Supporting Information

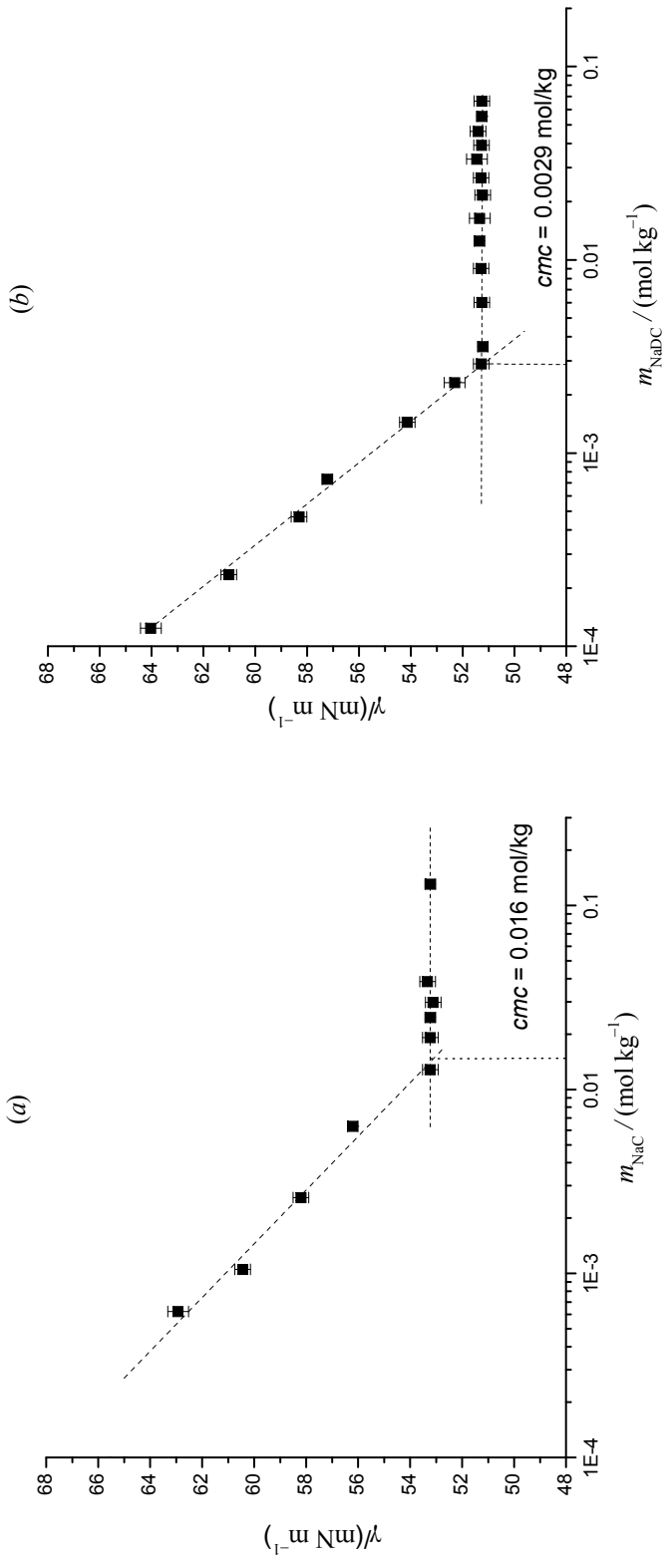


Figure S1 –Surface tension data at 25.0 °C for the systems NaC – H_2O (*a*) and NaDC – H_2O (*b*), as a function of the concentration.

