Supporting information for: Hydration and Counterion Binding of [C_{12}MIM] Micelles

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Densities, dynamic viscosities and conductivities

Table S1: Densities, ρ, dynamic viscosities, η, and conductivities, κ, of aqueous $[C_{12}MIM]Br$ solutions at 45 °C as a function of solute molality, b, and molarity, c.

b / mol·kg^{-1}	c / mol·dm^{-3}	ρ / g·cm^{-3}	η / mPa·s	κ / S·m^{-1}
0.0108	0.0106	0.99052	0.602	0.137
0.0202	0.0199	0.99072	0.617	0.184
0.0506	0.0494	0.99152	0.627	0.302
0.0772	0.0747	0.99221	0.649	0.410
0.1033	0.0992	0.99284	0.674	0.521
0.1313	0.1250	0.99354	0.736	0.632
0.1855	0.1738	0.99476	0.800	0.855
0.2147	0.1996	0.99550	0.846	0.978
0.2642	0.2421	0.99664	0.918	1.181

Table S2: Densities, ρ, dynamic viscosities, η, and conductivities, κ, of aqueous $[C_{12}MIM]I$ solutions at 45 °C as a function of solute molality, b, and molarity, c.

b / mol·kg^{-1}	c / mol·dm^{-3}	ρ / g·cm^{-3}	η / mPa·s	κ / S·m^{-1}
0.0074	0.0073	0.99067	0.599	0.0847
0.0202	0.0199	0.99143	0.623	0.116
0.0511	0.0498	0.99306	0.648	0.191
0.0771	0.0745	0.99479	0.679	0.252
0.1038	0.0995	0.99630	0.715	0.315
0.1307	0.1242	0.99784	0.763	0.375
0.1860	0.1739	1.00088	0.931	0.481
0.2144	0.1988	1.00242	1.128	0.536
0.2507	0.2301	1.00478	1.51	0.613

Table S3: Densities, ρ, dynamic viscosities, η, and conductivities, κ, of aqueous $[C_{12}MIM]OTf$ solutions at 45 °C as a function of solute molality, b, and molarity, c.

b / mol·kg^{-1}	c / mol·dm^{-3}	ρ / g·cm^{-3}	η / mPa·s	κ / S·m^{-1}
0.0043	0.0043	0.99042	0.598	0.0362
0.0151	0.0149	0.99086	0.631	0.0569
0.0302	0.0299	0.99148	0.703	0.0794
0.0502	0.0498	0.99232	1.224	0.110
0.0749	0.0744	0.99334	3.127	0.148
0.1000	0.0995	0.99438	8.45	0.190
0.1251	0.1245	0.99546	13.4	0.233
0.1743	0.1739	0.99742	14.6	0.311
0.2540	0.2305	0.99988	13.4	0.396

Table S4: Densities, ρ, dynamic viscosities, η, and conductivities, κ, of a [C12MIM]Br solution with b = 0.1033 mol·kg^{-1} as a function of temperature T.

T / K	c / mol·dm^{-3}	ρ / g·cm^{-3}	η / mPa·s	κ / S·m^{-1}
298.15	0.0999	1.00003	1.116	0.324
308.15	0.0996	0.99683	0.894	0.415
318.15	0.0992	0.99284	0.674	0.521
328.15	0.0987	0.98793	0.601	0.639
338.15	0.0981	0.98173	0.506	0.774

Table S5: Densities, ρ, dynamic viscosities, η, and conductivities, κ, of a [C12MIM]I solution with b = 0.1038 mol·kg^{-1} as a function of temperature T.

T / K	c / mol·dm^{-3}	ρ / g·cm^{-3}	η / mPa·s	κ / S·m^{-1}
298.15	0.1003	1.00353	1.31	0.164
308.15	0.0999	1.00032	0.903	0.233
318.15	0.0995	0.99630	0.715	0.315
328.15	0.0991	0.99161	0.598	0.403
338.15	0.0986	0.98639	0.508	0.501

Table S6: Densities, ρ, dynamic viscosities, η, and conductivities, κ, of a [C12MIM]OTf solution with b = 0.0749 mol·kg^{-1} as a function of temperature T.

