water was removed and the residue extracted with 30 mL MeOH/EtOAc (1:1 mixture). The crude product was purified by column chromatography (silica gel 60, MeOH/EtOAc 1:1 → MeOH, 3 × 10 cm). Halide-free fractions (tested with aq. $AgNO_3$) were combined and the solvent evaporated, resulting in 1.79 g (62% yield) of zwitterion-**1**.

^{1}H-NMR (400 MHz, D_2O, 298 K) δ [ppm]: 0.80–0.88 (m, 3H), 1.20–1.30 (m, 10H), 1.84 (t, J = 7.1 Hz, 2H), 4.15 (t, J = 7.1 Hz, 2H), 5.37 (s, 2H), 7.34 (d, J = 2.4 Hz, 1H), 7.36 (d, J = 2.6 Hz, 1H), 7.48 (q, J = 2.1 Hz, 2H), 7.69–7.78 (m, 2H). 8.84 (s, 1H).

^{13}C-NMR (101 MHz, D2O, 298 K) δ [ppm]: 13.42, 21.97, 25.27, 27.97, 28.18, 29.09, 30.97, 49.67, 52.55, 122.55, 122.59, 127.98 (d, J = 13.9 Hz), 131.06 (d, $J_{C–P}$ = 9.8 Hz), 135.20 (d, $J_{C–P}$ = 3.1 Hz), 135.39, 137.78 (d, $J_{C–P}$ = 174.4 Hz).

^{31}P-NMR (162 MHz, D_2O, 298 K) δ [ppm]: 10.33 (s). ESI-MS (negative mode, H_2O): measured: 349.6 m/z; calculated: $[1-Na]^-$ = 349.2 m/z.

Synthesis of zwitterion 2



Zwitterion **2**

3.00 mL 1-octylimidazole (2.72 g, 11.1 mmol, 1.0 equiv.) and 2.00 g diethyl-2-bromoethylphosphonate (11.1 mmol, 1.0 equiv.; synthesised according to a literature procedure[S4]) were heated to 50 °C for 24 h and then all volatiles removed at 60 °C for 4 h using a turbomolecular pump. Afterwards, 10 mL 48% aq. HBr was added and stirred for 4 h under reflux. After cooling to room temperature, HBr was evaporated and the residue dissolved in 20 mL water. The solution was neutralised with aq. Na_2CO_3. The water was removed and the residue extracted with 30 mL MeOH/EtOAc 1:1. The crude product was purified by column chromatography (silica gel 60, MeOH, 3 × 10 cm). Halide-free fractions (tested with aq. $AgNO_3$) were combined and the solvent evaporated, resulting in 1.00 g (30 % yield) of zwitterion-**2**.

^{1}H-NMR (400 MHz, D_2O, 298 K) δ [ppm]: 0.72 – 0.79 (m, 3H), 1.13 – 1.24 (m, 10H), 1.78 (q, J = 7.1 Hz, 2H), 1.96 – 2.09 (m, 2H), 4.09 (t, J = 7.1 Hz, 2H), 4.21 – 4.32 (m, 2H), 7.37 (t, J = 1.9 Hz, 1H), 7.44 (t, J = 1.9 Hz, 1H), 8.72 (s, 1H).

^{13}C-NMR (101 MHz, D_2O, 298 K) δ [ppm]: 13.33, 21.92, 25.24, 27.94, 28.12, 29.06, 29.80 (d, J = 127.9 Hz), 30.93, 45.94, 49.58, 122.11, 122.22, 135.09.

^{31}P-NMR (162 MHz, D_2O, 298 K) δ [ppm]: 16.41.

ESI-MS (negative mode, H_2O): Measured: 287.3 m/z; calculated: [**2**$-Na]^-$ = 287.2 m/z.