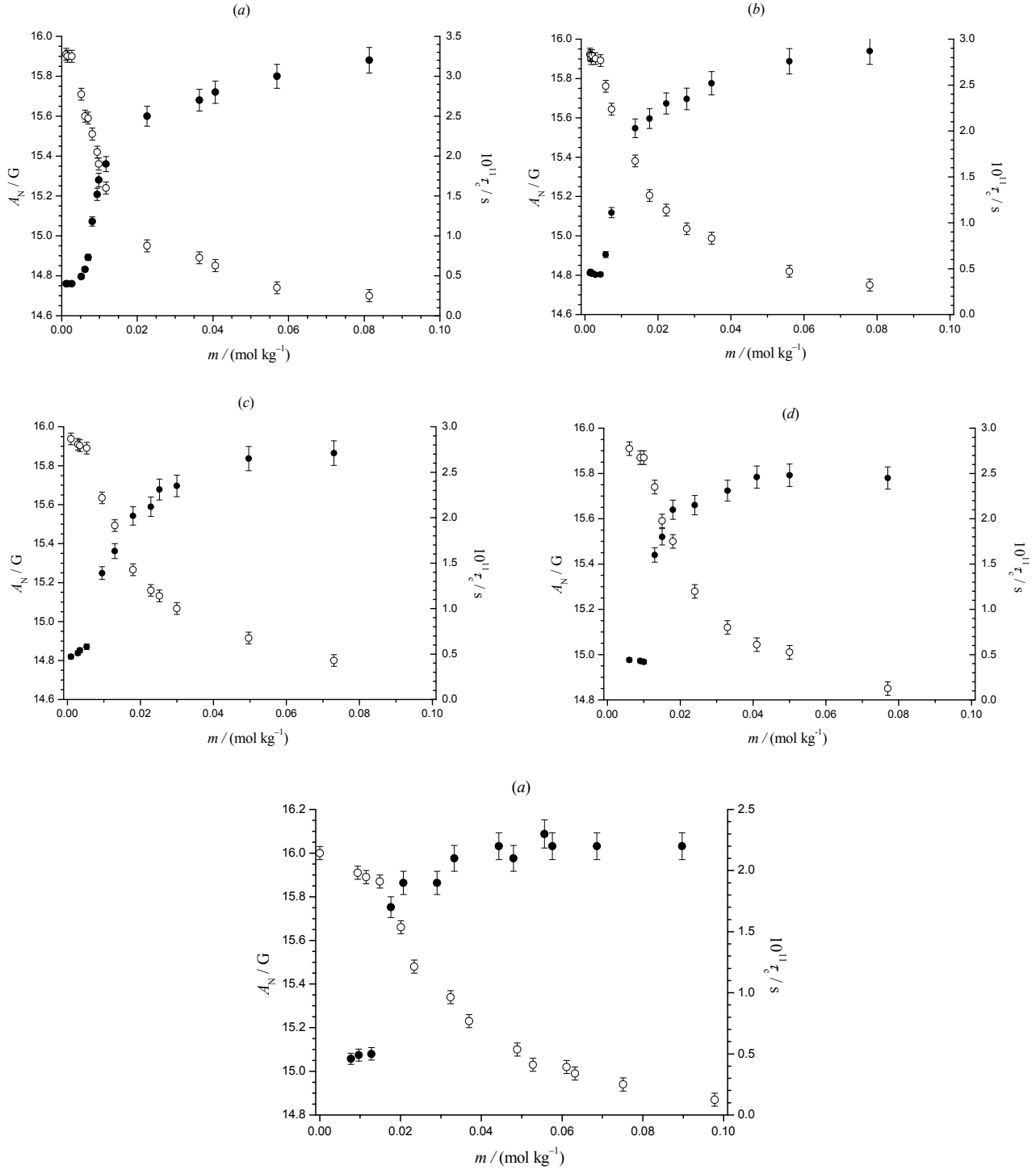


Figure S2 – Nitrogen hyperfine coupling constant A_N (–) and correlation time τ_c (,) of androstane in NaC – NaDC – H_2O systems at (*a*) $\alpha = 0$ NaDC binary aqueous system); (*b*) $\alpha = 0.100$; (*c*) $\alpha = 0.300$; (*d*) $\alpha = 0.700$; and (*e*) $\alpha = 1.000$ (NaC binary aqueous system), reported as a function of the total surfactant molality m at 25°C.

