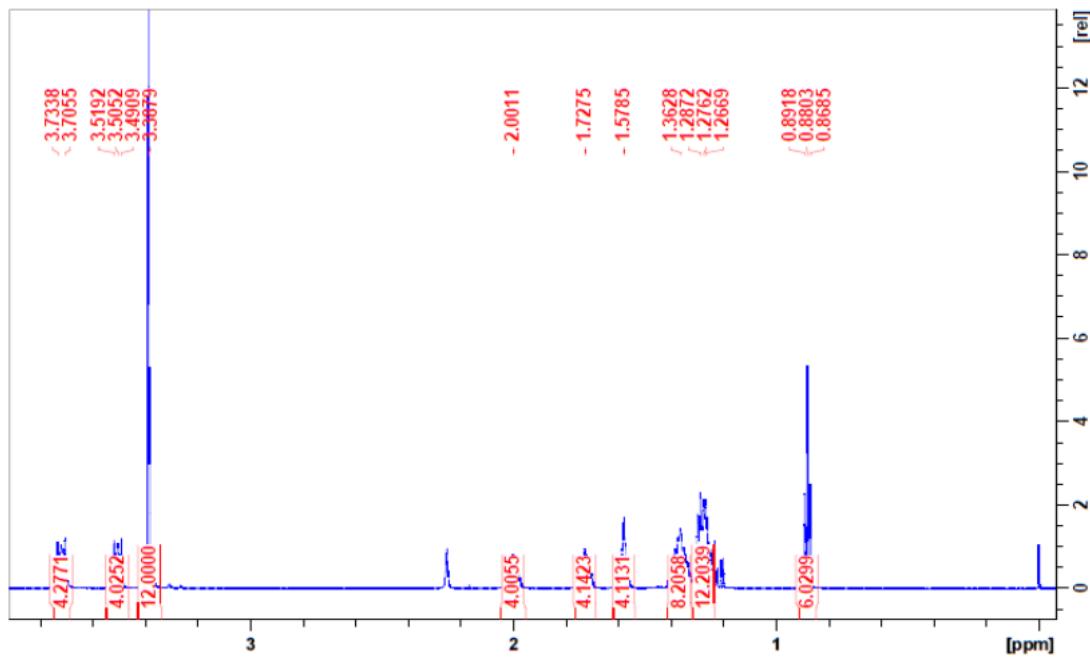
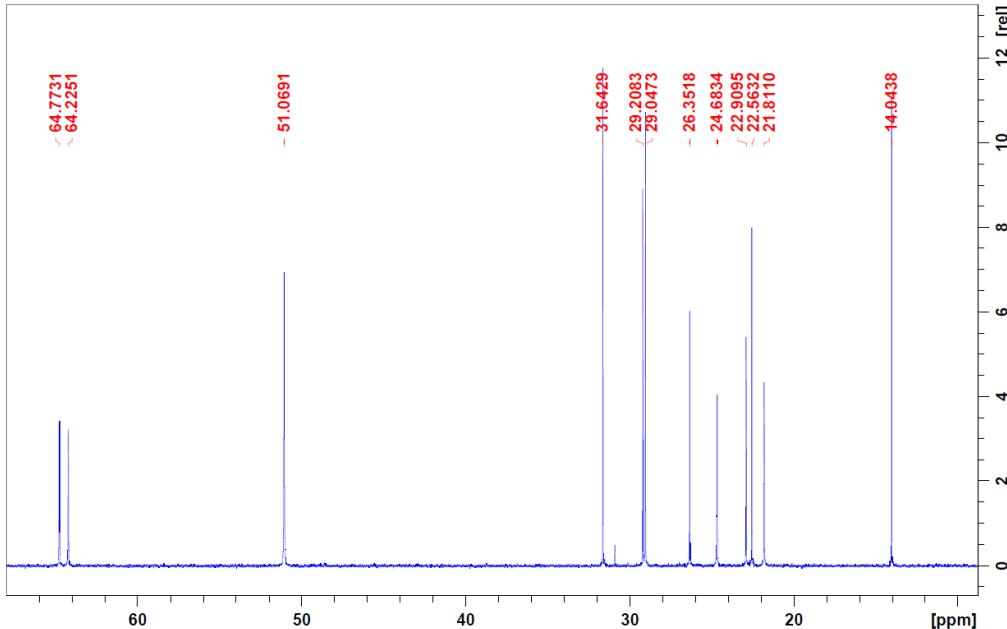


**Figure S1.**  $^1\text{H}$ -NMR spectra for heksylene-1,6-bis(dimethyloctylammonium) bromides.



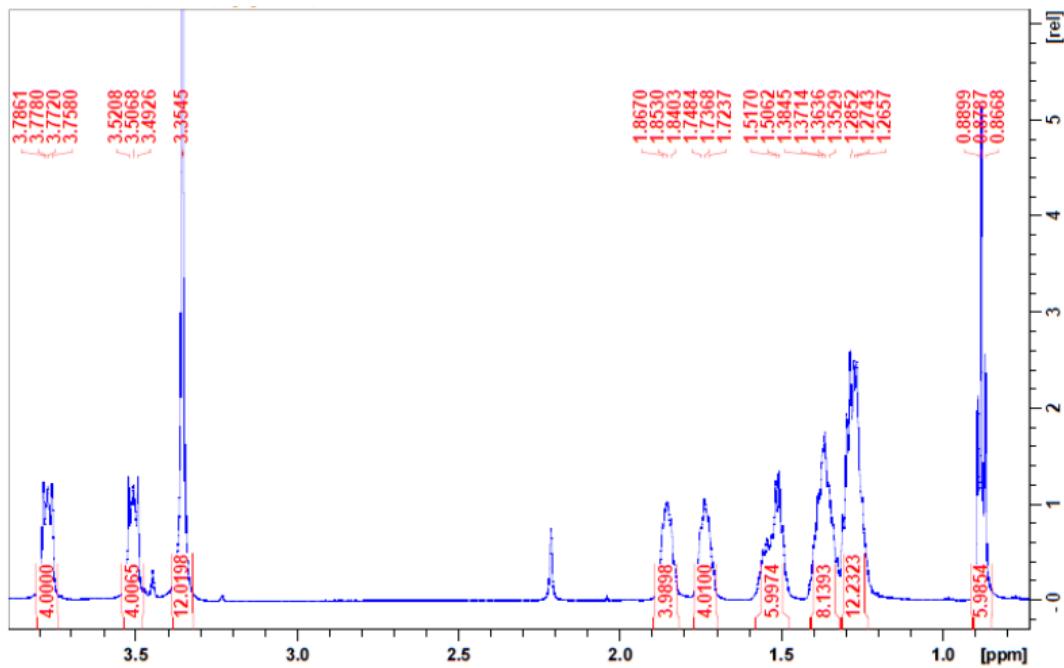
$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ ): 0.88 (t, 6H,  $J = 6.9$ , 2x $\text{CH}_3$ ), 1.22-1.26 (m, 12H, 6x $\text{CH}_2$ ), 1.26-1.31 (m, 8H, 4x $\text{CH}_2$ ), 1.56-1.61 (m, 4H, 2x $\text{CH}_2$ ), 1.64-1.68 (m, 4H, 2x $\text{CH}_2$ ), 1.80-2.05 (m, 4H, 2x $\text{CH}_2$ ), 3.39 (s, 12H, 4x $\text{CH}_3\text{N}$ ), 3.45-3.55 (m, 4H, 2x $\text{CH}_2\text{N}$ ), 3.65-3.75 (m, 4H, 2x $\text{CH}_2\text{N}$ ).

