# **Supporting Information**

# Designing the Head Group of CO<sub>2</sub>-Triggered Switchable Surfactants

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#### 1. Experimental section

### 1.1 Materials

Carbon dioxide (Praxair, 99.998%), nitrogen (Praxair, 99.998%), and argon (Praxair, 99.998%) were used as received. North Sea crude oil (API 19.5°, 129 cSt viscosity at 40 °C, 1.65 mg<sub>KOH</sub>/g total acid number) was obtained from Chevron and used for the demulsification experiments. Dimethylacetamide dimethyl acetal (90%) was received from TCI. All other reagents were received from Sigma Aldrich. All standard reagents and solvents were used without additional purification, unless otherwise noted.

Infrared spectra were recorded for liquid samples neat on an Avatar 360 FT-IR spectrometer. Solution <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Advance 400 MHz spectrometer. Thermogravimetric analyses were performed with a Thermal Sciences STA 1500 instrument. Heats of protonation were recorded using an isothermal mixing and reaction calorimeter, model superCRC 208-110. Height measurements for crude oil demulsifying experiments were made with an Eberbach cathetometer.

#### **1.2 Synthesis of amphiphiles**

#### <u>N'-Octyl-N,N-dimethylacetamidine (1a)</u>



Octyl amine (8.34 ml, 50.4 mmol) was added dropwise to *N*,*N*-dimethylacetamide dimethyl acetal (6.69 g, 50.2 mol) and the resulting mixture was heated to 65 °C for 20 min. The methanol byproduct was then removed under reduced pressure and the orange crude product was purified by vacuum distillation to produce a clear liquid (7.57 g, 38.2 mmol, 76%).

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 0.85$  (t, J = 7.2 Hz, 3H, C<sub>7</sub>H<sub>14</sub>CH<sub>3</sub>), 1.28 (m, 10H, C<sub>5</sub>H<sub>10</sub>), 1.47 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>N), 1.84 (s, 3H, CCH<sub>3</sub>), 2.84 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 3.14 (t, J = 7.2 Hz, 2H, C<sub>5</sub>H<sub>10</sub>CH<sub>2</sub>N);

<sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 12.3, 14.1, 22.7, 27.6, 29.3, 29.6, 31.9, 32.4. 37.9, 50.2, 158.6;

IR (neat, cm<sup>-1</sup>): 1008 (m), 1184 (m), 1259 (w), 1343 (m), 1455 (s), 1629 (s,  $\upsilon$  (C=N)), 2853 (m), 2925 (s); HRMS (EI<sup>+</sup>) m/z calc. for  $[C_{12}H_{27}N_2]^+$  199.2168, observed 199.2161.

# 2-Octyl-2-imidazoline (2a)



Ethylene diamine (13.4 ml, 200 mmol) was added to a solution of nonanoic acid (17.6 ml, 100 mmol) in toluene (100 ml). The reaction mixture was refluxed for 24 h employing a Dean-Stark trap to remove the water by-product. After completion of the reaction, toluene was removed under reduced pressure to yield a yellow powder. The crude product was crystallized from acetone to yield the pure product as white powder (11.68 g, 59%). The spectroscopic data obtained for this compound were consistent with those reported in the literature.<sup>1</sup>

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 0.88$  (t, J = 6.8 Hz, 3H, C<sub>7</sub>H<sub>14</sub>CH<sub>3</sub>), 1.27 (m, 10H, C<sub>5</sub>H<sub>10</sub>), 1.61 (m, 2H, C<sub>6</sub>H<sub>13</sub>CH<sub>2</sub>CH<sub>2</sub>C), 2.24 (t, J = 7.8 Hz, 2H, C<sub>7</sub>H<sub>14</sub>CH<sub>2</sub>C), 3.39 (s, 4H, NCH<sub>2</sub>CH<sub>2</sub>NH), 5.51 (s, 1H, NH);

<sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 14.0, 22.6, 26.7, 29.1, 29.2, 29.3, 29.4, 31.8, 49.4, 168.3;

IR (KBr, cm<sup>-1</sup>): 723 (m), 817 (m), 1051 (m), 1117 (m), 1223 (m), 1351 (m), 1466 (m), 1647 (s,  $\upsilon$  (C=N)), 2853 (s), 2924 (s), 3301 (w); HRMS (EI<sup>+</sup>) m/z calc. for  $[C_{11}H_{23}N_2]^+$  183.1861, observed 183.1901.