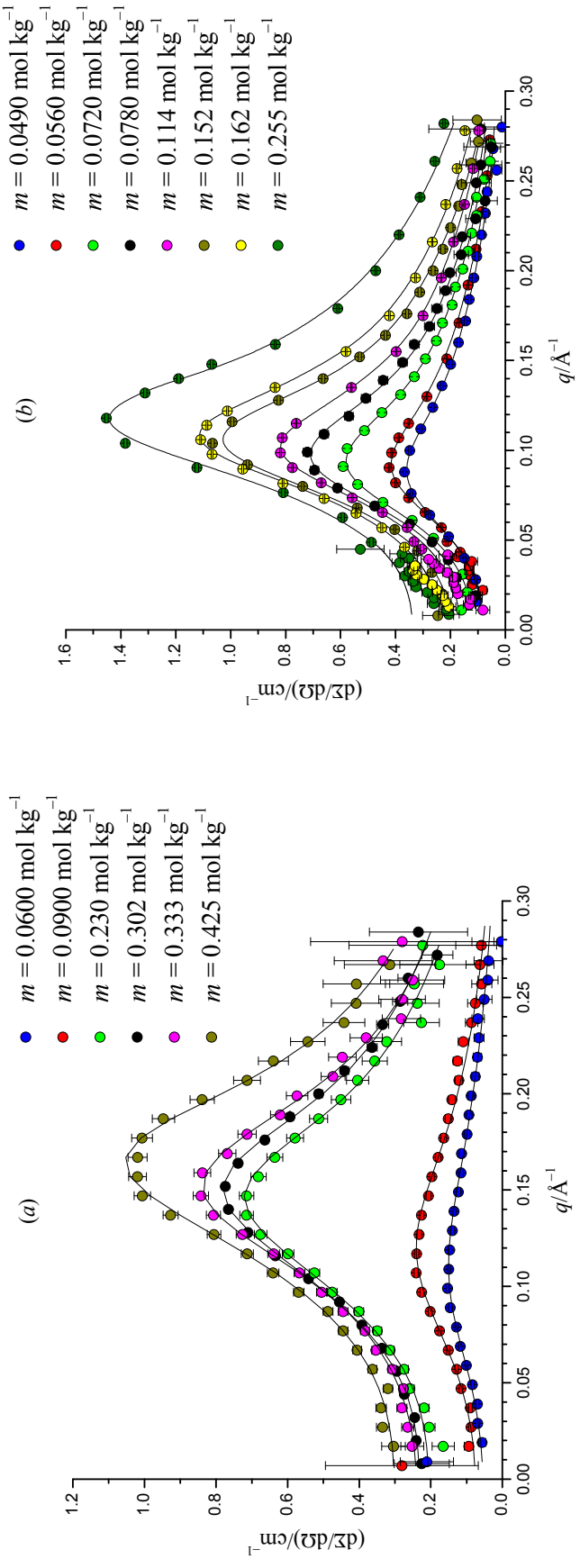


Figure S3 – Scattering cross sections at 25°C for the systems NaC – D_2O (*a*); NaDC – D_2O (*b*) at various solute concentrations, as indicated in the own legends. Solid lines represent the curves obtained by the fitting procedure described in the text.

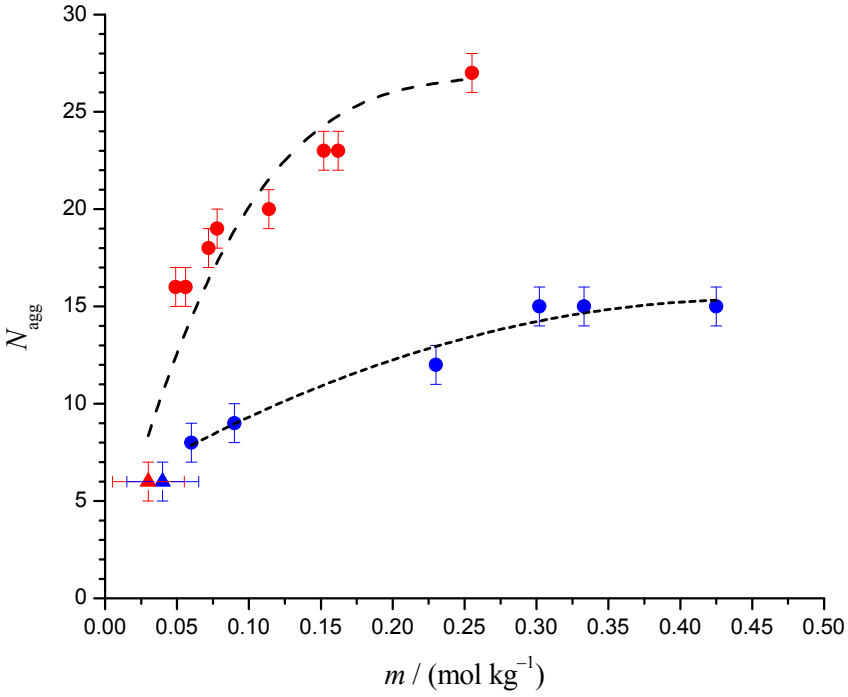


Figure S4 – Aggregation numbers N_{agg} reported as a function of the molality, obtained from analysis of SANS data for NaC – D_2O (,) and NaDC – D_2O (,) binary systems. Triangular symbols indicates the N_{agg} values obtained from fitting of equation (14) to experimental diffusion data for NaC – D_2O (7) and NaDC – D_2O (7) systems.

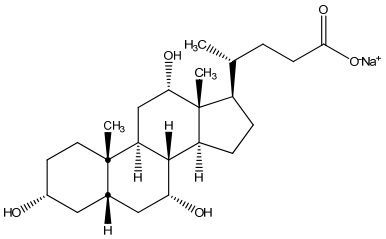
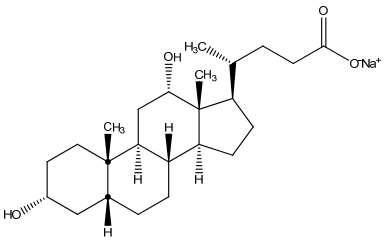
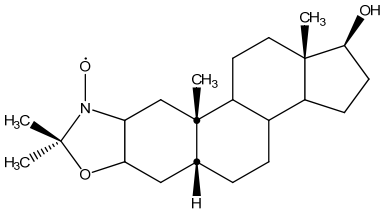
Molecule	"Dry" molar volume v	Scattering length Σb_i
Sodium cholate (NaC) 	550 Å^3	$8.43 \cdot 10^{-7}$ Å
Sodium deoxycholate (NaDC) 	570 Å^3	$7.09 \cdot 10^{-7}$ Å
Androstane nitroxide 		

Chart S1 – Structure of sodium cholate, sodium deoxycholate, and androstane nitroxide.