**Figure S2.**  $^{13}\text{C-NMR}$  spectra for heksylene-1,6-bis(dimethyloctylammonium) bromides.



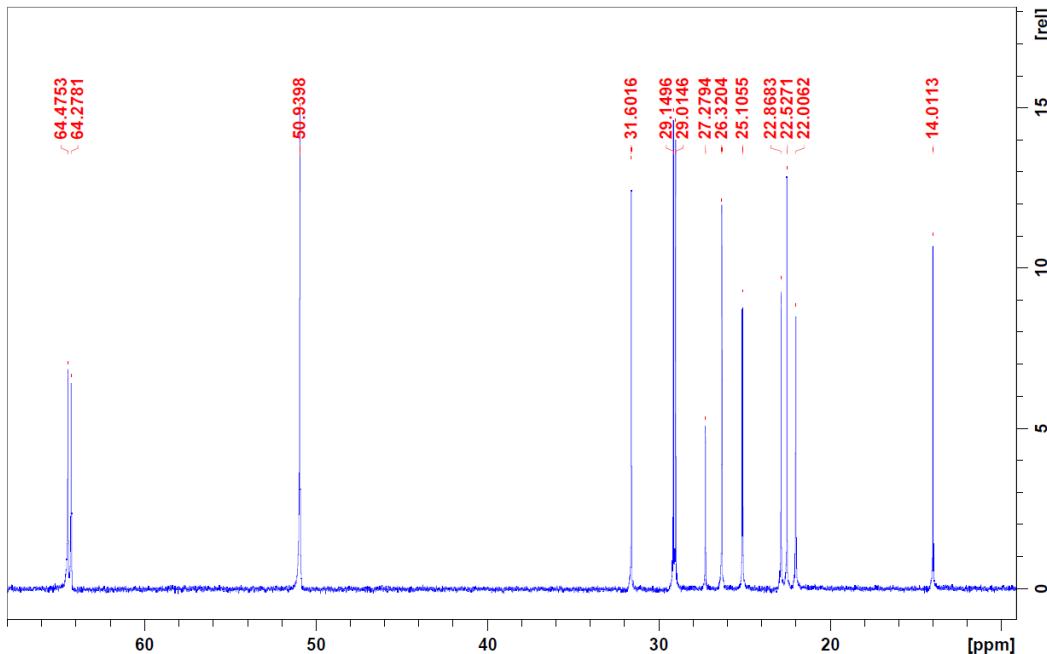
$^{13}\text{C-NMR}$  (150 MHz,  $\text{CDCl}_3$ ): 14.04 (2x $\text{CH}_3$ ), 21.81, 22.65, 22.90, 24.63, 26.35, 29.05, 29.21, 31.64 (16x $\text{CH}_2$ ), 51.06 (4x $\text{CH}_3\text{N}$ ), 64.23 (2x $\text{CH}_2\text{N}$ ), 64.77 (2x $\text{CH}_2\text{N}$ ).

**Figure S3.**  $^1\text{H}$ -NMR spectra for heptylene-1,7-bis(dimethyloctylammonium) bromides.



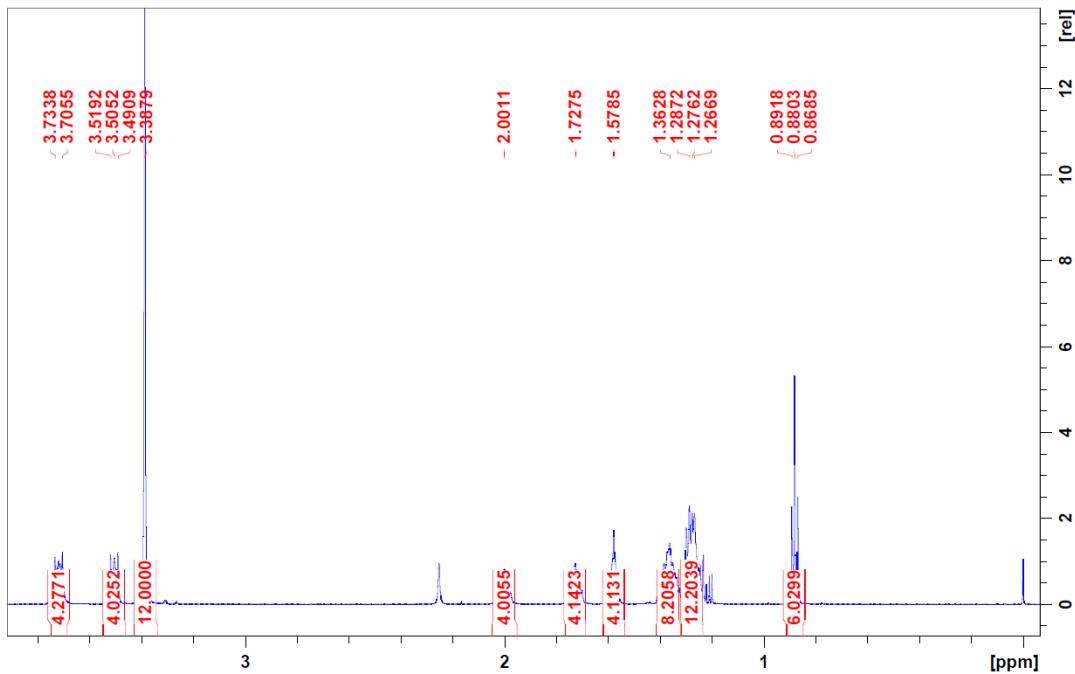
$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ ): 0.88 (t, 6H,  $J = 6.7$ , 2x $\text{CH}_3$ ), 1.22-1.31 (m, 12H, 6x $\text{CH}_2$ ), 1.31-1.41 (m, 8H, 4x $\text{CH}_2$ ), 1.47-1.58 (m, 6H, 3x $\text{CH}_2$ ), 1.70-1.77 (m, 4H, 2x $\text{CH}_2$ ), 1.82-1.89 (m, 4H, 2x $\text{CH}_2$ ), 3.35 (s, 12H, 4x $\text{CH}_3\text{N}$ ), 3.48-3.54 (m, 4H, 2x $\text{CH}_2\text{N}$ ), 3.74-3.81 (m, 4H, 2x $\text{CH}_2\text{N}$ ).

