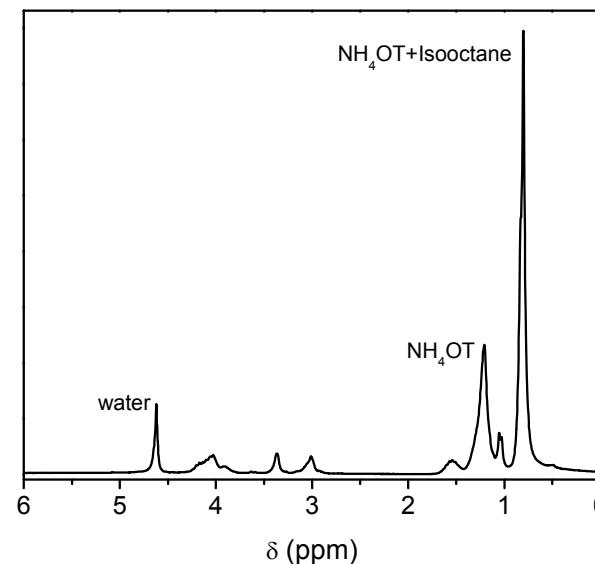


## SUPPORTING INFORMATION

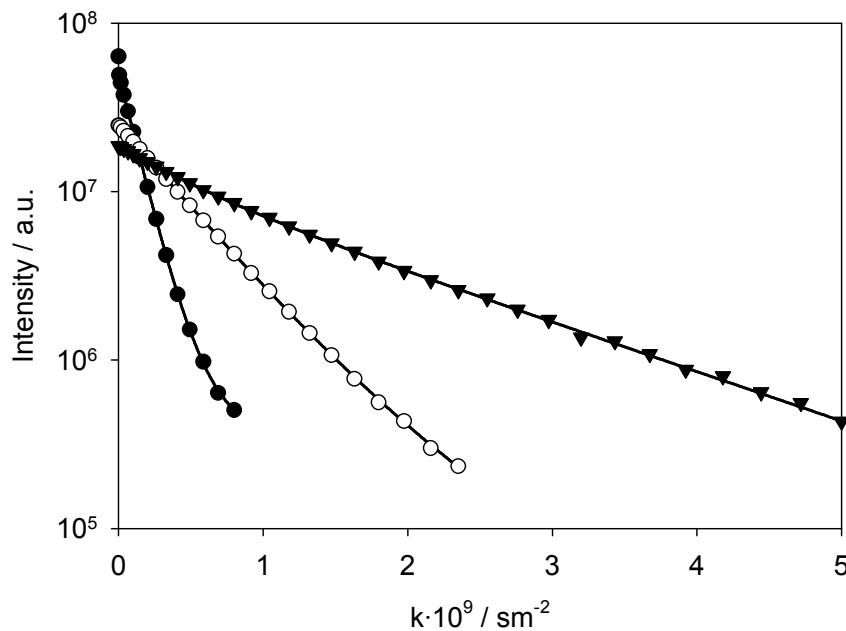
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### THE EFFECT OF CHANGING THE MICROSTRUCTURE OF A MICROEMULSION ON CHEMICAL REACTIVITY

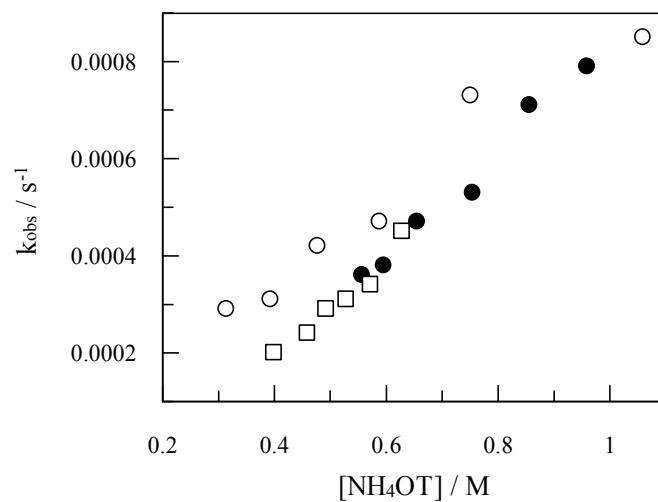
C. Cabaleiro-Lago, L. García-Río, P. Hervella