2. Cryo-TEM Images

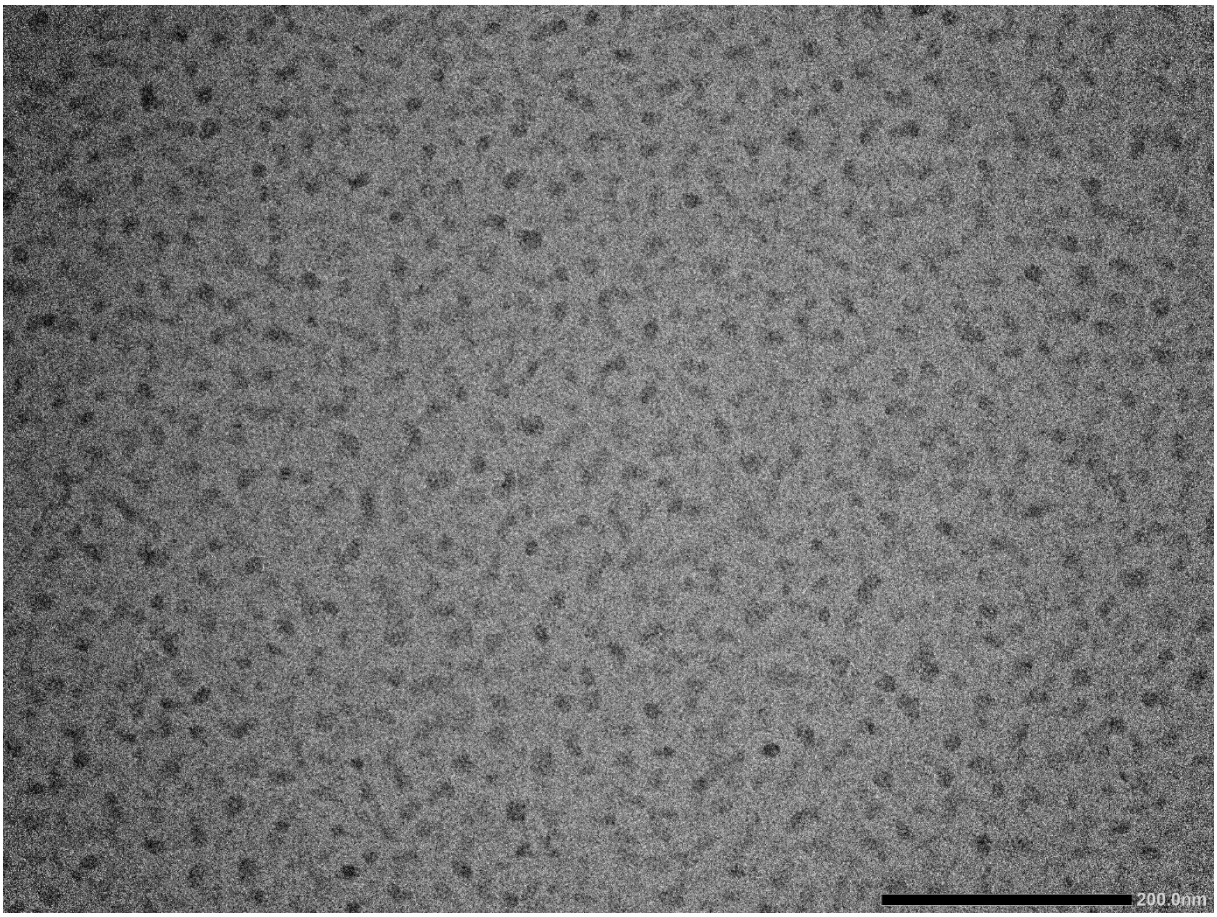


Figure S1. Cryo-TEM image of 178 mM $[OMIM]_2[WO_4]$ in 50 wt.% H_2O_2.

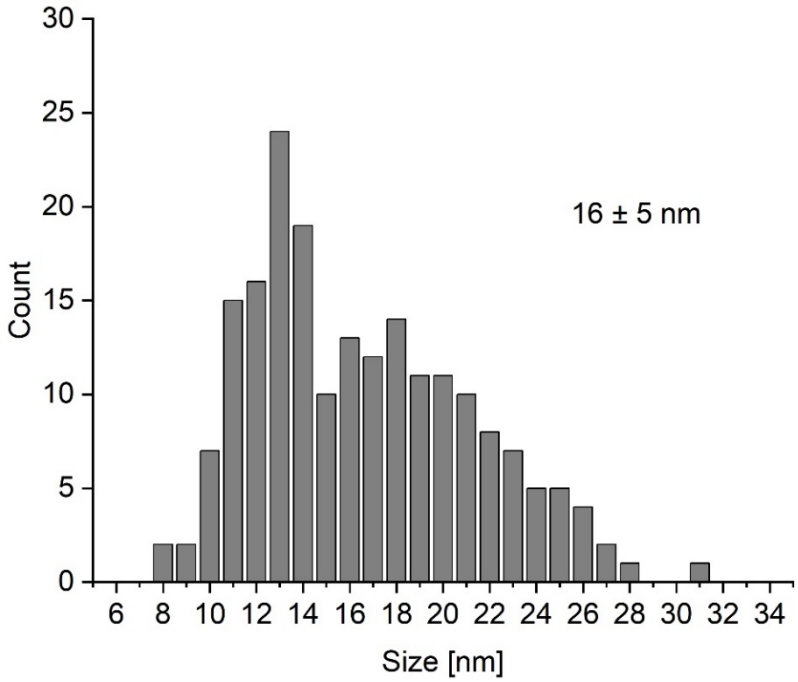


Figure S2. Micelle diameter distribution in Figure S1 evaluated for a total of 200 micelles.