# 1-Methyl-2-octyl-2-imidazoline (3a)



Nonanoic acid (5.34 ml, 33.8 mmol) was added to *N*-methylethylenediamine (5.0 ml, 67.6 mmol) in toluene (60 ml) in a round bottom flask. The colourless reaction mixture was refluxed for 18 h employing a Dean-Stark trap to remove the water by-product. Removal of the toluene under reduced pressure led to a yellow oil. The crude product was purified by vacuum distillation to yield a pale yellow liquid (5.54 g, 76%).

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta = 0.88$  (t, J = 6.60 Hz, 3H, C<sub>7</sub>H<sub>14</sub>CH<sub>3</sub>), 1.28 (m, 10H, C<sub>5</sub>H<sub>10</sub>), 1.62 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>C), 2.21 (t, J = 7.81 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>C), 2.79 (s, 3H, NCH<sub>3</sub>), 3.28 (t, J = 9.61 Hz, 2H, =NCH<sub>2</sub>CH<sub>2</sub>N-), 3.65 (t, J = 9.61 Hz, 2H, =NCH<sub>2</sub>CH<sub>2</sub>N-);

<sup>13</sup>**C NMR** (100 MHz, DMSO-d<sub>6</sub>): δ = 13.1, 21.6, 25.3, 26.6, 28.1, 28.3, 28.6, 30.8, 32.8, 50.4, 52.2, 167.6;

**IR** (neat, cm<sup>-1</sup>): 1004 (m), 1267 (m), 1456 (s), 1618 (s,  $\upsilon$  (C=N)), 2855 (s), 2925 (s), 3208 (w); HRMS (EI<sup>+</sup>) m/z calc. for  $[C_{12}H_{24}N_2]^+$  196.1939, observed 196.1940.

# N'-(4-Heptylphenyl)-N,N-dimethylacetamidine (4a)



4-Heptyl-aniline (5.11 g, 26.7 mmol) was added dropwise to *N*,*N*-dimethylacetamide dimethyl acetal (3.55 g, 26.7 mmol) and the resulting mixture was heated to 65 °C for 20 min. The resulting methanol was then removed under reduced pressure and the residual liquid was purified by vacuum distillation to yield a pale yellow liquid (6.26 g, 24.1 mmol, 90%).

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta = 0.87$  (t, J = 6.8 Hz, 3H, C<sub>6</sub>H<sub>12</sub>CH<sub>3</sub>), 1.29 (m, 8H, C<sub>4</sub>H<sub>8</sub>), 1.58 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>C), 1.85 (s, 3H, CCH<sub>3</sub>), 2.53 (t, J = 7.8 Hz, 2H, C<sub>6</sub>H<sub>13</sub>CH<sub>2</sub>C), 3.00 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 6.61 (d, J = 8.0 Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 7.02 (d, J = 8.0 Hz, 2H, C<sub>6</sub>H<sub>4</sub>);

<sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 14.1, 14.9, 22.7, 29.2, 29.3, 31.7, 31.9, 35.4, 37.9, 122.2, 128.6, 135.6, 149.8, 157.3;

IR (neat, cm<sup>-1</sup>): 1008 (m), 1184 (m), 1259 (m), 1343 (m), 1455 (s), 1629 (s,  $\upsilon$  (C=N)), 2853 (m), 2925 (s); HRMS (EI<sup>+</sup>) m/z calc. for  $[C_{17}H_{29}N_2]^+$  261.2330, observed 261.2333.





Tetramethyl urea (8.16 ml, 68.0 mmol) was dissolved in methylene chloride (15 ml) and then oxalyl chloride (9.8 ml, 116 mmol) was added slowly to the mixture. After the reaction mixture was refluxed for 24 h, the solvent was removed under reduced pressure yielding a white powder. In a separate flask, octyl amine (20.0 ml, 121 mmol, having been dried over solid KOH overnight and distilled prior to use) was dissolved in dry acetonitrile (20 ml). The white powder was dissolved in dry acetonitrile (30 ml). The octyl amine solution was added dropwise and the reaction mixture was heated to 60 °C for 20 h, resulting in a yellow solution. The solvent was removed under reduced pressure and ether (300 ml) was added. The solution was cooled in an ice bath. An aqueous solution of 3.75 M sodium hydroxide (100 ml) was saturated with potassium carbonate and was slowly added to the cooled solution. The organic layer was removed and the aqueous phase was extracted with ether (2 x 100 ml). The organic layers were combined, dried over MgSO<sub>4</sub> and the solvents were removed under reduced pressure. The pale vellow liquid was purified by vacuum distillation to yield a clear liquid (11.8 g, 51.8 mmol, 76%). The spectroscopic data obtained for this compound were consistent with those reported in the literature.<sup>2</sup>