**Figure S4.**  $^{13}\text{C-NMR}$  spectra for heptylene-1,7-bis(dimethyloctylammonium) bromides.



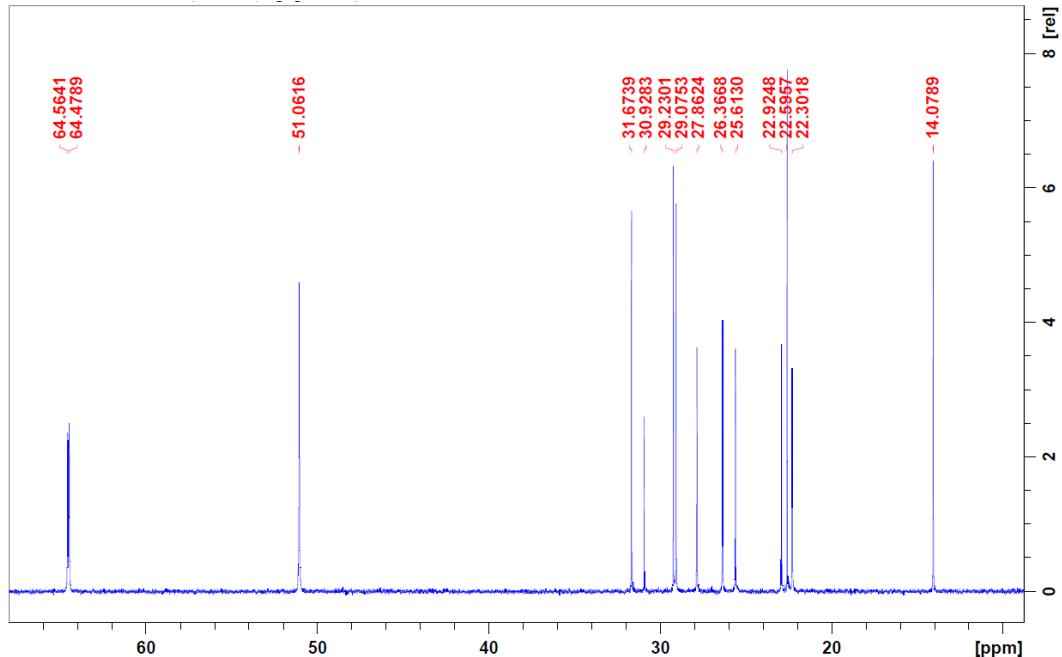
$^{13}\text{C-NMR}$  (150 MHz,  $\text{CDCl}_3$ ): 14.08 (2x $\text{CH}_3$ ), 22.03, 22.60, 22.93, 25.11, 26.39, 27.23, 29.08, 29.22, 31.67 (17x $\text{CH}_2$ ), 50.98 (4x $\text{CH}_3\text{N}$ ), 64.39 (2x $\text{CH}_2\text{N}$ ), 64.57 (2x $\text{CH}_2\text{N}$ ).

**Figure S5.**  $^1\text{H}$ -NMR spectra for oktylene-1,8-bis(dimethyloctylammonium) bromides



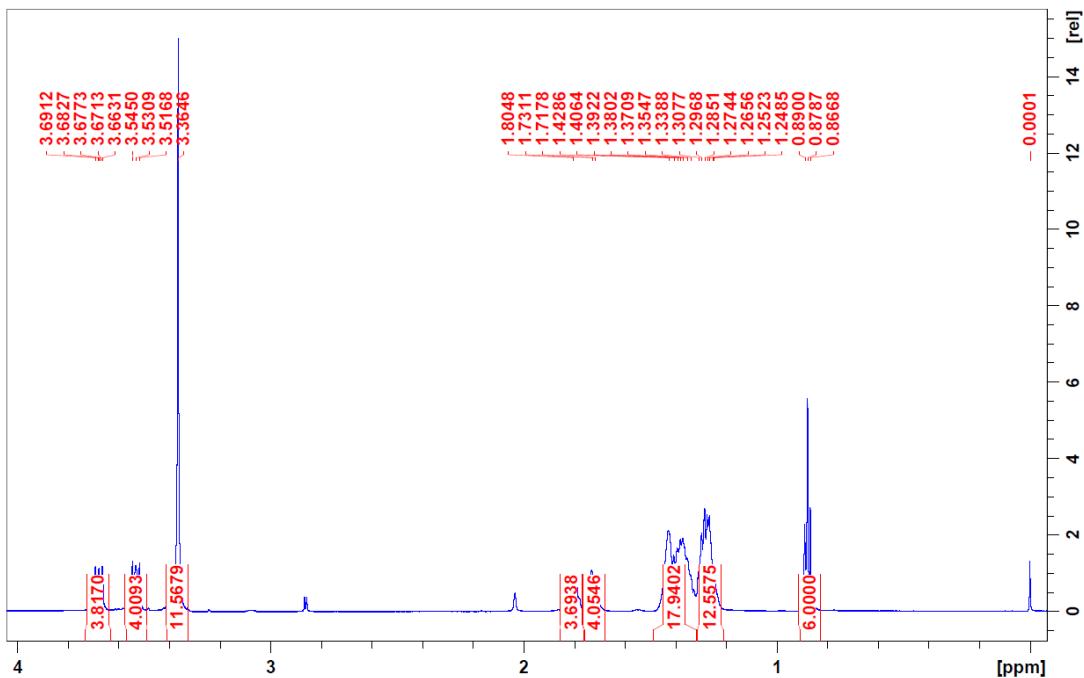
$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ ): 0.88 (t, 6H,  $J = 7.0$ , 2x $\text{CH}_3$ ), 1.22-1.32 (m, 12H, 6x $\text{CH}_2$ ), 1.32-1.42 (m, 8H, 4x $\text{CH}_2$ ), 1.43-1.50 (m, 8H, 4x $\text{CH}_2$ ), 1.69-1.75 (m, 4H, 2x $\text{CH}_2$ ), 1.83-1.89 (m, 4H, 2x $\text{CH}_2$ ), 3.37 (s, 12H, 4x $\text{CH}_3\text{N}$ ), 3.50-3.56 (m, 4H, 2x $\text{CH}_2\text{N}$ ), 3.66-3.74 (m, 4H, 2x $\text{CH}_2\text{N}$ ).

**Figure S6.**  $^{13}\text{C}$ -NMR spectra for oktylene-1,8-bis(dimethyloctylammonium) bromides



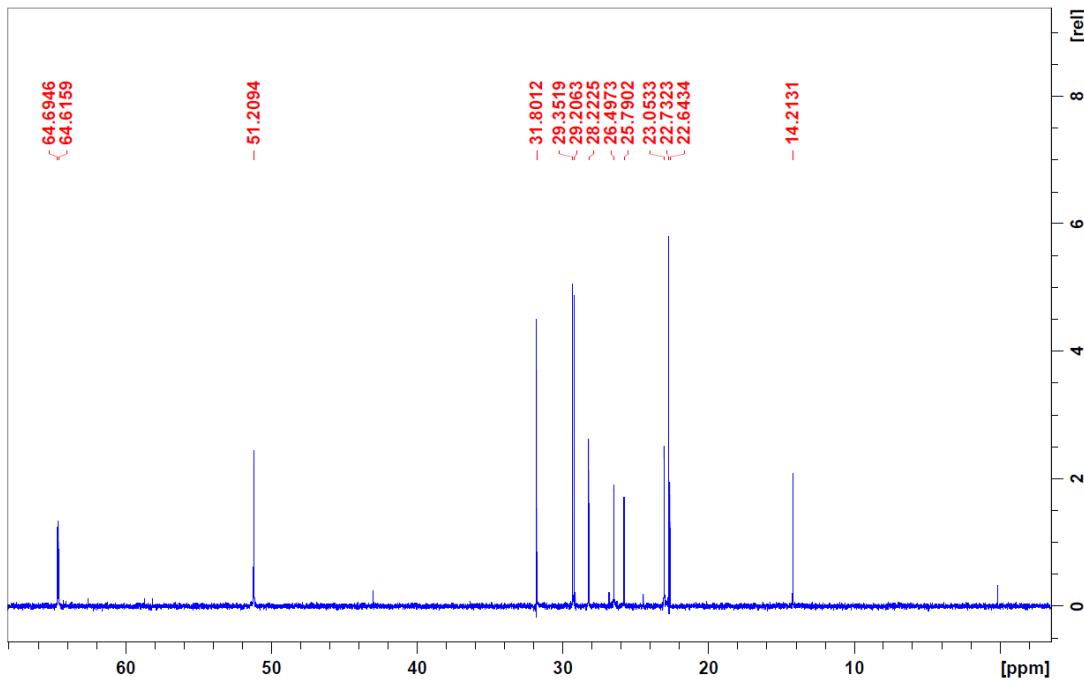
$^{13}\text{C-NMR}$  (150 MHz,  $\text{CDCl}_3$ ): 14.09 (2x $\text{CH}_3$ ), 22.32, 22.62, 22.95, 25.62, 26.39, 27.85, 29.09, 29.25, 31.70 (18x $\text{CH}_2$ ), 51.06 (4x $\text{CH}_3\text{N}$ ), 64.52 (2x $\text{CH}_2\text{N}$ ), 64.62 (2x $\text{CH}_2\text{N}$ ).