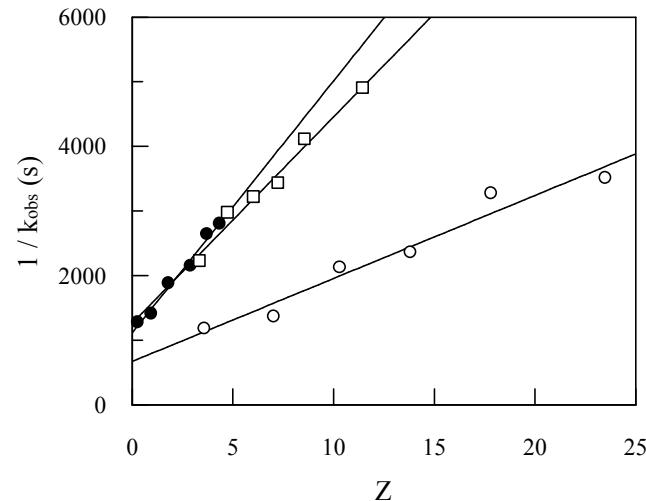
**Figure S-1:** <sup>1</sup>H-NMR spectrum of a NH<sub>4</sub>OT/isooctane/water microemulsion (46% water). Spectral width 2003.1 Hz, number of points 1024. Labels show peaks for different components.



**Figure S-2.** Representative echo decays of (●) Water (○) isoctane and (▼) NH<sub>4</sub>OT in microemulsion. The data have been fitted to a biexponential function (the solid lines). k is defined as  $k = \gamma^2 G^2 \delta^2 (\Delta - \delta/3)$ .

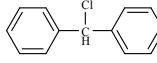
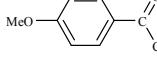
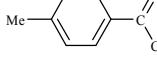
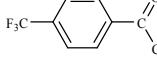
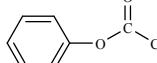
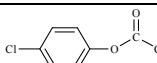


**Figure S-3.** Influence of the surfactant concentration on the solvolysis rate constant of PhOCOCl in microemulsions of water/NH<sub>4</sub>OT/isoctane at 25.0°C. (○) W=5.53; (●) W=25.9 and (□) W=42.9.



**Figure S-4.** Linealization of data from figure S-3 according to equation 3 (see manuscript). (○) W=5.53; (●) W=25.9 and (□) W=42.9.

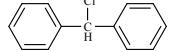
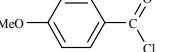
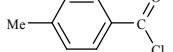
**Table S-1.** Values of the distribution constant for different substrates of the microemulsion,  $K_{oi}$ , for different W values.

	W											<b>Mean</b>	
	2.6	4.0	5.5	5.8	9.7	15.0	20.8	25.9	40.0	41.8	54.1	87.2	
 DPhMeCl			3.8±0.4					3.6±0.4			2.5±0.3	3.2±0.4	<b>3.3±0.4</b>
 4-MeO		4.8±0.5		5.2±0.6		5.0±0.6	5.2±0.6		5.1±0.6				<b>5.1±0.6</b>
 4-Me	3.2±0.3				2.1±0.3			2.5±0.3					<b>2.6±0.3</b>
 4-Cl	2.3±0.3				2.5±0.4			2.3±0.3					<b>2.6±0.3</b>
 4-CF <sub>3</sub>			6.3±0.6					4.1±0.5		5.5±0.6			<b>5.3±0.6</b>
 PhOCOCl			5.2±0.5					2.8±0.6		3.9±0.5			<b>4.0±0.5</b>
 4-Cl-PhOCOCl	3.2±0.3				2.1±0.4			3.6±0.4	3.0±0.4				<b>3.0±0.4</b>

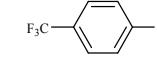
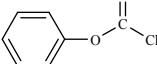
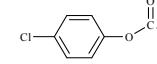
**Table S-2.** Influence of W on the solvolysis rate constant at the interphase of NH<sub>4</sub>OT-based microemulsions,  $k_i$ , for processes that take place via a dissociative mechanism. The uncertainty in the  $k_i$  values is smaller than 10%.