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 0.88$  (t, J = 6.8, 3H, C<sub>7</sub>H<sub>14</sub>CH<sub>3</sub>), 1.29 (m, 10H, C<sub>5</sub>H<sub>10</sub>), 1.51 (m, 2H, C<sub>6</sub>H<sub>13</sub>CH<sub>2</sub>CH<sub>2</sub>N=), 2.65 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.74 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 3.10 (t, J = 7.0, 2H, CH<sub>2</sub>N);

<sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ = 14.0, 22.6, 27.4, 29.3, 29.5, 31.8, 32.8, 38.7, 39.5, 49.6, 159.8;

IR (neat): 914 (m), 1037 (w), 1065 (m), 1138 (m), 1237 (m), 1237 (m), 1363 (s), 1455 (m), 1494 (m), 1625 (s,  $\upsilon$  (C=N)), 2854 (m), 2925 (s); HRMS (EI<sup>+</sup>) calc. for  $[C_{13}H_{30}N_3]^+$  228.2434, observed 228.2428.

# Dimethyloctylamine (6a)

NMe<sub>2</sub>

This compound was obtained commercially but its spectroscopic data are included here for comparison to those of the bicarbonate salt.

<sup>1</sup>**H** NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta = 0.86$  (t, J = 6.6 Hz, 3H, C<sub>7</sub>H<sub>14</sub>CH<sub>3</sub>), 1.25 (m, 10H, C<sub>5</sub>H<sub>10</sub>CH<sub>3</sub>), 1.37 (m, 2H, C<sub>6</sub>H<sub>13</sub>CH<sub>2</sub>CH<sub>2</sub>N), 2.09 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.16 (t, J = 7.0 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>N);

<sup>13</sup>**C NMR** (100 MHz, DMSO-d<sub>6</sub>): δ = 13.88, 22.01, 26.70, 26.76, 28.59, 28.83, 31.18, 44.85, 58.95;

**IR** (neat, cm<sup>-1</sup>): 1042 (m), 1170 (m), 1267 (w), 1379 (w), 1466 (s), 2359 (m), 2762 (s), 2813 (m), 2854 (m), 2927 (s).

# 1.3 In Situ Spectra of the Bicarbonate Salts

The amidine, guanidine, or amine was dissolved in DMSO- $d_6$  with 10 equivalents of distilled H<sub>2</sub>O in an NMR tube. CO<sub>2</sub> was bubbled through the solution for 20 min and NMR spectra were recorded immediately. CDCl<sub>3</sub> was used for compound **2b** as the <sup>13</sup>C NMR spectrum in DMSO was not clear. Due to the low solubility in DMSO, the NMR spectra of compound **4b** were recorded in D<sub>2</sub>O. In general, the NMR spectra of the bicarbonate salts could not be acquired using the same solvent as was used for the neutral compounds because of insufficient solubility.

IR spectra were obtained after bubbling  $CO_2$  through a solution of equimolar amounts of surfactant and water in  $CH_2Cl_2$  until most of the solvent was evaporated. An IR spectrum of the viscous residue was then acquired.

# N'-Octyl-N,N-dimethylacetamidinium bicarbonate (1b)



<sup>1</sup>**H NMR** (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 0.83$  (t, 3H, C<sub>7</sub>H<sub>14</sub>C*H*<sub>3</sub>), 1.29 (m, 10H, C<sub>5</sub>*H*<sub>10</sub>), 1.52 (2H, C<sub>6</sub>H<sub>13</sub> C*H*<sub>2</sub>CH<sub>2</sub>N), 2.20 (3H, CC*H*<sub>3</sub>), 3.10 (s, 6H, N(C*H*<sub>3</sub>)<sub>2</sub>), 3.29 (2H, C<sub>5</sub>H<sub>10</sub>C*H*<sub>2</sub>N);