**Figure S7.**  $^1\text{H}$ -NMR spectra for nonylene-1,9-bis(dimethyloctylammonium) bromides



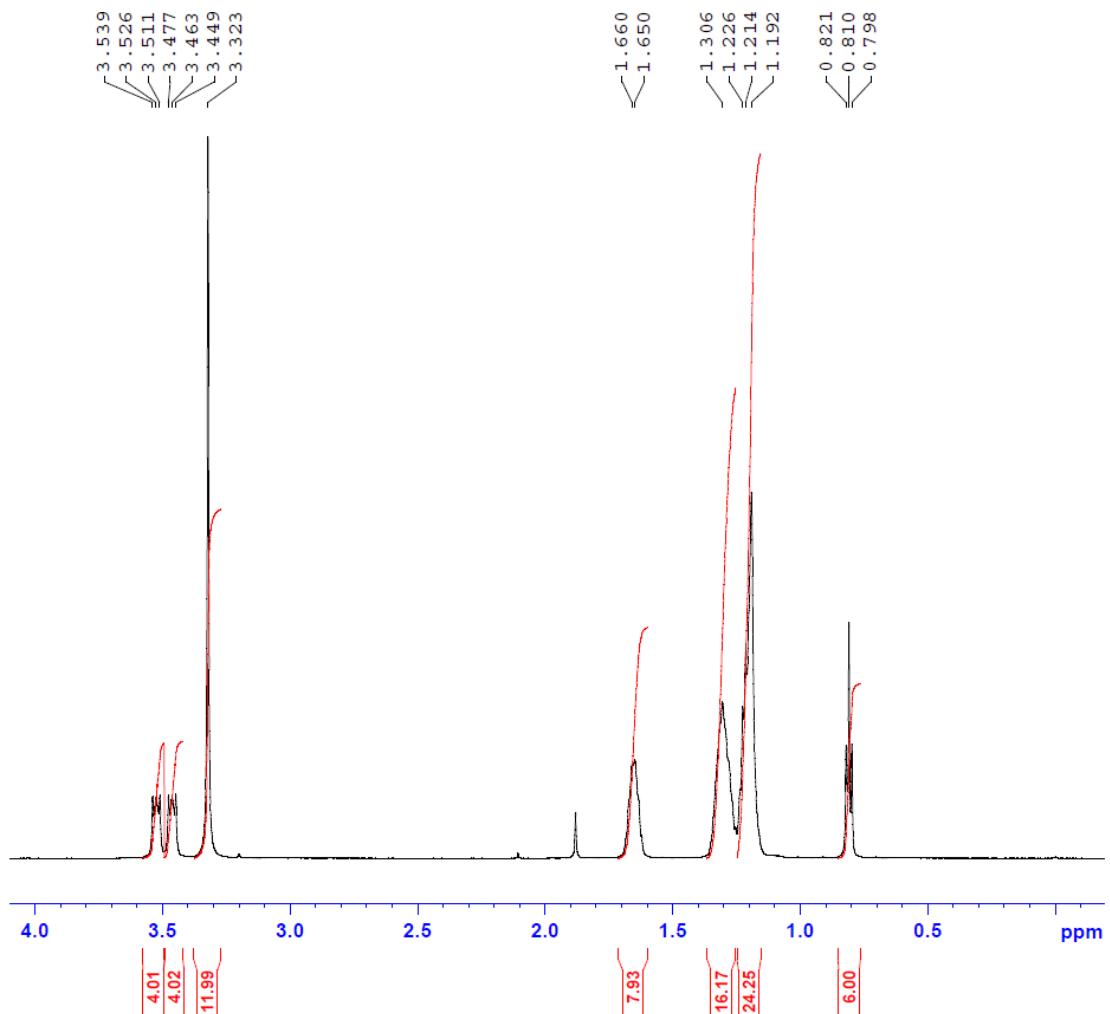
$^1\text{H}$ -NMR (600 MHz,  $\text{CDCl}_3$ ): 0.88 (t, 6H,  $J = 7.0$ ,  $2\times\text{CH}_3$ ), 1.21-1.32 (m, 12H,  $6\times\text{CH}_2$ ), 1.32-1.48 (m, 18H,  $4\times\text{CH}_2$ ), 1.68-1.75 (m, 4H,  $2\times\text{CH}_2$ ), 1.76-1.85 (m, 4H,  $2\times\text{CH}_2$ ), 3.36 (s, 12H,  $4\times\text{CH}_3\text{N}$ ), 3.50-3.57 (m, 4H,  $2\times\text{CH}_2\text{N}$ ), 3.64-3.72 (m, 4H,  $2\times\text{CH}_2\text{N}$ )