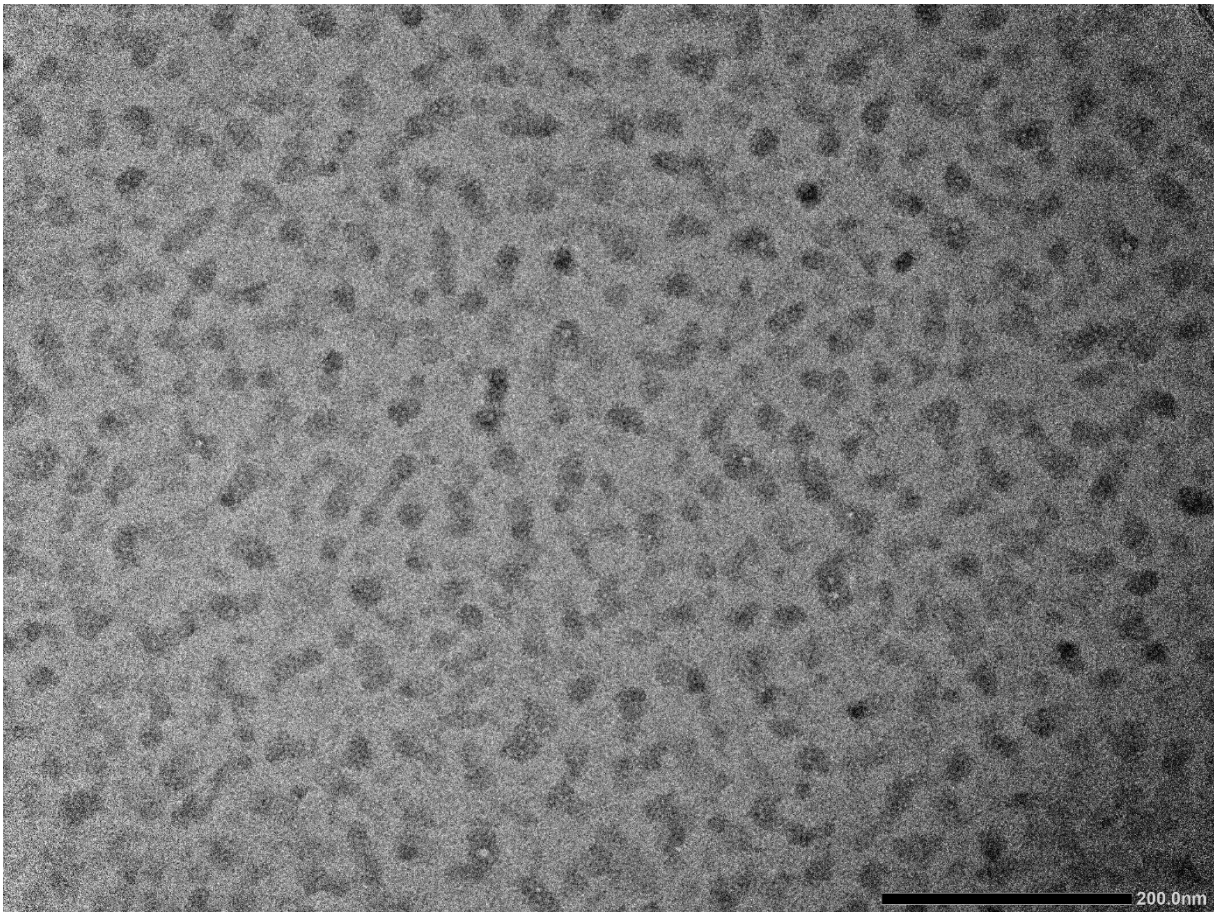


Figure S3. Cryo-TEM image of 178 mM $[OMIM]_2[WO_4]$ in 50 wt.% H_2O_2 saturated with COE.