<sup>13</sup>**C NMR** (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 14.37, 14.61, 22.55, 26.52, 29.13, 29.19, 30.17, 31.73, 44.81, 44.88, 159.61 (HCO<sub>3</sub><sup>-</sup>), 164.00;

IR (neat, cm<sup>-1</sup>): 689 (m), 834 (m,  $\upsilon$  out-of-plane (HCO<sub>3</sub><sup>-</sup>)), 1005 (m,  $\upsilon$  C-OH stretch (HCO<sub>3</sub><sup>-</sup>)), 1380 (s,  $\upsilon$  C-OH bend (HCO<sub>3</sub><sup>-</sup>)), 1650 (s,  $\upsilon$  (C=N)), 1924 (w), 2664 (w),

2855 (m), 2925 (m).

# 2-Octyl-2-imidazolinium bicarbonate (2b)



<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta = 0.833$  (t, 3H, C<sub>7</sub>H<sub>14</sub>CH<sub>3</sub>), 1.22 (m, 10H, C<sub>5</sub>H<sub>10</sub>), 1.47 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C), 2.38 (2H, CH<sub>2</sub>CH<sub>2</sub>C), 3.69 (s, 4H, NC<sub>2</sub>H<sub>4</sub>NH); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta = 14.08$ , 22.64, 26.68, 29.15, 29.17, 29.29, 29.40, 31.83, 49.23, 155.41 (HCO<sub>3</sub><sup>-</sup>), 168.52;

**IR** (neat): 706 (m), 833 (m, υ out-of-plane (HCO<sub>3</sub><sup>-</sup>)), 996 (m, υ C-OH stretch (HCO<sub>3</sub><sup>-</sup>)), 1377 (s, υ C-OH bend (HCO<sub>3</sub><sup>-</sup>)), 1617 (s), 1695 (s, υ (C=N)), 1923 (w), 2546 (w), 2855(w), 2925 (m), 3446 (s).

# 1-Methyl-2-octyl-2-imidazolinium bicarbonate (3b)



<sup>1</sup>**H NMR** (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  0.84 (t, 3H, C<sub>7</sub>H<sub>14</sub>CH<sub>3</sub>), 1.17-1.32 (m, 10H, C<sub>5</sub>H<sub>10</sub>), 1.51 (t, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>C), 2.32 (t, 2H, CH<sub>2</sub>CH<sub>2</sub>C), 2.85 (s, 3H, NCH<sub>3</sub>), 3.44-3.51 (m, 2H, CH<sub>2</sub> ethylene), 3.53-3.61 (m, 2H, CH<sub>2</sub> ethylene);

<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 14.02, 22.22, 25.55, 25.72, 28.72, 28.78, 28.79, 31.40, 33.06, 47.18, 52.08, 158.75 (HCO<sub>3</sub><sup>-</sup>), 168.52;

**IR** (neat, cm<sup>-1</sup>): 703 (m), 833 (m, υ out-of-plane (HCO<sub>3</sub><sup>-</sup>)), 1006 (m, υ C-OH stretch (HCO<sub>3</sub><sup>-</sup>)), 1372 (s, υ C-OH bend (HCO<sub>3</sub><sup>-</sup>)), 1400 (s), 1622 (s), 1659 (s, υ (C=N)), 1922 (w), 2623 (w), 2855 (m), 2925 (m), 3400 (m).

# <u>N'-(4-Heptylphenyl)-N,N-dimethylacetamidinium bicarbonate (4b)</u>



<sup>1</sup>**H NMR** (400 MHz, D<sub>2</sub>O):  $\delta = 0.89$  (t, 3H, C<sub>6</sub>H<sub>12</sub>CH<sub>3</sub>), 1.29 (m, 8H, C<sub>4</sub>H<sub>8</sub>), 1.52 (m,

2H, CH<sub>2</sub>CH<sub>2</sub>C), 1.84 (s, 3H, CCH<sub>3</sub>), 2.47 (m, 2H, CH<sub>2</sub>C), 3.11 (m, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 6.90 (m, 2H, C<sub>6</sub>H<sub>4</sub>), 7.04 (m, 2H, C<sub>6</sub>H<sub>4</sub>);

<sup>13</sup>**C NMR** (100 MHz, D<sub>2</sub>O):  $\delta = 13.05$ , 21.67, 28.05, 28.37, 30.44, 31.24, 34.65, 38.57, 122.17, 127.59, 159.30 (HCO<sub>3</sub><sup>-</sup>), 161.67 (the missing aromatic carbons could not be observed);

**IR** (neat, cm<sup>-1</sup>): 704 (m), 833 (m, υ out-of-plane (HCO<sub>3</sub><sup>-</sup>)), 1009 (m, υ C-OH stretch (HCO<sub>3</sub><sup>-</sup>)), 1391(s, υ C-OH bend (HCO<sub>3</sub><sup>-</sup>)), 1622 (s, υ (C=N)), 1924 (w), 2579 (w), 2855 (m), 2926 (m), 3431 (w).