**Figure S8.**  $^{13}\text{C}$ -NMR spectra for nonylene-1,9-bis(dimethyloctylammonium) bromides



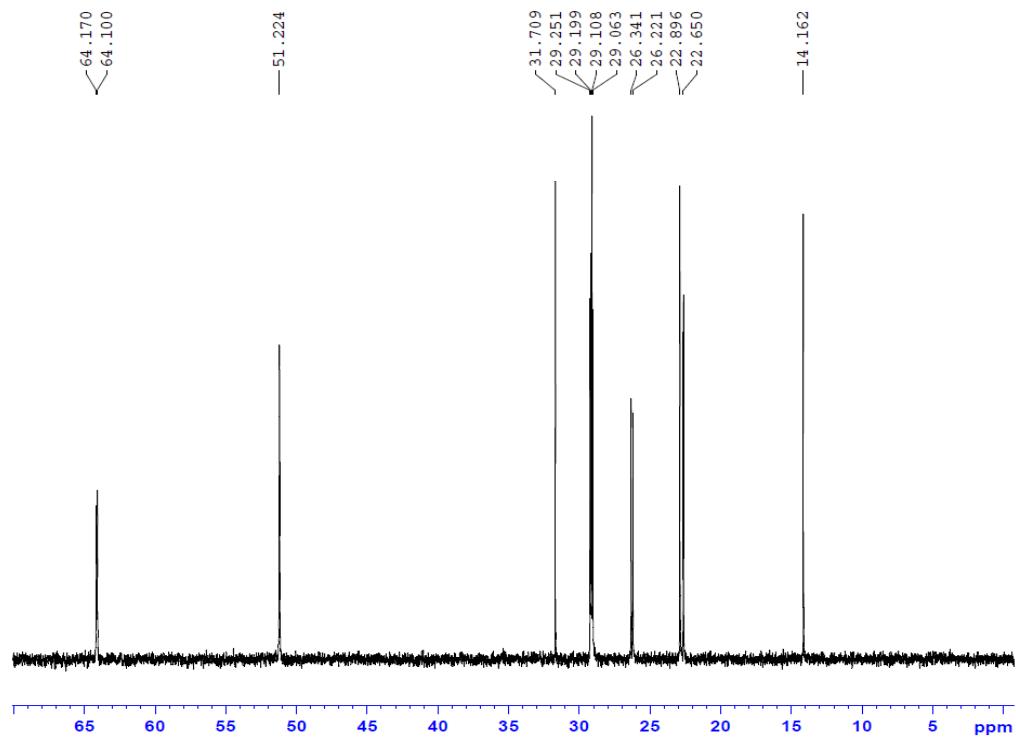
$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ ): 14.21 ( $2\times\text{CH}_3$ ), 22.64, 22.73, 223.05, 25.79, 26.50, 28.22, 29.21, 29.35, 31.80 ( $18\times\text{CH}_2$ ), 51.21 ( $4\times\text{CH}_3\text{N}$ ), 64.62 ( $2\times\text{CH}_2\text{N}$ ), 64.69 ( $2\times\text{CH}_2\text{N}$ ).

**Figure S9.**  $^1\text{H}$ -NMR spectra for tetradecene-1,14-bis(dimethyloctylammonium) bromides



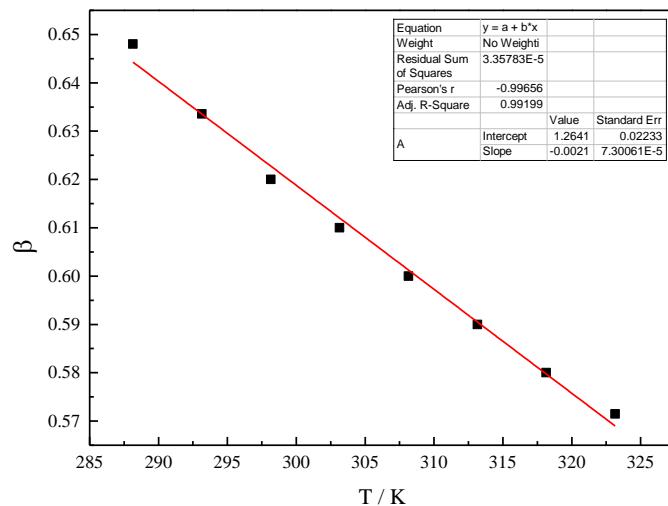
**$^1\text{H-NMR}$**  (600 MHz,  $\text{CDCl}_3$ ): 0.81 (t, 6H,  $J = 6.7$ , 2x $\text{CH}_3$ ), 1.14-1.25 (m, 24H, 12x $\text{CH}_2$ ), 1.25-1.37 (m, 16H, 8x $\text{CH}_2$ ), 1.59-1.71 (m, 8H, 4x $\text{CH}_2$ ), 3.32 (s, 12H, 4x $\text{CH}_3\text{N}$ ), 3.42-3.49 (m, 4H, 2x $\text{CH}_2\text{N}$ ), 3.49-3.57 (m, 4H, 2x $\text{CH}_2\text{N}$ ).

**Figure S10.**  $^{13}\text{C}$ -NMR spectra for tretadecylene-1,14-bis(dimethyloctylammonium) bromide

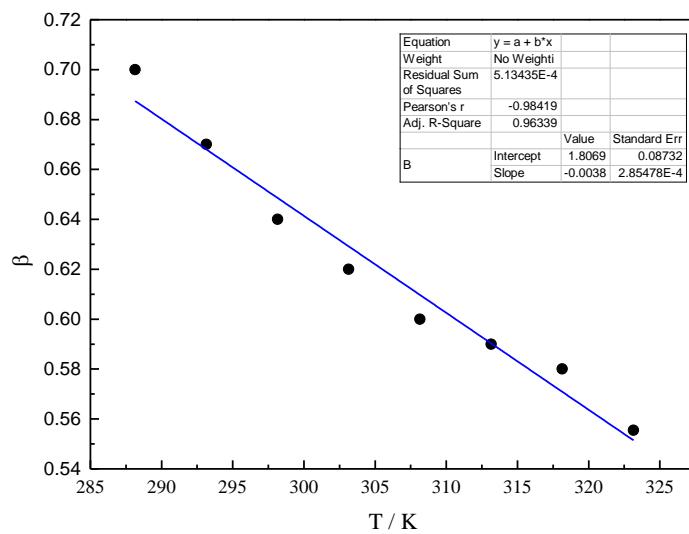


$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ ): 14.16 (2x $\text{CH}_3$ ), 22.65, 22.89, 26.22, 26.34, 29.06, 29.11, 29.20, 29.25, 31.71 (24x $\text{CH}_2$ ), 51.22 (4x $\text{CH}_3\text{N}$ ), 64.10 (2x $\text{CH}_2\text{N}$ ), 64.17 (2x $\text{CH}_2\text{N}$ ).

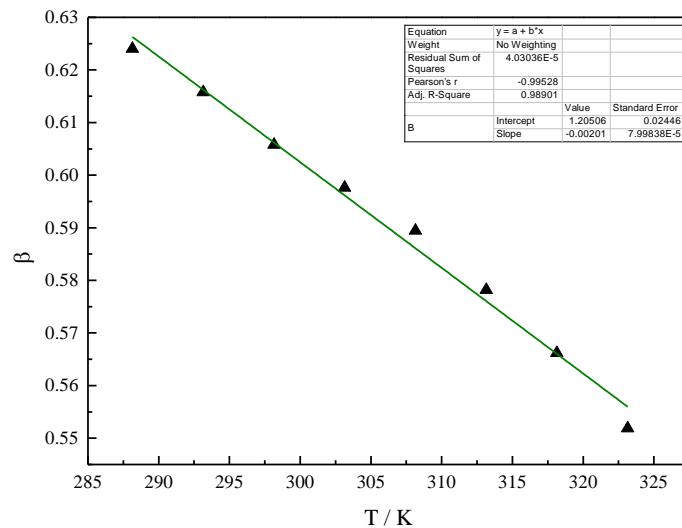
**Figure S11.** Temperature dependence of counterion binding to micelles,  $\beta$ , determined for aqueous solutions of heksylene-1,6 bis(dimethyloctylammonium) bromides by the slope ratio method conductometrically.