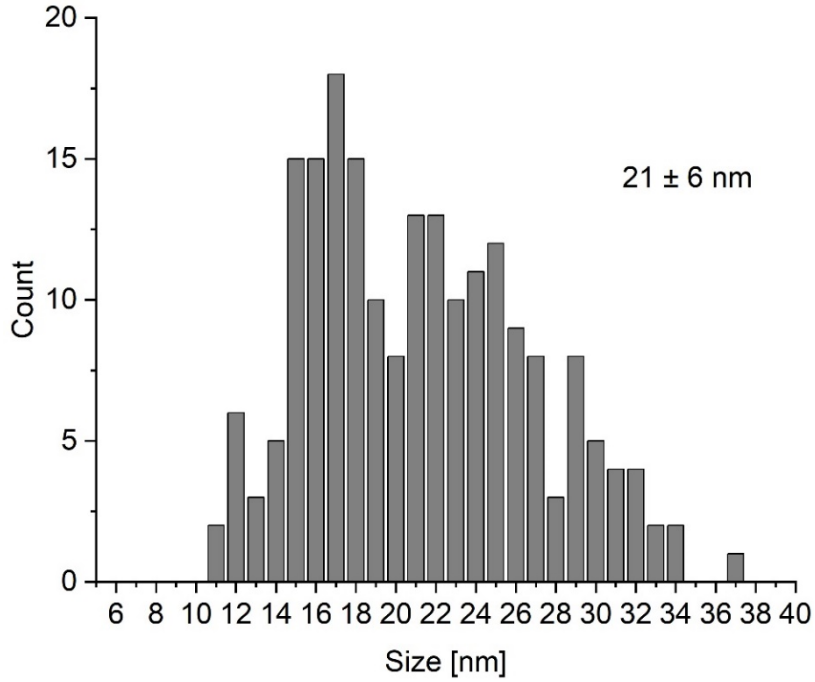


Figure S4. Micelle diameter distribution of Figure S3 evaluated for a total of 200 micelles.