W	$k_i / \text{s}^{-1}$	W	$k_i / \text{s}^{-1}$	W	$k_i / \text{s}^{-1}$
1.5	$4.55 \times 10^{-5}$	1.5	$1.34 \times 10^{-3}$	1.4	$2.51 \times 10^{-4}$
2.6	$5.95 \times 10^{-3}$	3.1	$3.62 \times 10^{-3}$	2.6	$3.16 \times 10^{-4}$
3.1	$6.97 \times 10^{-5}$	4	$7.30 \times 10^{-3}$	2.9	$3.58 \times 10^{-4}$
4.8	$1.55 \times 10^{-4}$	4.8	$8.39 \times 10^{-3}$	3.5	$4.36 \times 10^{-4}$
5.5	$4.40 \times 10^{-4}$	5.8	$1.36 \times 10^{-2}$	4.5	$5.21 \times 10^{-4}$
6.5	$4.92 \times 10^{-4}$	6.5	$1.75 \times 10^{-2}$	5.3	$6.65 \times 10^{-4}$
10.4	$8.93 \times 10^{-4}$	10.4	$3.71 \times 10^{-2}$	6.1	$7.83 \times 10^{-4}$
14.7	$1.75 \times 10^{-3}$	14.7	$5.57 \times 10^{-2}$	7.9	$1.12 \times 10^{-3}$
19.6	$2.55 \times 10^{-3}$	15	$5.94 \times 10^{-2}$	9.3	$1.09 \times 10^{-3}$
25.2	$3.00 \times 10^{-3}$	19.6	$7.92 \times 10^{-2}$	9.7	$1.46 \times 10^{-3}$
25.9	$3.07 \times 10^{-3}$	20.8	$9.85 \times 10^{-2}$	11.7	$1.69 \times 10^{-3}$
31.7	$3.90 \times 10^{-3}$	25.2	$1.04 \times 10^{-1}$	17.6	$3.41 \times 10^{-3}$
39.2	$4.55 \times 10^{-3}$	31.6	$1.21 \times 10^{-1}$	25	$5.38 \times 10^{-3}$
48.2	$6.19 \times 10^{-3}$	39.1	$1.41 \times 10^{-1}$	28.4	$6.10 \times 10^{-3}$
48.2	$5.96 \times 10^{-3}$	40	$1.79 \times 10^{-1}$	36.7	$7.97 \times 10^{-3}$
54.1	$1.08 \times 10^{-2}$	48	$1.68 \times 10^{-1}$	45	$1.02 \times 10^{-2}$
62.9	$1.01 \times 10^{-2}$	58.7	$2.11 \times 10^{-1}$	52.7	$9.68 \times 10^{-3}$

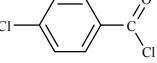
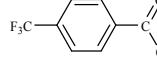
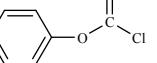
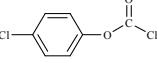
**Table S-2.** Continuation.

					
<b>W</b>	$k_i / \text{s}^{-1}$	<b>W</b>	$k_i / \text{s}^{-1}$	<b>W</b>	$k_i / \text{s}^{-1}$
71.7	$1.09 \times 10^{-2}$	67.3	$2.40 \times 10^{-1}$	76.4	$1.95 \times 10^{-2}$
80.5	$1.21 \times 10^{-2}$	79.4	$2.75 \times 10^{-1}$	99.4	$1.95 \times 10^{-2}$
87.2	$1.26 \times 10^{-2}$	104.8	$2.99 \times 10^{-1}$	120.1	$3.62 \times 10^{-2}$
89.3	$1.57 \times 10^{-2}$	131.8	$2.92 \times 10^{-1}$	148.9	$4.25 \times 10^{-2}$
98.1	$1.59 \times 10^{-2}$	134.5	$3.05 \times 10^{-1}$	194.7	$6.26 \times 10^{-2}$
108	$1.51 \times 10^{-2}$	149.4	$3.18 \times 10^{-1}$	235.7	$8.03 \times 10^{-2}$
172	$2.04 \times 10^{-2}$	202.5	$3.38 \times 10^{-1}$	288.1	$9.12 \times 10^{-2}$
204	$2.58 \times 10^{-2}$	356.5	$3.49 \times 10^{-1}$		
209	$2.48 \times 10^{-2}$				

**Table S-3.** Influence of W on the solvolysis rate constant at the interphase of NH<sub>4</sub>OT-based microemulsions,  $k_i$ , for processes that take place via a dissociative mechanism. The uncertainty in the  $k_i$  values is smaller than 10%.