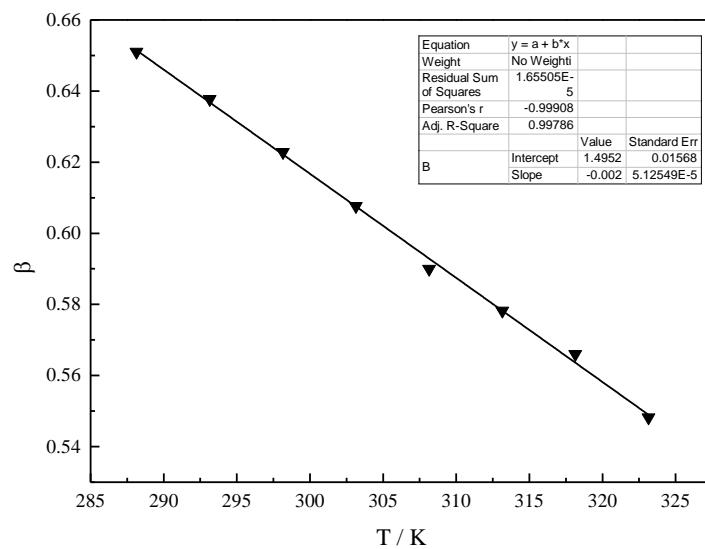
**Figure S12.** Temperature dependence of counterion binding to micelles,  $\beta$ , determined for aqueous solutions of heptylene -1,7 bis(dimethyloctylammonium) bromides by the slope ratio method conductometrically.



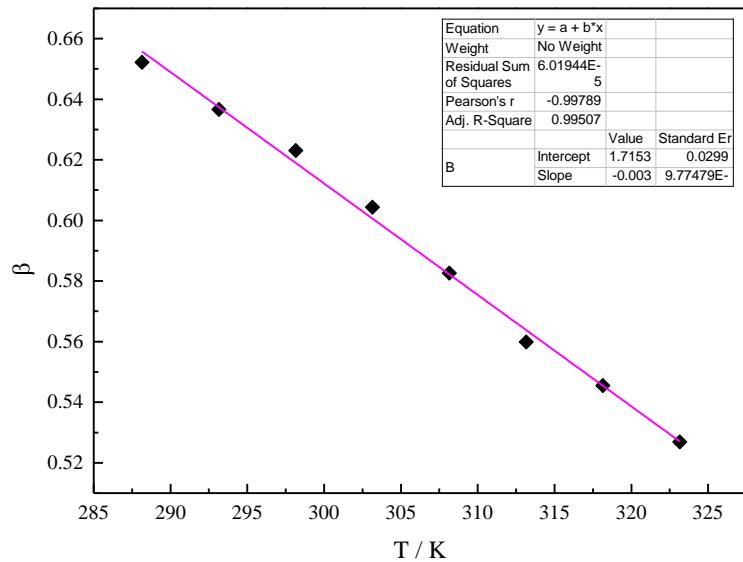
**Figure S13.** Temperature dependence of counterion binding to micelles,  $\beta$ , determined for aqueous solutions of oktylene -1,8 bis(dimethyloctylammonium) bromides by the slope ratio method conductometrically.



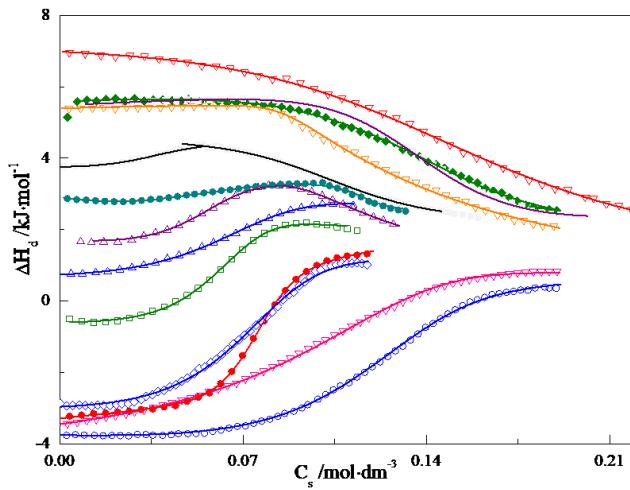
**Figure S14.** Temperature dependence of counterion binding to micelles,  $\beta$ , determined for aqueous solutions of nonylene -1,9 bis(dimethyloctylammonium) bromides by the slope ratio method conductometrically.



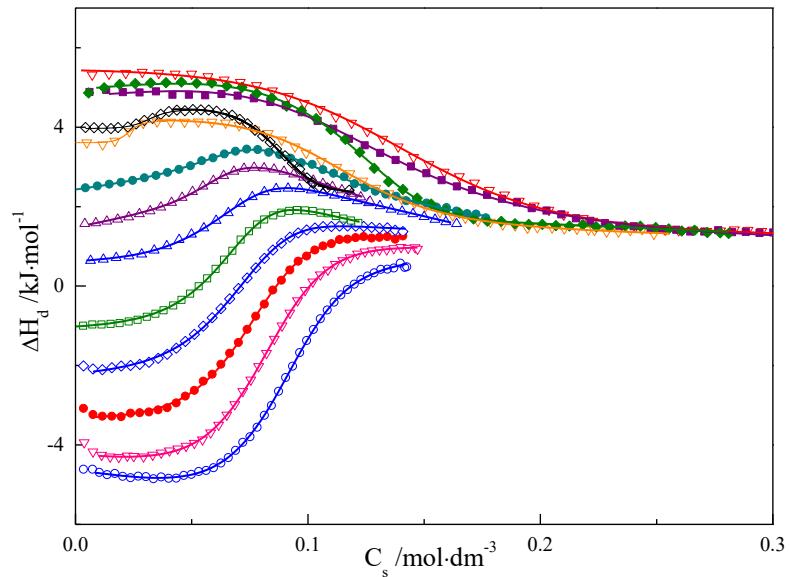
**Figure S15.** Temperature dependence of counterion binding to micelles,  $\beta$ , determined for aqueous solutions of tetradecylene -1,14 bis(dimethyloctylammonium) bromides by the slope ratio method conductometrically.



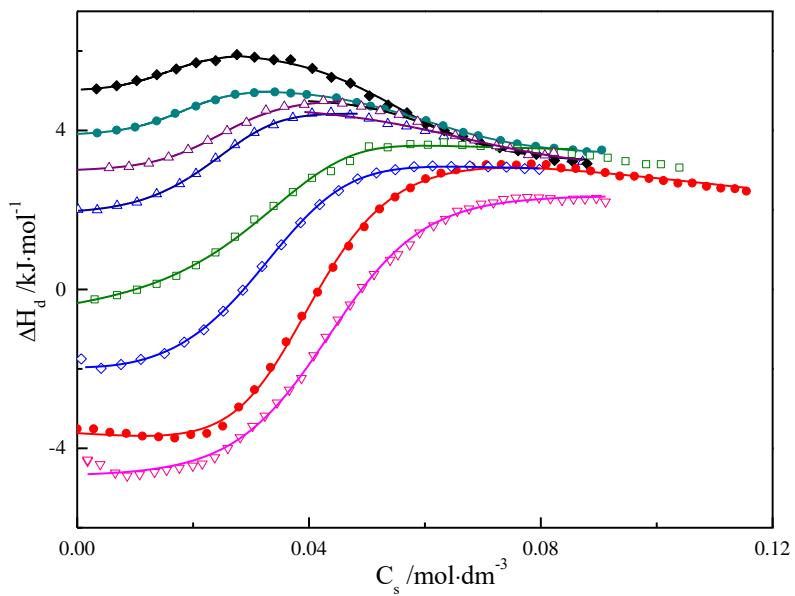
**Figure S16.** Calorimetric titration curve from additions 8-6-8 surfactant to water for temperatures: ○ - 283.15 K, ▽ - 288.15 K, • - 293.15 K, Ⓢ - 298.15 K, □ - 303.15 K, Δ - 308.15 K, △ - 313.15 K, ● - 318.15 K, ♦ - 323.15 K, ▷ - 328.15 K, ◆ - 333.15 K, P - 338.15 K, ▽ - 343.15 K