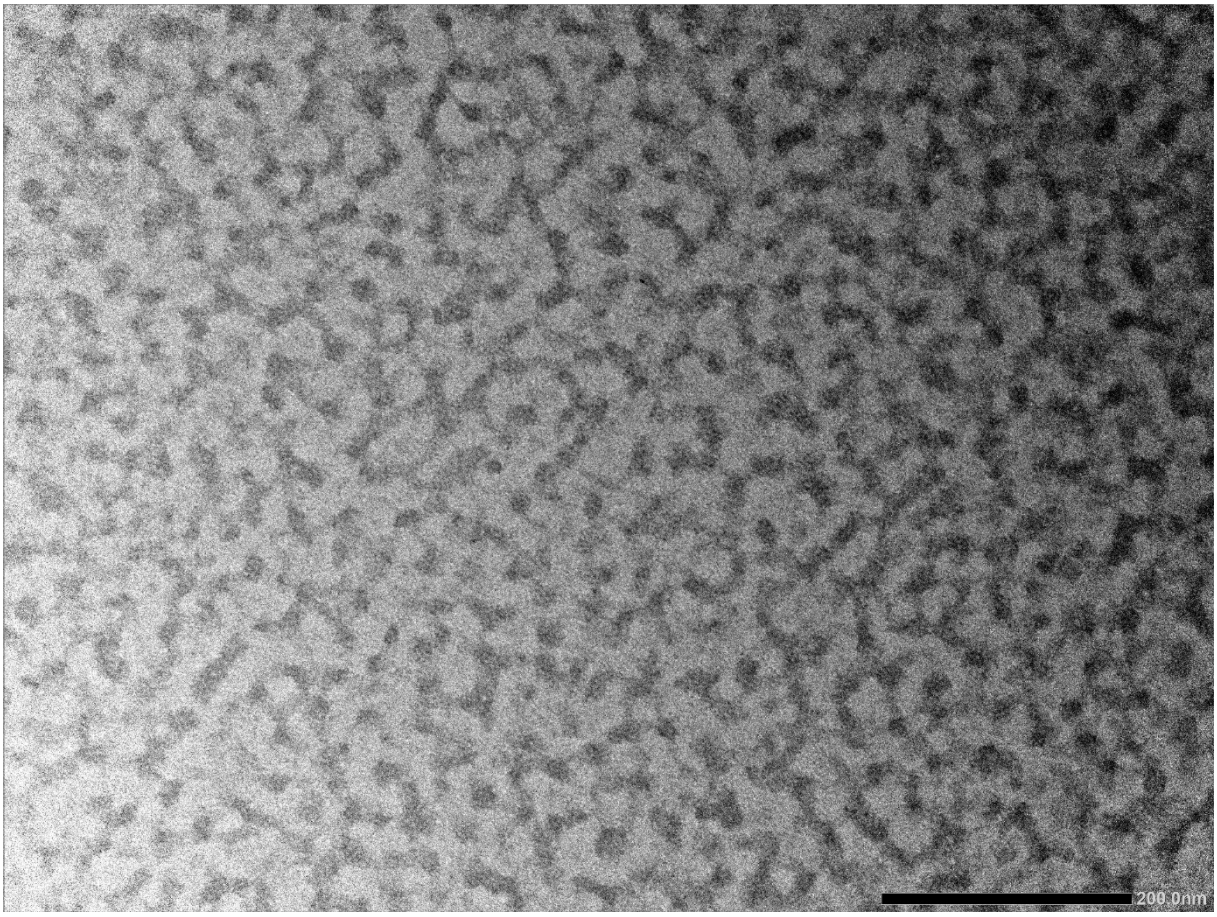


Figure S5. Cryo-TEM image of 356 mM $[OMIM]_2[WO_4]$ in 50 wt% H_2O_2.

3. Calculation of COE-uptake in micelles

The excess-concentration Γ, which gives the molar concentration of the surfactant on the surface/interphase is described by the Gibbs-adsorption isotherm:

$$\Gamma = \frac{n}{A} = -\frac{1}{RT} * \frac{d\gamma}{d \ln c}$$

Input of the values 323 K for the measurement at 50 °C and $\frac{d\gamma}{d \ln c}$ by −6.255 (see Figure S6) results in an excess-concentration of 2.33 µmol/m² or 1.4 surfactant moieties per nm², speaking for 2.8 $[OMIM]^+$ cations per nm².
As the slopes of the Gibbs-isotherm with and without COE are identical, we conclude that the surfactant surface concentration is constant. Therefore, the average number of surfactant molecules N per micelle is calculated by

$$N = \Gamma * A_{micelle} * N_A = \Gamma * 4\pi r^2 * N_A$$

The surface area of the COE-saturated micelles is larger by a factor of 1.63 than the 'empty' micelles, corresponding to a 2.08-fold volume increase of the micelles upon COE uptake (Table S1). Subtraction of the swollen micelles' volume occupied by the surfactant molecules results in an average void of 1083 nm³, which has to be filled with COE. Taking the molecular volume of COE 4.63/nm³ into account, the number of COE molecules inside the swollen micelle is 5017. This means, that each catalyst moiety on average dissolves 2.54 molecules of COE in the aqueous phase (1.27 molecules per $[OMIM]^+$ cation).

Table S1. Micelle parameter calculated from Images Figure S1 (without COE) and S2 (with COE).

Micelle parameter	Without COE	With COE
r	8.3 ± 2.2 nm	10.6 ± 2.8 nm
A	865 ± 459 nm²	1411 ± 745 nm²
V	2394 ± 1903 nm³	4989 ± 1897 nm³
$N_{[OMIM]^+}$	1211 ± 642	1975 ± 1043
Γ	2.33 µmol/m²	2.33 µmol/m²

Table S2. Parameters and the corresponding units for the calculation.

Parameter	Symbol	Unit
Radius	r	nm
Area	A	nm^2
Volume	V	nm^3
Aggregation number	N	---
Amount of substance	n	µmol
Gas constant	R	J/(K·mol)
Avogadro constant	N_A	mol^{-1}
Temperature	T	K
Concentration	c	mmol
Surface Tension	γ	mN/m
Excess conentration	Γ	µmol/m^2

