Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary materials

A. Densities, electron densities and neutron scattering length densities used

	Density	Electron density	Neutron scattering length density
	g/cm³	Å^{-2} (10^{-6})	Å^{-2}
water	0.997	9.43	$-5.596\ 10^{-7}$
D_2O	1.104	-	6.35810^{-6}
ethanol	0.789	7.56	-3.45610^{-7}
C_2D_6O	0.89	-	6.08110^{-6}
1-octanol	0.822	7.95	$-3.179\ 10^{-7}$
$C_8D_{17}OH$	0.936	-	$6.452\ 10^{-6}$

B. Table summing up the important results

Table S1: Data for the investigated salts and surfactants. Concentrations of anions or cations in the surfactant-free microemulsion in mol/kg and wt%. From **SAXS**: correlation length ξ_X in Å, absolute intensity at q→0 I(0) in cm^{-1}, mean radius R_{MV} in Å, distance D* in Å; from **SANS**: correlation length ξ_N in Å for the three contrasts. OR means octanol-rich contrast, WR means water-rich contrast, and ER means ethanol-rich contrast; and from **DLS/SLS**: characteristic time τ (inverse of the decay rate) in µs, Rayleigh ratio R in mm^{-1}.

			SAXS				**SANS**			**DLS - SLS**	
Ions	**Concentration**		ξ_X	**I(0)**	R_{MV}	**D***	ξ_N			**τ**	**R**
-	*mol/kg*	*wt%*	*Å*	*cm^{-1}*	*Å*	*Å*	OR *(Å)*	WR *(Å)*	ER *(Å)*	*µs*	*mm^{-1}*
reference	0	0	6.8	0.145	15.23	∞	16.3	6.35	16.0	40.2	1.62
Cl^-	0.18	1	10.2	0.275	22.85	∞	-	-	-	48.6	1.85
	0.35	2	12.3	0.45	27.55	∞	18.8	5.1	22.0	57.1	2.06
	0.51	3	16.7	0.76	37.41	∞	-	-	-	66.4	2.13
	0.68	4	27.7	2.25	62.05	∞	-	-	-	100.0	2.97
NO_3^-	0.06	0.5	7.75	0.155	17.36	∞	-	-	-	40.6	1.55
	0.84	7	15.8	1.18	35.39	∞	-	-	-	63.9	1.80
	0.93	8	19.5	1.79	43.79	∞	-	-	-	72.1	1.98
	1.10	9	30.2	4.62	67.65	∞	-	-	-	107.4	2.72
	1.17	10	46.2	11.25	103.49	∞	-	-	-	170.6	4.45
CH_3COO^-	0.11	1	8.65	0.207	19.38	∞	-	-	-	44.5	1.62
	1.18	10	16.1	1.35	36.06	∞	-	-	-	69.7	1.01
	1.50	12	40.6	8.6	90.94	∞	-	-	-	-	0.71
SCN^-	0.13	1	5.39	0.13	12.07	∞	-	-	-	33.8	1.28
	0.49	4	3.78	0.13	8.47	∞	-	-	-	24.2	1.52
	0.86	7	4.01 (3)	-	29.39	85.98	-	-	-	↘	1.01
	1.23	10	3.94 (3)	-	20.00	57.57	-	-	-	↘	0.71
Br^-	0.10	1	-	-	-	-	-	-	-	41.5	1.52
	0.48	5	-	-	-	-	-	-	-	40.8	1.14
	0.91	9	-	-	-	-	-	-	-	↘	0.67
	2.00	20	-	-	-	-	-	-	-	↘	0.49
ClO_4^-	0.10	1	-	-	-	-	-	-	-	39.1	1.49
	0.46	6	-	-	-	-	8.6	5.8	9.4	32.6	1.18
	1.26	15	-	-	-	-	-	-	-	↘	0.78
	1.60	20	-	-	-	-	-	-	-	↘	0.68