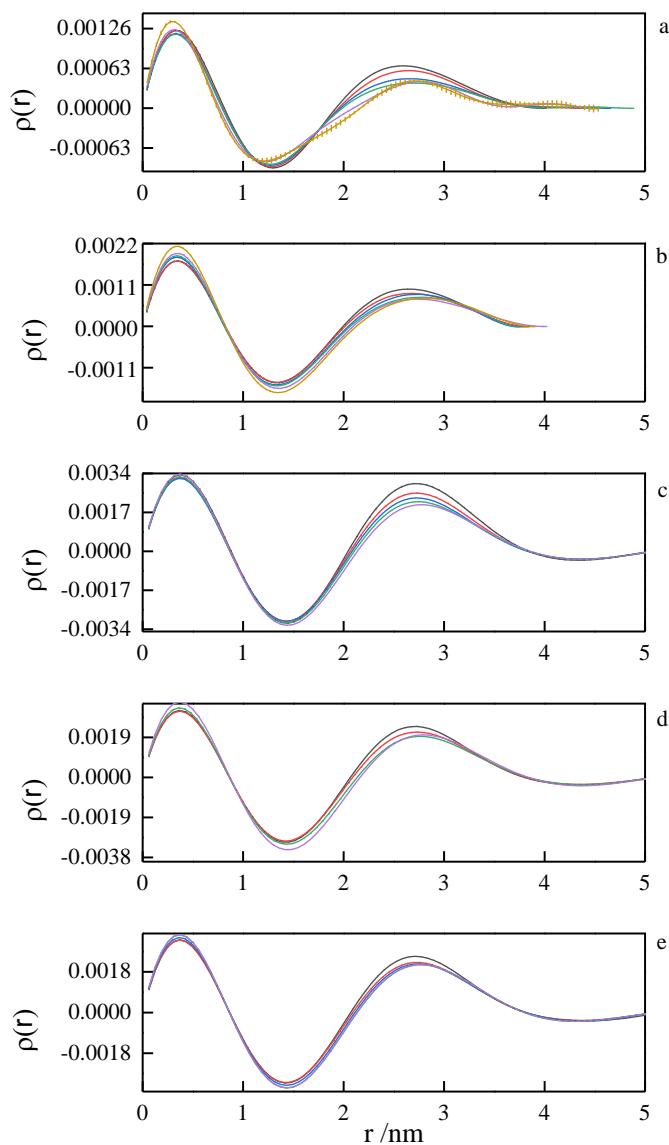
**Figure S17.** Calorimetric titration curve from additions 8-7-8 surfactant to water for temperatures: ○ - 283.15 K, ▼ - 288.15 K, ● - 293.15 K, ○ - 298.15K, □ - 303.15K, Δ - 308.15K, Δ - 313.15K, ● - 318.15K, ♦ - 323.15 K, △ - 328.15K, ♦ - 333.15 K, P - 338.15K, ▽ - 343.15 K



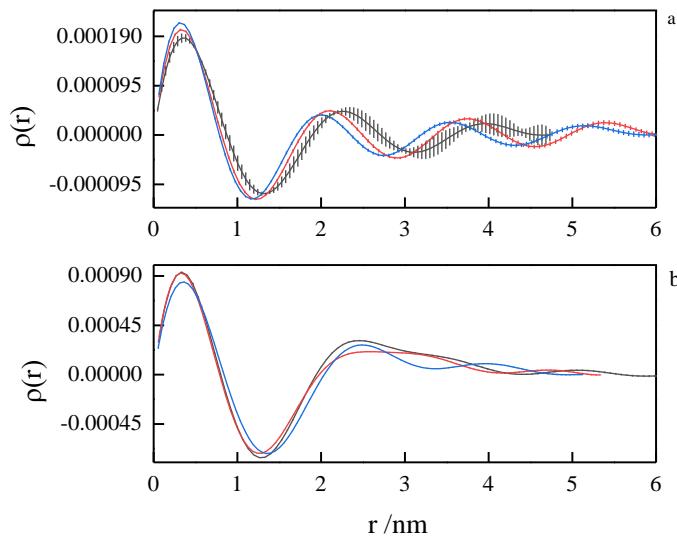
**Figure S18.** Calorimetric titration curve from additions 8-9-8 surfactant to water for temperatures: ▼ - 288.15 K, ● - 293.15 K, ○ - 298.15K, □ - 303.15K, Δ - 308.15K, Δ - 313.15K, ● - 318.15K, ♦ - 323.15 K



**Figure S19.** Pair distance distribution functions derived from SAXS data by indirect Fourier transform for 8-7-8 surfactant system at concentrations: a)  $0.150 \text{ mol dm}^{-3}$ , b)  $0.214 \text{ mol dm}^{-3}$ , c)  $0.331 \text{ mol dm}^{-3}$ , d)  $0.342 \text{ mol dm}^{-3}$ , e)  $0.352 \text{ mol dm}^{-3}$  at  $293.15 \text{ K}$ , **298.15 K**, **303.15 K**, **308.15 K**, **313.15 K**, **318.15 K**.



**Figure S20.** Pair distance distribution functions derived from SAXS data by indirect Fourier transform for 8-9-8 surfactant system at concentrations a)  $0.40 \text{ mol dm}^{-3}$ , b)  $0.107 \text{ mol dm}^{-3}$  at 293.15 K, 298.15 K, 303.15 K.



**Table S1.** Temperature dependence of micellisation parameters: c.m.c,  $C_{m,\text{trans}}$  and thermodynamic quantities of the micellisation and transformation process for aqueous surfactant solution 8-6-8 determined on the basis of calorimetric titration. The values for the micelle transformation process are shown in bold.

$T$ /K	$c.m.c / \text{mol} \cdot \text{dm}^{-3}$ $C_{m,\text{trans}} / \text{mol} \cdot \text{dm}^{-3}$	Thermodynamic Functions for 8-6-8			
		$\Delta G_m / \Delta G_{m,\text{trans}}$ /kJ · mol <sup>-1</sup>	$\Delta H_m / \Delta H_{m,\text{trans}}$ /kJ · mol <sup>-1</sup>	$T\Delta S_m / T\Delta S_{m,\text{trans}}$ /kJ · mol <sup>-1</sup>	$\Delta S_m / \Delta S_{m,\text{trans}}$ /J · mol <sup>-1</sup> · K <sup>-1</sup>
283.15	$0.126 \pm 0.01$	-16.57	4.11	20.68	73.04
288.15	$0.106 \pm 0.01$	-17.17	3.70	20.86	72.41
293.15	$0.077 \pm 0.007$	-18.12	3.60	21.72	74.10
298.15	$0.070 \pm 0.007$	-18.59	3.55	22.14	74.25
303.15	$0.063 \pm 0.005$	-19.00	3.03	22.04	72.25
308.15	$0.065 \pm 0.006$	-19.06	2.30	21.35	69.28
313.15	$0.057 \pm 0.006$	-19.55	1.68	21.23	67.80
	<b><math>0.107 \pm 0.01</math></b>	<b>-17.76</b>	<b>-1.13</b>	<b>16.63</b>	<b>53.12</b>
318.15	$0.053 \pm 0.005$	-19.87	0.51	20.38	64.07
	<b><math>0.114 \pm 0.01</math></b>	<b>-17.69</b>	<b>-0.49</b>	<b>17.20</b>	<b>54.06</b>
323.15	$0.037 \pm 0.005$	-20.94	0.58	21.42	66.29
	<b><math>0.113 \pm 0.01</math></b>	<b>-17.89</b>	<b>-2.57</b>	<b>15.28</b>	<b>47.28</b>
328.15	$0.116 \pm 0.01$	-17.83	-3.90	13.93	42.44
333.15	$0.138 \pm 0.01$	-17.42	-3.56	13.86	41.60
338.15	$0.136 \pm 0.01$	-17.54	-4.07	13.46	39.81
343.15	$0.147 \pm 0.01$	-17.39	-4.95	12.43	36.23