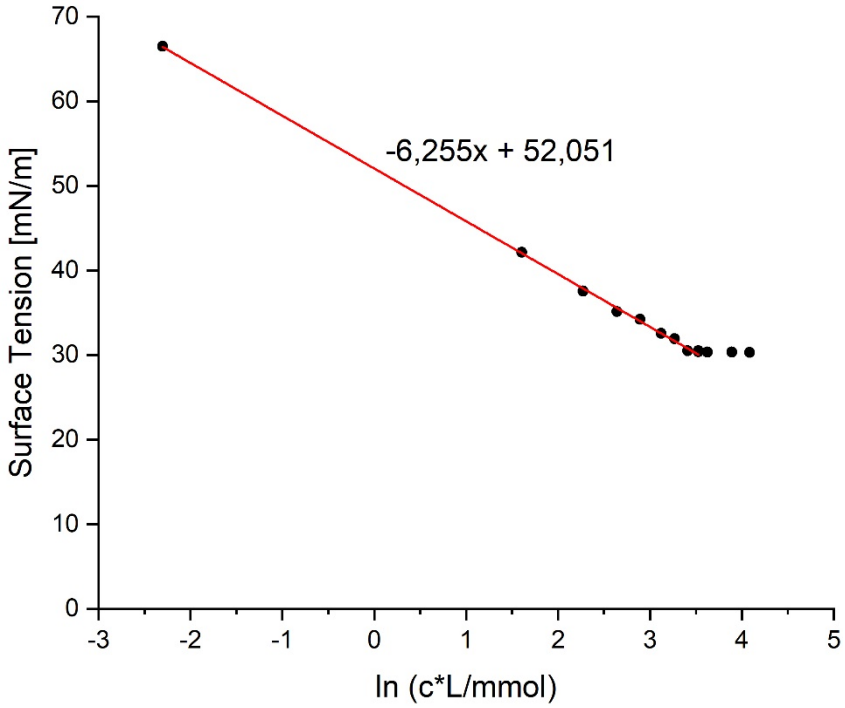


Figure S6. Semilogarithmic plot of the surface tension of $[OMIM]_2[WO_4]$ in aq. H_2O_2 (50 wt.%) at 50 °C and various IL concentrations.

4. Tensiometry measurements of $[RMIM]_2[WO_4]$ (R = Octyl, Decyl, Dodecyl)

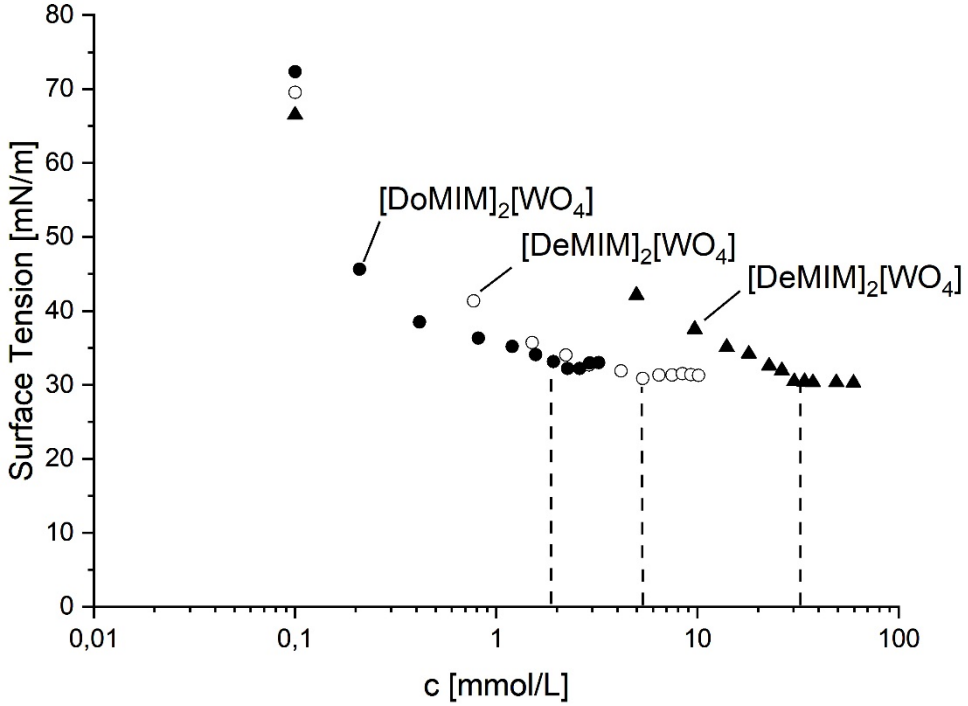


Figure S7. Tensiometry data for $[RMIM]_2[WO_4]$ (R = Octyl, Decyl, Dodecyl) in 50 wt.% aq. H_2O_2 at 50 °C.