α	cmc / mmol kg^{-1} Surface tension	cmc / mmol kg^{-1} EPR
0.	3.0 ± 0.1	3 ± 1
0.100		4 ± 1
0.196	3.1 ± 0.1	
0.300		5 ± 1
0.486	5.5 ± 0.1	
0.500		7 ± 1
0.581	5.8 ± 0.1	
0.651	7.2 ± 0.1	
0.700		10 ± 1
1.	13.0 ± 0.1	15 ± 1

Table S1 – Critical micellar concentration cmc obtained at 25°C for ternary aqueous systems of NaC and NaDC as a function of the stoichiometric molar fraction α of NaC defined in equation (1).

c_{NaC} / mol dm^{-3}	$10^5 D$ / cm^2 s^{-1}	c_{NaDC} / mol dm^{-3}	$10^5 D$ / cm^2 s^{-1}
$9.97\cdot10^{-4}$	0.649 ± 0.013	$1.00\cdot10^{-5}$	0.720 ± 0.014
$2.99\cdot10^{-3}$	0.642 ± 0.013	$2.99\cdot10^{-3}$	0.698 ± 0.014
$4.98\cdot10^{-3}$	0.646 ± 0.013	$3.98\cdot10^{-3}$	0.587 ± 0.014
$9.94\cdot10^{-3}$	0.635 ± 0.013	$4.98\cdot10^{-3}$	0.613 ± 0.012
$1.19\cdot10^{-2}$	0.608 ± 0.012	$7.95\cdot10^{-3}$	0.470 ± 0.012
$1.59\cdot10^{-2}$	0.552 ± 0.011	$1.19\cdot10^{-2}$	0.441 ± 0.010
$1.78\cdot10^{-2}$	0.530 ± 0.011	$1.98\cdot10^{-2}$	0.446 ± 0.010
$1.98\cdot10^{-2}$	0.528 ± 0.011	$2.47\cdot10^{-2}$	0.454 ± 0.010
$2.47\cdot10^{-2}$	0.484 ± 0.010	$2.96\cdot10^{-2}$	0.464 ± 0.010
$2.96\cdot10^{-2}$	0.486 ± 0.010	$3.45\cdot10^{-2}$	0.447 ± 0.010
$3.94\cdot10^{-2}$	0.492 ± 0.010	$3.93\cdot10^{-2}$	0.453 ± 0.010
$4.90\cdot10^{-2}$	0.487 ± 0.010	$4.42\cdot10^{-2}$	0.461 ± 0.010
$5.87\cdot10^{-2}$	0.492 ± 0.010	$5.38\cdot10^{-2}$	0.442 ± 0.010
		$5.86\cdot10^{-2}$	0.459 ± 0.010
		$6.82\cdot10^{-2}$	0.465 ± 0.010
		$7.76\cdot10^{-2}$	0.459 ± 0.010
		$8.71\cdot10^{-2}$	0.467 ± 0.010

Table S2 – Mutual diffusion coefficients obtained at 25°C for NaC and NaDC aqueous binary systems, by means of the Taylor dispersion technique

$\frac{c}{\text{mol dm}^{-3}}$	$\frac{10^5 D_{1,1}}{\text{cm}^2\ \text{s}^{-1}}$	$\frac{10^5 D_{2,2}}{\text{cm}^2\ \text{s}^{-1}}$	$\frac{10^5 D_{1,2}}{\text{cm}^2\ \text{s}^{-1}}$	$\frac{10^5 D_{2,1}}{\text{cm}^2\ \text{s}^{-1}}$
0	*0.533*	*0.598*	*0.101*	*0.123*
0.008	0.524 ±0.015	0.199 ± 0.008	0.318 ± 0.002	0.073 ± 0.002
0.018	0.486 ± 0.013	0.209 ± 0.008	0.225 ± 0.011	0.052 ± 0.009
0.040	0.373 ± 0.006	0.311 ± 0.005	0.077 ± 0.006	0.153 ± 0.006
0.060	0.353 ± 0.003	0.290 ± 0.002	0.099 ± 0.003	0.166 ± 0.003

Table S3 – Main and cross diffusion coefficients obtained at 25°C for NaC – NaDC – H_2O system at $\alpha = 0.500$ (*i.e.* $c_1 = c_2 = c$), by means of the Gouy interferometric method. Infinite dilution values, reported in italic, have been evaluated through the Nernst–Hartley equation.