T / K	c / mol·dm^{-3}	ρ / g·cm^{-3}	η / mPa·s	κ / S·m^{-1}
298.15	0.0750	1.00042	48.6	0.095
308.15	0.0747	0.99728	10.59	0.120
318.15	0.0744	0.99334	3.127	0.148
328.15	0.0741	0.98870	1.355	0.181
338.15	0.0737	0.98349	0.723	0.221

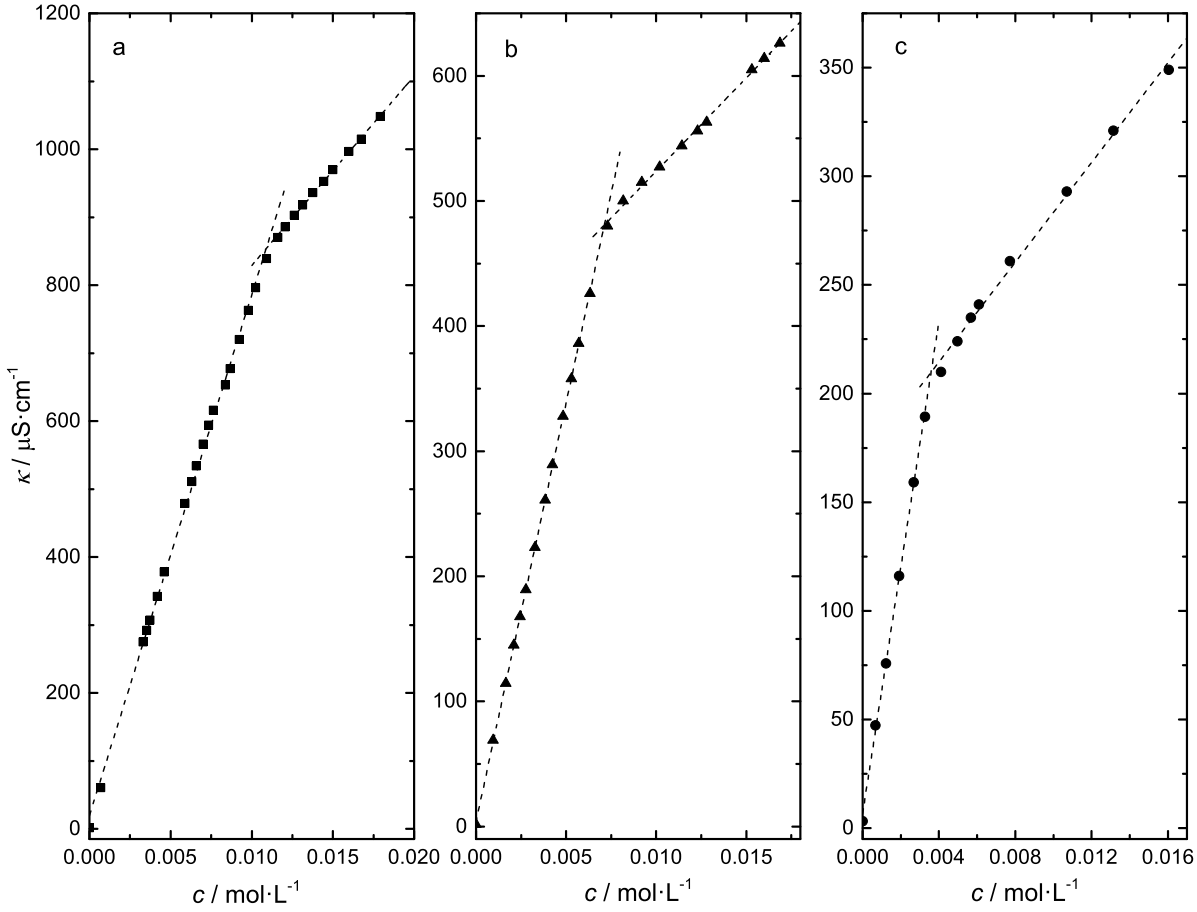

Figure S1: Conductivity, κ, *vs.* concentration, c, profiles for the determination of the critical micellar concentration, *cmc*, and the degree of counterion binding, β, for solutions of (a) [C_{12}MIM]Br, (b) [C_{12}MIM]I and (c) [C_{12}MIM]OTf in water at 45 °C (see main manuscript for details).