5. Conductometry measurements of $[RMIM]_2[WO_4]$ (R = Octyl, Decyl, Dodecyl)

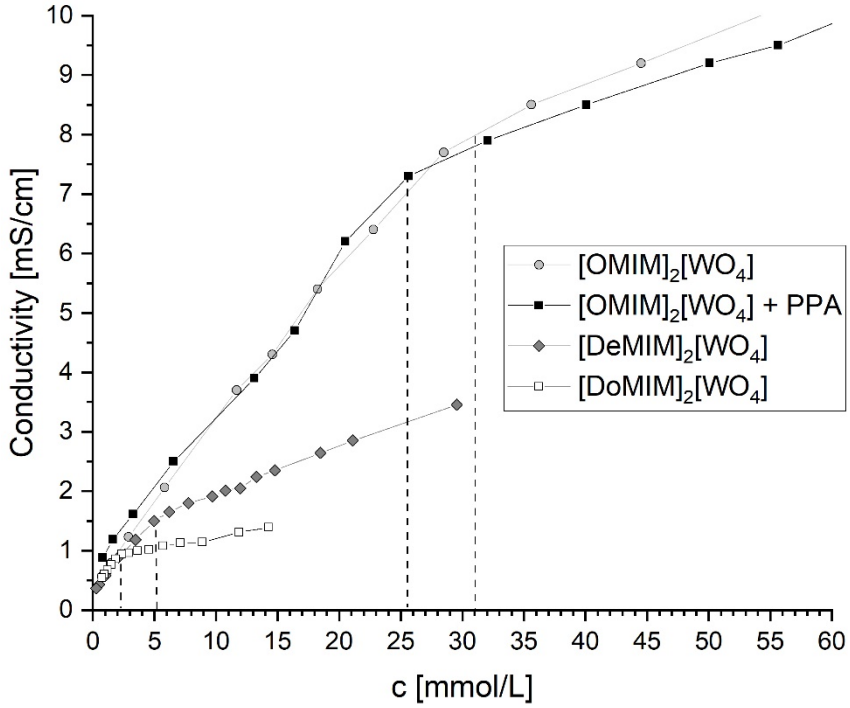


Figure S8. Conductivity data for $[RMIM]_2[WO_4]$ (R = Octyl, Decyl, Dodecyl) in 50 wt% aq. H_2O_2 at 50 °C. PPA = Phenylphosphonic acid.

6. Determination of the activation energy

The activation energy of the epoxidation of COE by $[OMIM]_2[WO_4]$ was determined by an Arrhenius-plot for temperatures of 30, 40, 50, 60 and 70 °C.

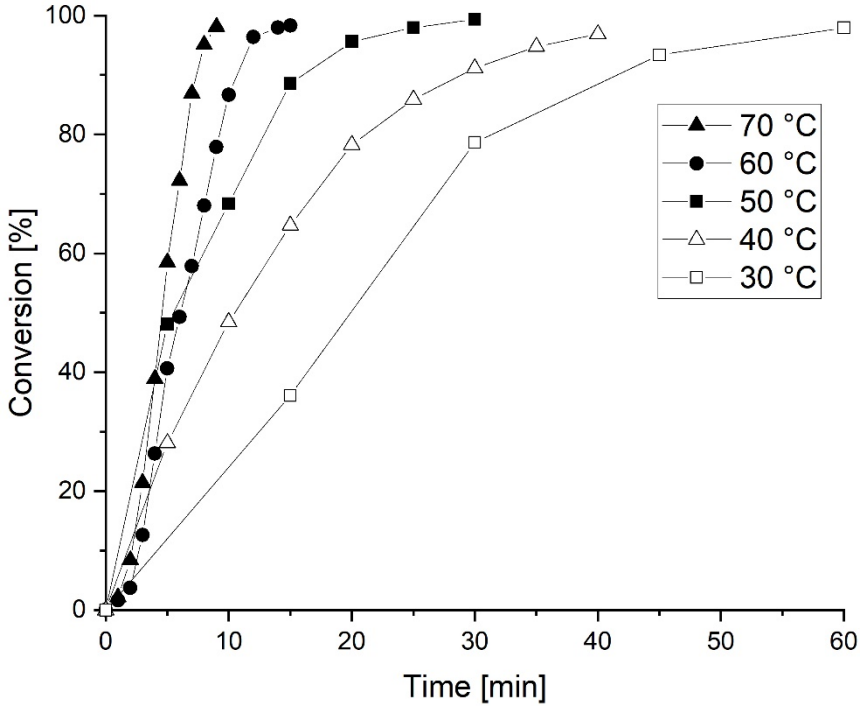


Figure S9. Kinetic plots for the epoxidation of COE. Conditions: Molar ratio $[OMIM]_2[WO_4]$:PPA:COE:H_2O_2 = 2.5:5:100:250.

Temperature [°C]	Temperature [1/K]	Rate [mmol*mL^{-1}*min^{-1}]	ln(rate)
70	0.002915	0.908	-0.09685
60	0.003003	0.631	-0.46082
50	0.003096	0.456	-0.78436
40	0.003195	0.300	-1.20397
30	0.003300	0.203	-1.59669