							
W	$k_i / \text{s}^{-1}$	W	$k_i / \text{s}^{-1}$	W	$k_i / \text{s}^{-1}$	W	$k_i / \text{s}^{-1}$
1.1	$2.39 \times 10^{-3}$	2	$1.04 \times 10^{-2}$	1.5	$2.37 \times 10^{-3}$	1.4	$7.48 \times 10^{-3}$
2.6	$2.92 \times 10^{-3}$	4	$7.53 \times 10^{-3}$	3.1	$1.86 \times 10^{-3}$	2.6	$5.95 \times 10^{-3}$
6.2	$1.19 \times 10^{-3}$	5.5	$1.18 \times 10^{-2}$	4.8	$1.58 \times 10^{-3}$	2.9	$5.81 \times 10^{-3}$
9.2	$9.93 \times 10^{-4}$	8	$4.61 \times 10^{-3}$	5.5	$1.49 \times 10^{-3}$	4.5	$4.26 \times 10^{-3}$
9.7	$9.89 \times 10^{-4}$	16	$3.51 \times 10^{-3}$	6.5	$1.45 \times 10^{-3}$	6.1	$3.92 \times 10^{-3}$
12.4	$8.87 \times 10^{-4}$	20	$3.86 \times 10^{-3}$	10.3	$1.18 \times 10^{-3}$	7.9	$3.64 \times 10^{-3}$
19.8	$8.16 \times 10^{-4}$	25	$3.39 \times 10^{-3}$	14.6	$1.07 \times 10^{-3}$	9.7	$3.41 \times 10^{-3}$
24.3	$8.03 \times 10^{-4}$	25.9	$3.46 \times 10^{-3}$	19.5	$9.95 \times 10^{-4}$	11.7	$3.14 \times 10^{-3}$
25.9	$1.16 \times 10^{-3}$	30	$3.07 \times 10^{-3}$	25.1	$9.28 \times 10^{-4}$	17.6	$2.54 \times 10^{-3}$
29.2	$7.98 \times 10^{-4}$	35	$2.80 \times 10^{-3}$	25.9	$9.00 \times 10^{-4}$	25.9	$2.46 \times 10^{-3}$
34.8	$8.09 \times 10^{-4}$	40	$2.62 \times 10^{-3}$	31.5	$8.68 \times 10^{-4}$	28.4	$2.24 \times 10^{-3}$
48.6	$8.54 \times 10^{-4}$	45	$2.73 \times 10^{-3}$	39.1	$8.19 \times 10^{-4}$	36.7	$2.06 \times 10^{-3}$
57.3	$1.51 \times 10^{-3}$	50	$2.90 \times 10^{-3}$	47.9	$7.80 \times 10^{-4}$	40	$1.95 \times 10^{-3}$
63	$1.28 \times 10^{-3}$	60	$3.33 \times 10^{-3}$	58.6	$7.43 \times 10^{-4}$	45	$1.89 \times 10^{-3}$
72	$1.32 \times 10^{-3}$	70	$3.60 \times 10^{-3}$	62.7	$7.94 \times 10^{-4}$	55.1	$2.02 \times 10^{-3}$
81	$1.38 \times 10^{-3}$	80	$2.72 \times 10^{-3}$	71.5	$7.83 \times 10^{-4}$	86	$2.29 \times 10^{-3}$

**Table S-3.** Influence of W

							
<b>W</b>	$k_i / \text{s}^{-1}$	<b>W</b>	$k_i / \text{s}^{-1}$	<b>W</b>	$k_i / \text{s}^{-1}$	<b>W</b>	$k_i / \text{s}^{-1}$
132	$1.49 \times 10^{-3}$	90	$2.66 \times 10^{-3}$	80.7	$7.93 \times 10^{-4}$	276.9	$1.45 \times 10^{-3}$
173	$2.11 \times 10^{-3}$	100	$2.38 \times 10^{-3}$	89.3	$7.56 \times 10^{-4}$		
185	$2.23 \times 10^{-3}$	120	$3.21 \times 10^{-3}$	98.8	$7.08 \times 10^{-4}$		
193	$1.93 \times 10^{-3}$	130	$3.45 \times 10^{-3}$	107.1	$7.80 \times 10^{-4}$		
285	$2.69 \times 10^{-3}$	140	$2.71 \times 10^{-3}$	171.4	$8.72 \times 10^{-4}$		
324	$3.85 \times 10^{-3}$	150	$2.82 \times 10^{-3}$	268.1	$1.02 \times 10^{-3}$		
		160	$2.77 \times 10^{-3}$	308.9	$1.07 \times 10^{-3}$		
		170	$2.64 \times 10^{-3}$	342.8	$1.13 \times 10^{-3}$		
		190	$2.83 \times 10^{-3}$	344.3	$1.36 \times 10^{-3}$		
		200	$2.87 \times 10^{-3}$				