NH_4^+	0.10	0.5	18.4	0.48	41.22	∞	-	-	-	42.5	1.59
	1.00	5	21.1	0.9	47.26	∞	-	-	-	74.7	1.79
	1.39	7	28.5	1.51	63.84	∞	-	-	-	125.8	2.33
	1.47	8	45.8	4.5	102.59	∞	-	-	-	150.0	2.70
Cs^+	0.10	2	10.5	0.308	23.52	∞	-	-	-	44.7	1.65
	0.46	8	15.3	2.43	34.27	∞	-	-	-	70.0	2.06
	0.60	10	22.2	1.05	49.73	∞	-	-	-	106.0	2.79
	0.62	10.5	45.9	13.5	102.82	∞	-	-	-	146.3	3.92
Na^+	0.18	1	10.2	0.275	22.85	∞	-	-	-	48.6	1.85
	0.35	2	12.3	0.45	27.55	∞	18.8	5.1	22.0	57.1	2.06
	0.51	3	16.7	0.76	37.41	∞	-	-	-	66.4	2.13
	0.68	4	27.7	2.25	62.05	∞	-	-	-	100.0	2.97
K^+	0.01	0.1	7.7	0.147	17.25	∞	-	-	-	39.7	1.57
	0.15	1	10.4	0.275	23.30	∞	-	-	-	46.4	1.81
	0.43	3	17.8	0.89	39.87	∞	-	-	-	65.6	2.34
	0.53	4	24.1	1.62	53.98	∞	-	-	-	82.0	2.93
Li^+	0.05	0.2	10.6	0.24	23.74	∞	-	-	-	44.8	1.75
	0.50	2	10.6	0.302	23.86	∞	16.4	6.55	19.0	49.5	1.50
	1.85	8	10.2	0.46	22.85	∞	-	-	-	↗	0.78
	2.25	10	9.2	0.42	20.61	∞	-	-	-	↗	0.61
Ca^{2+}	0.10	1	9.6	0.262	21.62	∞	-	-	-	46.3	1.50
	0.47	5	13.6	0.86	30.46	∞	-	-	-	↗	0.92
	0.90	10	12.2	1.2	27.33	∞	-	-	-	-	0.39
BPh_4^-	0.03	1	5.7	0.108	12.77	∞	-	-	-	28.6	1.32
	0.06	2	4.73	0.1	10.59	∞	-	-	-	-	-
	0.10	3	4.42	0.09	9.90	∞	-	-	-	21.0	1.25
	0.12	4	3.55	0.08	7.95	∞	-	-	-	-	-
	0.14	5	4.73 (3)	-	22.63	70.47	-	-	-	20.3	1.31
	0.17	6	6.27 (3)	-	19.85	59.22	-	-	-	-	-
	0.20	7	6.12 (3)	-	18.47	53.85	-	-	-	-	-
	0.23	8	4.91 (3)	-	16.80	47.56	-	-	-	15.5	1.27
	0.27	9	5.38 (3)	-	16.29	45.96	-	-	-	15.2	1.33
SDS	0.005	0.1	-	-	-	-	-	-	-	37.8	1.48
	0.05	1	-	-	-	-	-	-	-	28.5	1.03
	0.07	2	3.95 (3)	-	36.47	110.21	-	-	-	25.9	0.95
	0.14	4	5.06 (3)	-	21.20	55.00	-	-	-	19.8	1.07
	0.20	6	6.20 (3)	-	17.95	45.13	-	-	-	↘	0.68
	0.35	10	8.40 (3)	-	15.44	38.87	-	-	-	↘	0.61
	0.42	12	8.52 (3)	-	14.77	37.03	-	-	-	-	-
	0.50	14	9.55 (3)	-	14.42	36.33	-	-	-	↘	0.60
	0.55	16	10.5 (3)	-	14.51	36.31	-	-	-	-	-
	0.70	20	12.8 (3)	-	13.82	35.19	-	-	-	↘	0.62
HDEHP	0.03	1	6.95	0.144	15.59	∞	-	-	-	-	-
	0.07	2	8.2	0.153	18.37	∞	-	-	-	-	-
	0.09	3	8.65	0.165	19.38	∞	-	-	-	-	-
	0.12	4	10.15	0.177	22.74	∞	-	-	-	-	-
	0.16	5	12.9	0.227	28.90	∞	-	-	-	-	-
NaDEHP	0.32	10	3.75 (3)	-	20.42	50.32	-	-	-	-	-
	0.63	20	7.18 (3)	-	10.96	27.56	-	-	-	-	-
	0.95	30	6.14 (3)	-	10.81	26.18	-	-	-	-	-
	1.26	40	2.88 (3)	-	7.37	18.33	-	-	-	-	-