# **N-Octyl-N',N',N'',N''-tetramethylguanidinium bicarbonate (5b)**



<sup>1</sup>**H NMR** (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 0.833$  (t, 3H, C<sub>7</sub>H<sub>14</sub>CH<sub>3</sub>), 1.23 (m, 10H, C<sub>5</sub>H<sub>10</sub>), 1.50 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>N), 2.86 (s, 12H, (N(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), 3.07 (t, 2H, CH<sub>2</sub>CH<sub>2</sub>N);

<sup>13</sup>**C NMR** (100 MHz, DMSO-d<sub>6</sub>): δ = 14.22, 22.36, 26.41, 28.87, 28.88, 29.48, 31.49, 39.60, 44.67, 159.06 (HCO<sub>3</sub><sup>-</sup>), 161.27;

**IR** (neat, cm<sup>-1</sup>): 703 (m), 834 (m, υ out-of-plane (HCO<sub>3</sub><sup>-</sup>)), 1005 (m, υ C-OH stretch (HCO<sub>3</sub><sup>-</sup>)), 1378 (s, υ C-OH bend (HCO<sub>3</sub><sup>-</sup>)), 1625 (s, υ (C=N)), 1924 (w), 2636 (w), 2855 (m), 2926 (m).

# Dimethyloctylammonium bicarbonate (6b)



<sup>1</sup>**H** NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta = 0.86$  (t, J = 6.6 Hz, 3H, C<sub>7</sub>H<sub>14</sub>CH<sub>3</sub>), 1.25 (m, 10H, C<sub>5</sub>H<sub>10</sub>), 1.38 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>N), 2.13 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.21 (t, J = 7.0 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>N);

<sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ ):  $\delta = 159.32$  (HCO<sub>3</sub><sup>-</sup>). All other signals were identical to those in the <sup>13</sup>C NMR spectrum of the neutral form;

**IR** (neat, cm<sup>-1</sup>): 832 (m, υ out-of-plane (HCO<sub>3</sub><sup>-</sup>)), 999 (m, υ C-OH stretch (HCO<sub>3</sub><sup>-</sup>)), 1377 (s, υ C-OH bend (HCO<sub>3</sub><sup>-</sup>)), 1466 (m), 1660 (s, C=O asym. stretch), 2076 (w), 2342 (m), 2360 (m), 2762 (m), 2856 (m), 2927 (m), 3446 (s).

#### **1.4 Solubility measurements**

The amidine, guanidine or amine (0.20 mmol) was mixed with 3 ml of D<sub>2</sub>O and stirred vigorously for 30 min in a sample vial. The mixture was allowed to stand for 30 min to ensure sedimentation of the undissolved solids. A 200  $\mu$ L aliquot of the saturated aqueous solution was combined in an NMR tube with DMF as an internal standard. The NMR tube was topped up with D<sub>2</sub>O to a total volume of 0.6 ml and a <sup>1</sup>H NMR spectrum was recorded. The amount of internal standard was 10  $\mu$ l for octylamine and compounds **1a**, **2a**, and **3a**, 5  $\mu$ L for compound **4a** and 2.5  $\mu$ l for compound **6a**. Because 0.20 mmol of compound **5a** was fully miscible with 3 ml of D<sub>2</sub>O, an increased amount of the compound was needed as well as an increased amount of the internal standard (25  $\mu$ l). The solubility of each compound was measured at least three times and reported as the average.

#### 1.5 Prediction of logKow Values

The logK<sub>ow</sub> values were predicted using the ALOGPS 2.1 software, which calculates the logK<sub>ow</sub> value for the given structure using nine different algorithms and then averages these values.<sup>3-5</sup> A comparison of predicted and experimental values for 9 amines showed that the ALOGPS predictions are typically slightly too low, by up to 0.26 units (average error is 0.15 units).