Correction of Raw Dielectric Spectra

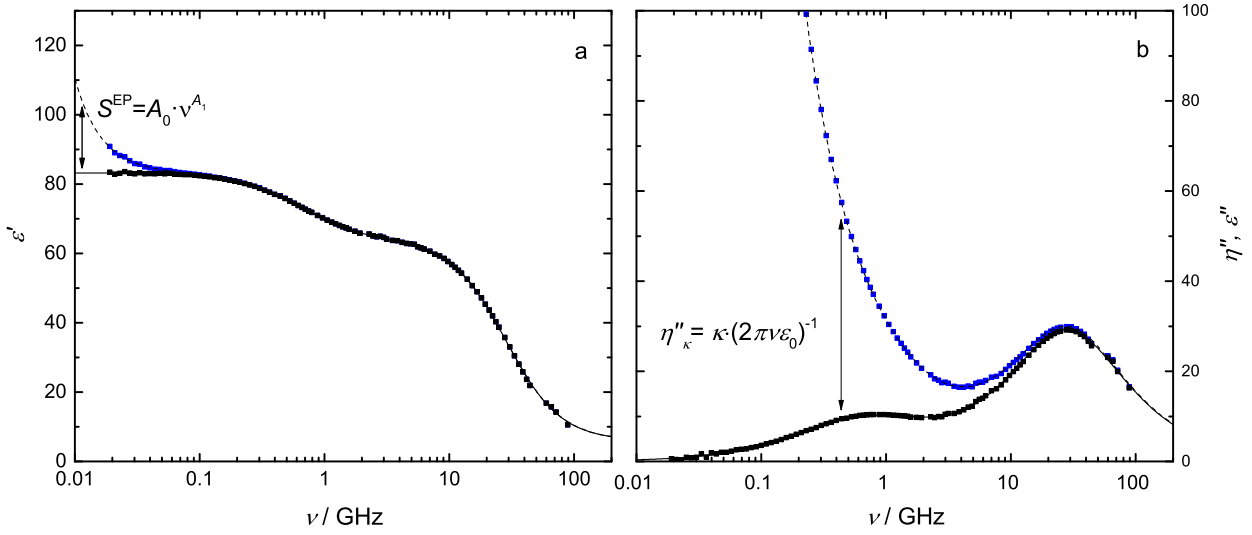

Figure S2: (a) Relative permittivity spectrum, $\varepsilon'(\nu)$, of 0.2421 mol·L^{-1} [C_{12}MIM]Br(aq) before (■) and after (■) correction for electrode polarization (EP, amplitude $S^{EP} = A_0 \times \nu^{A_1}$). (b) Spectra of the total, $\eta''(\nu)$ (■), and the dielectric, $\varepsilon''(\nu)$ (■), loss of this solution, as well as the associated contribution from dc conductivity, $\eta''_\kappa = \kappa/(2\pi\nu\varepsilon_0)$. The lines in both panels indicate the fit with the D+D+D+D model.

Relaxation Time Distribution Functions

The relaxation-time distribution functions, $P(\tau)$, of Figs. S3–S8 were obtained by fitting $N_\tau = 601$ Debye basis functions equidistantly spaced on a log τ scale between 0.1 ps and 100,000 ps to the experimental data as described in detail in Ref. S1.

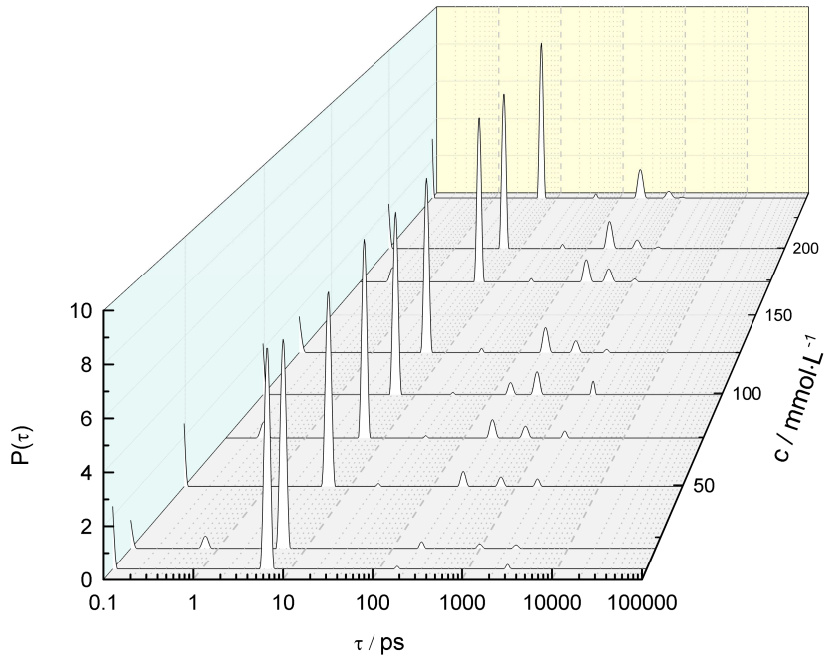

Figure S3: Zasetsky plots[S1] of the relaxation-time distribution functions, $P(\tau)$, for the dielectric spectra of aqueous $[C_{12}MIM]Br$ solutions at 45 °C.