C. DLS of composition α with increasing the anion concentration

As observed in **Figure A**, two different behaviours are observed with DLS when increasing the concentration of the sodium salts. For CH_3COO^-, Br^-, ClO_4^-, and SCN^- the intensity of the correlation functions decreases from 0 to respectively 1.50, 2.00, 1.60, and 1.30 mol/kg of the respective salt. The intensity of the correlation functions increases for Cl^- and NO_3^- from 0 to respectively 0.67 and 1.17 mol/kg.

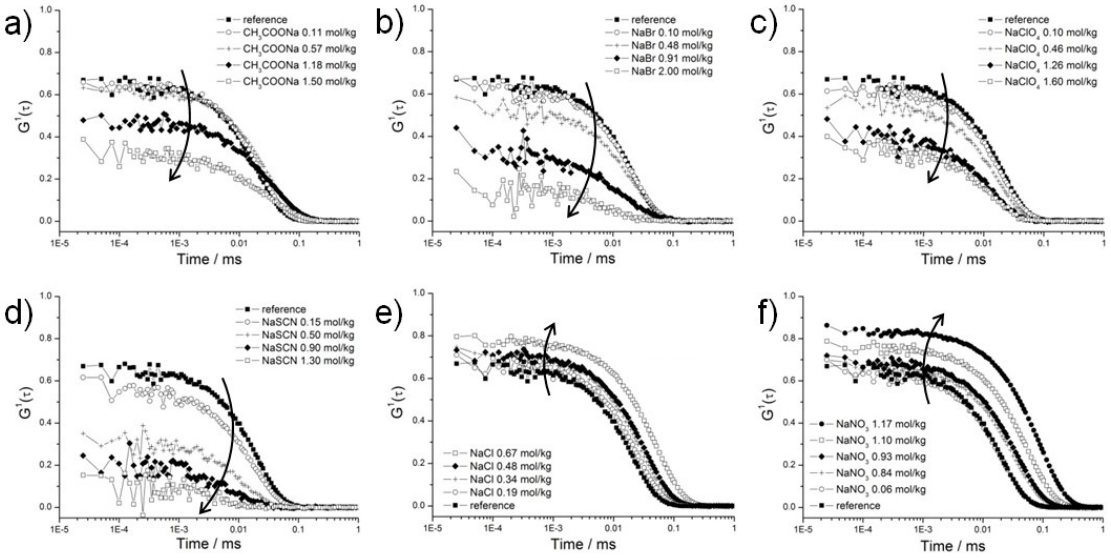

Figure A. Time-dependent self-correlation functions as obtained by DLS for the system water/ethanol/1-octanol in presence of different sodium salts: a) CH_3COONa; b) NaBr; c) $NaClO_4$; d) NaSCN; e) NaCl; f) $NaNO_3$, at 25 °C. The investigated salts were added to the composition α, see figure 1.

D. DLS of composition α with increasing the cation concentration

Regarding the DLS measurements performed with chloride salts and presented in **Figure B**, following observations can be made: the intensity of the correlations functions decreases with Li^+ and Ca^{2+} as cations, from 0 to 2.25 and 0.90 mol/kg of the respective salts. For NH_4^+, Cs^+, K^+, and Na^+ the intensity of the correlation functions increases from 0 to respectively 1.47, 0.62, 0.53, and 0.67 mol/kg.