### 1.6 Determination of conversion to the bicarbonate salt by CO<sub>2</sub>

The extent of conversion of each base to the bicarbonate salt by  $CO_2$  was determined by <sup>1</sup>H NMR spectroscopy. Compounds **1a**, **2a**, **3a**, **5a**, and **6a** were tested at 40 °C and compounds **1a** and **5a** were also tested at 60 °C, although the method below is written for 40 °C only. Each compound was tested twice by method A and twice by method B to ensure consistent results for each compound. Method A was designed so that the equilibrium would be approached from below (from low conversion). Method B was designed so that the equilibrium would be approached from below (from above (from high conversion)

Method A: The base (0.11 mmol) was placed into a 5 mm NMR tube, after which

25.0  $\mu$ L of distilled H<sub>2</sub>O was added along with 0.60 ml of DMSO-*d*<sub>6</sub>. The tube was set in a 40 °C water bath and CO<sub>2</sub> was bubbled through the mixture for 4 min. A <sup>1</sup>H NMR spectrum was taken immediately with the internal temperature of the NMR being kept constant at 40 °C. The tube was then placed back into the 40 °C water bath and bubbled again with CO<sub>2</sub> for 2 min. A second <sup>1</sup>H NMR spectrum was obtained at 40 °C and this procedure was repeated twice more to ensure that equilibrium had been reached.

<u>Method B:</u> The base (0.11 mmol) was placed into a 5 mm NMR tube, after which 25.0  $\mu$ L of distilled H<sub>2</sub>O was added along with 0.60 ml of DMSO-*d*<sub>6</sub>. CO<sub>2</sub> was bubbed through the solution for 20 min at room temperature and then for 3 min at 40 °C in the water bath. A <sup>1</sup>H NMR spectrum was obtained at 40 °C. The tube was then placed back into the 40 °C water bath and bubbled again with CO<sub>2</sub> for 2 min. A second <sup>1</sup>H NMR spectrum was obtained at 40 °C and this procedure was repeated twice more to ensure that equilibrium had been reached.

# **1.7 Calorimetry**

In a typical experiment, the base (amine, amidine or guanidine) (0.3 mmol) was placed into a sample vial, which was then filled with DMSO to a total volume of 2.0 ml. A reference vial was filled with 2.0 ml of the same solvent. Both samples were placed in an Omnical SuperCRC calorimeter. Once the system was equilibrated, a mixture of 0.15 ml HCl (12 M) and 0.85 ml DMSO was added simultaneously to both the sample and reference vial. The method was validated by determining the  $\Delta H_{rxn}$  for two common nitrogen bases, triethylamine in water (observed value 43.6±0.5 kJ/mol) and aniline in DMSO (30.8±0.5) and comparing them with known literature values (43.2 and 31.0, respectively).<sup>6,7</sup>

# **1.8** Conductivity measurements

Conductivity of surfactant solutions was measured using a JENWAY conductivity meter 4071.  $CO_2$  was purged through a 20 mM solution (20 mL) of the surfactant in EtOH or EtOH/water mixtures using a needle (flow rate 80 mL/min). The change in conductivity was monitored over time. Once the conductivity had reached a constant value, the addition of  $CO_2$  was stopped and Ar was bubbled through the solution. Again, the change in conductivity was monitored over time. This cycle was repeated

twice; any solvent lost to evaporation was replaced after every cycle.

### 1.9 Emulsion stability experiments

Two samples of 0.2 mmol of the amidine, guanidine or amine in 0.25 ml of decane were prepared. In one sample 8 ml deionized water and in the second 8 ml of carbonated water were added. Both samples were shaken by hand for 1 min and then sonicated in a Fisher Scientific FS 30 sonication bath for 15 min. Phase separation was monitored over time.

#### **1.10 Demulsification**

Crude oil (Chevron, North Sea, 4 ml), deionized water (2 ml) and amidine, guanidine or amine (0.29 mmol) were added to a vial. The vial was shaken in a Retsch MM2 mixer mill at a speed setting of 100 for 10 min. The vial was placed on the bench top and was monitored for separation by height measurements at certain time intervals with a cathetometer. All tests were performed twice and the average reported. In some tests, no switchable surfactant (amidine/guanidine/amine) was added.

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