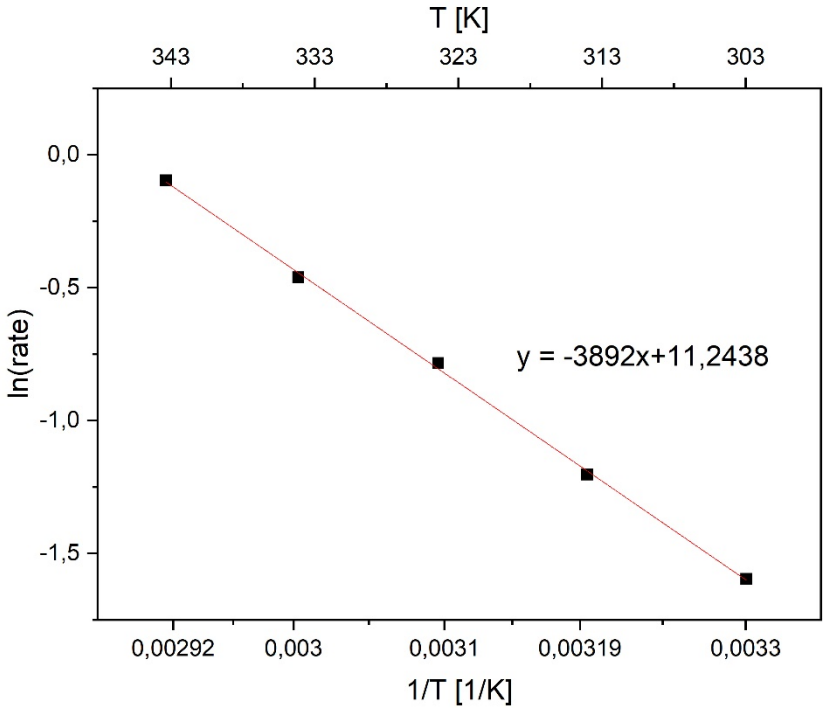


Figure S10. Arrhenius plot for the Epoxidation of COE with $[OMIM]_2[WO_4]$.

Multiplication of the slope with the ideal gas constant R results in an activation energy of 32.34 kJ/mol.

7. ESI-MS spectra of zwitterions 1 and 2 in H_2O_2

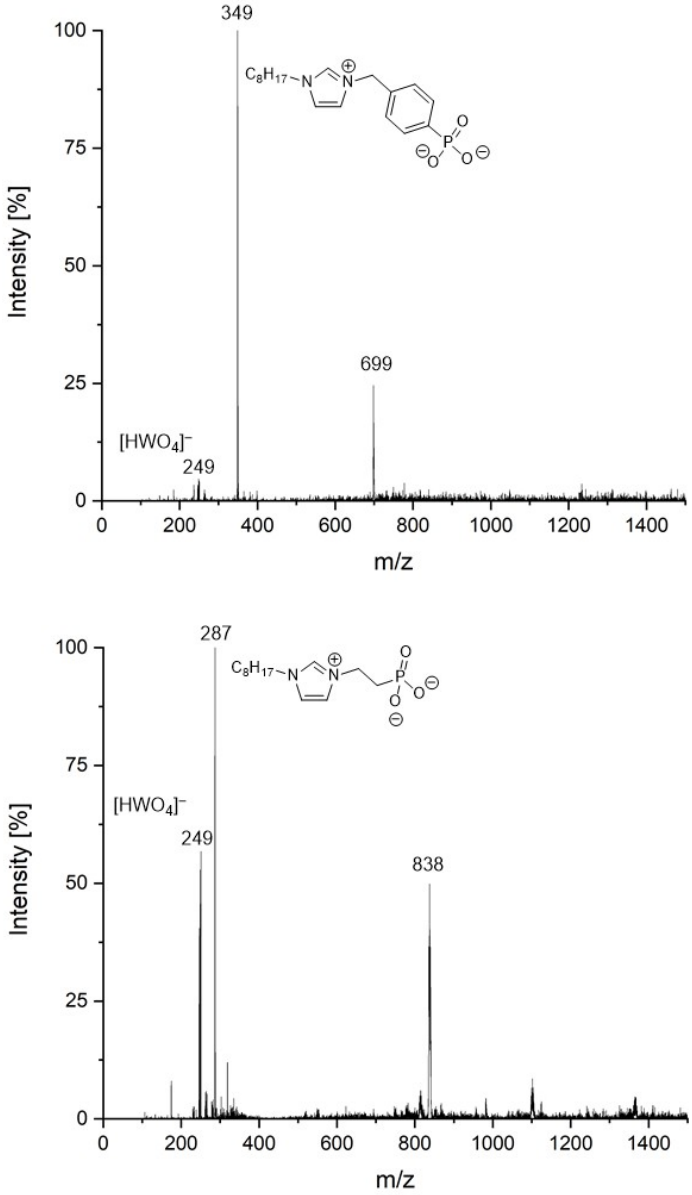


Figure S11. ESI-MS spectra of zwitterions **1** (top) and **2** (bottom) with equimolar amounts of H_2WO_4 in 50 wt.% aq. H_2O_2.

8. References

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