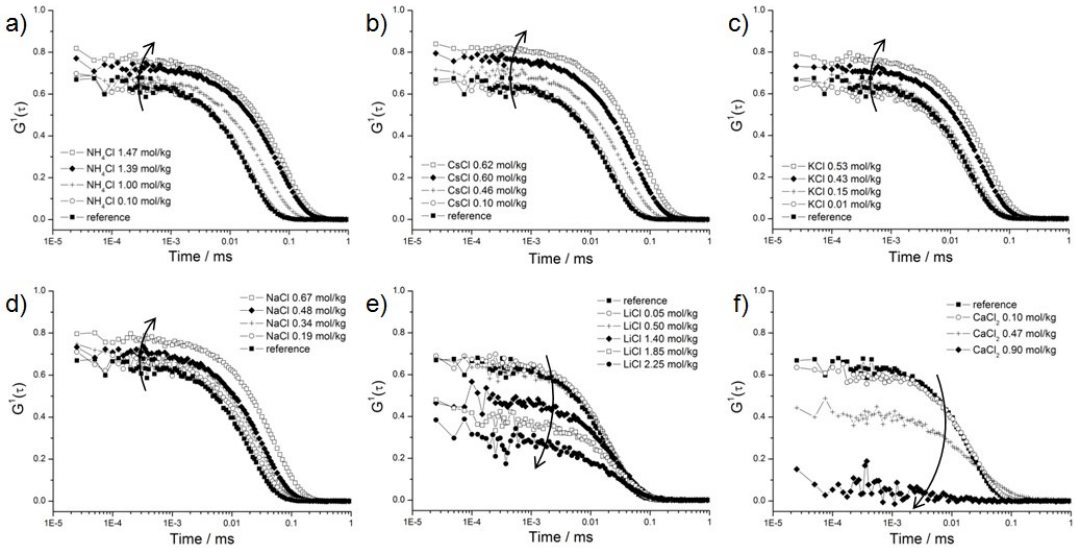

Figure B. Time-dependent self-correlation functions as obtained by DLS for the systems water/ethanol/1-octanol in presence of different chloride salts: a) NH_4Cl; b) CsCl; c) KCl; d) NaCl; e) LiCl; and f) $CaCl_2$, at 25 °C. The investigated salts were added to the composition α, see figure 1.

E. DLS of composition α with increasing concentration of $NaBPh_4$ and SDS

As can be seen in **Figure C**.a, the time-correlation becomes less and less pronounced when the concentration of $NaBPh_4$ increases from 0 to 0.27 mol/kg. The same trend was observed with increasing concentration of SDS from 0 to 0.70 mol/kg (see **Figure C**.b).

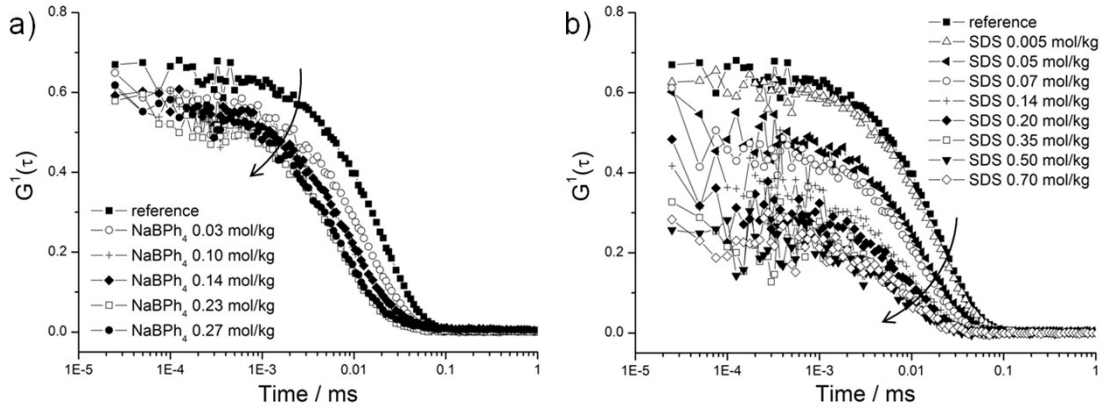

Figure C. Time-dependent self-correlation functions as obtained by DLS for the systems water/ethanol/1-octanol/additive, where the additive is a) $NaBPh_4$; and b) SDS, at 25 °C. The investigated salts were added to the ternary system of composition α, see figure 1.