**Table S2.** Temperature dependence of micellisation parameters: c.m.c,  $C_{m,trans}$  and thermodynamic quantities of the micellisation and transformation process for aqueous surfactant solution 8-7-8 determined on the basis of calorimetric titration. The values for the micelle transformation process are shown in bold.

T /K	Thermodynamic Functions for 8-7-8				
	c.m.c /mol · dm <sup>-3</sup>	$\Delta G_m / \Delta G_{m,trans}$ /kJ · mol <sup>-1</sup>	$\Delta H_m / \Delta H_{m,trans}$ /kJ · mol <sup>-1</sup>	$T\Delta S_m / T\Delta S_{m,trans}$ /kJ · mol <sup>-1</sup>	$\Delta S_m / \Delta S_{m,trans}$ /J · mol <sup>-1</sup> · K <sup>-1</sup>
283.15	0.130±0.01	-17.19	3.58	20.77	73.35
288.15	0.116±0.01	-17.53	3.52	21.05	73.05
293.15	0.096±0.01	-18.08	3.28	21.36	72.86
298.15	0.090±0.01	-18.27	2.88	21.15	70.43
303.15	0.081±0.008	-18.55	2.41	20.96	69.14
308.15	0.079±0.008	-18.61	1.34	19.95	64.74
313.15	0.074±0.007	-18.77	0.73	19.50	62.27
318.15	0.055±0.005	-19.57	0.43	20.00	62.86
	<b>0.130±0.01</b>	<b>-17.14</b>	<b>-0.48</b>	<b>16.66</b>	<b>52.37</b>
323.15	0.049±0.005	-19.84	0.36	20.20	62.51
	<b>0.139±0.01</b>	<b>-16.90</b>	<b>-1.14</b>	<b>15.76</b>	<b>48.77</b>
328.15	0.136±0.01	-16.91	-1.90	15.01	45.74
333.15	0.142±0.01	-16.72	-1.80	14.92	44.78
338.15	0.147±0.01	-16.55	-1.83	14.72	43.53
343.15	0.160±0.01	-16.23	-1.67	14.56	42.43

**Table S3.** Temperature dependence of micellisation parameters: c.m.c,  $C_{m,trans}$  and thermodynamic quantities of the micellisation and transformation process for aqueous surfactant solution 8-9-8 determined on the basis of calorimetric titration. The values for the micelle transformation process are shown in bold.

T /K	Thermodynamic Functions for 8-9-8				
	c.m.c /mol · dm <sup>-3</sup>	$\Delta G_m / \Delta G_{m,trans}$ /kJ · mol <sup>-1</sup>	$\Delta H_m / \Delta H_{m,trans}$ /kJ · mol <sup>-1</sup>	$T\Delta S_m / T\Delta S_{m,trans}$ /kJ · mol <sup>-1</sup>	$\Delta S_m / \Delta S_{m,trans}$ /J · mol <sup>-1</sup> · K <sup>-1</sup>
288.15	0.043±0.004	-19.98	7.15	27.13	95.81
293.15	0.039±0.004	-20.09	7.89	27.98	95.44
298.15	0.034±0.003	-20.56	6.06	26.62	89.28
303.15	0.032±0.003	-20.80	3.92	24.72	81.54
308.15	0.025±0.002	-21.57	2.67	24.24	78.68
	<b>0.065±0.006</b>	<b>-18.88</b>	<b>-1.46</b>	<b>17.42</b>	<b>56.52</b>
313.15	0.024±0.002	-21.69	1.80	23.49	75.02
	<b>0.062±0.006</b>	<b>-19.06</b>	<b>-1.49</b>	<b>17.57</b>	<b>56.12</b>
318.15	0.018±0.001	-22.59	1.14	23.73	74.59
	<b>0.060±0.006</b>	<b>-19.21</b>	<b>-2.02</b>	<b>17.19</b>	<b>54.03</b>
323.15	0.015±0.001	-23.08	0.93	24.02	74.32
	<b>0.058±0.005</b>	<b>-19.49</b>	<b>-2.80</b>	<b>16.69</b>	<b>51.65</b>

**Table S4.** Temperature dependence of micellisation parameters: c.m.c,  $C_{m.trans}$  and thermodynamic quantities of the micellisation and transformation process for aqueous surfactant solution 8-14-8 determined on the basis of calorimetric titration. The values for the micelle transformation process are shown in bold.

Thermodynamic Functions for 8-14-8					
$T$ /K	$c.m.c / \text{mol} \cdot \text{dm}^{-3}$	$\Delta G_m / \Delta G_{m.trans}$ /kJ · mol <sup>-1</sup>	$\Delta H_m / \Delta H_{m.trans}$ /kJ · mol <sup>-1</sup>	$T\Delta S_m / T\Delta S_{m.trans}$ /kJ · mol <sup>-1</sup>	$\Delta S_m / \Delta S_{m.trans}$ /J · mol <sup>-1</sup> · K <sup>-1</sup>
283.15	0.022±0.001	-21.58	10.46	32.04	113.2
288.15	0.021±0.001	-21.83	8.92	30.75	106.7
293.15	0.020±0.001	-22.04	6.77	28.81	98.27
298.15	0.017±0.001	-22.36	5.72	28.08	94.19
303.15	0.017±0.001	-22.44	3.61	26.05	85.92
	<b>0.044±0.001</b>	<b>-19.73</b>	<b>-2.33</b>	<b>17.40</b>	<b>57.40</b>
308.15	0.011±0.001	-23.63	3.39	27.02	87.68
	<b>0.041±0.001</b>	<b>-19.98</b>	<b>-2.57</b>	<b>17.41</b>	<b>56.51</b>
313.15	0.007±0.001	-24.86	2.82	27.67	88.37
	<b>0.028±0.001</b>	<b>-21.02</b>	<b>-4.85</b>	<b>16.17</b>	<b>51.62</b>
318.15	0.026±0.002	-21.18	-6.02	15.16	47.66
323.15	0.027±0.003	-21.04	-7.22	13.82	42.76
328.15	0.028±0.003	-20.88	-8.70	12.18	37.12
333.15	0.028±0.003	-20.81	-10.56	10.24	30.76
338.15	0.029±0.003	-20.63	-10.57	10.06	29.76
343.15	0.030±0.003	-20.45	-12.08	8.37	24.40