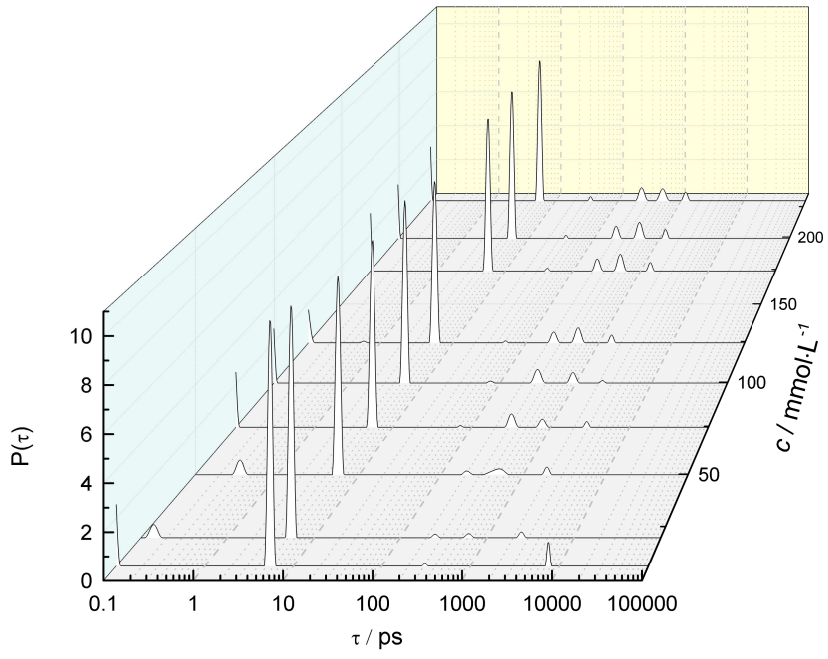

Figure S4: Zasetsky plots[S1] of the relaxation-time distribution functions, $P(\tau)$, for the dielectric spectra of aqueous $[C_{12}MIM]I$ solutions at 45 °C.

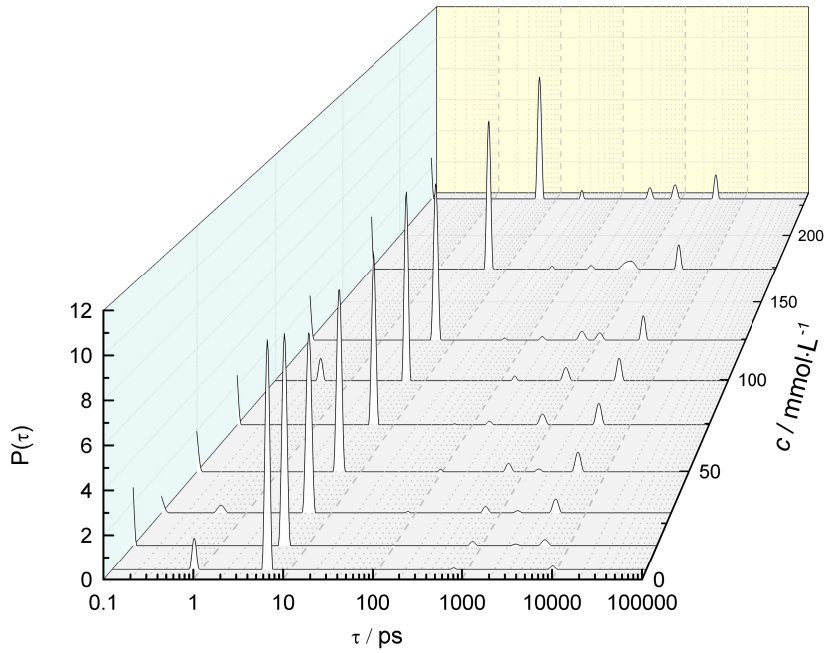

Figure S5: Zasetsky plots[S1] of the relaxation-time distribution functions, $P(\tau)$, for the dielectric spectra of aqueous $[C_{12}MIM]OTf$ solutions at 45 °C.

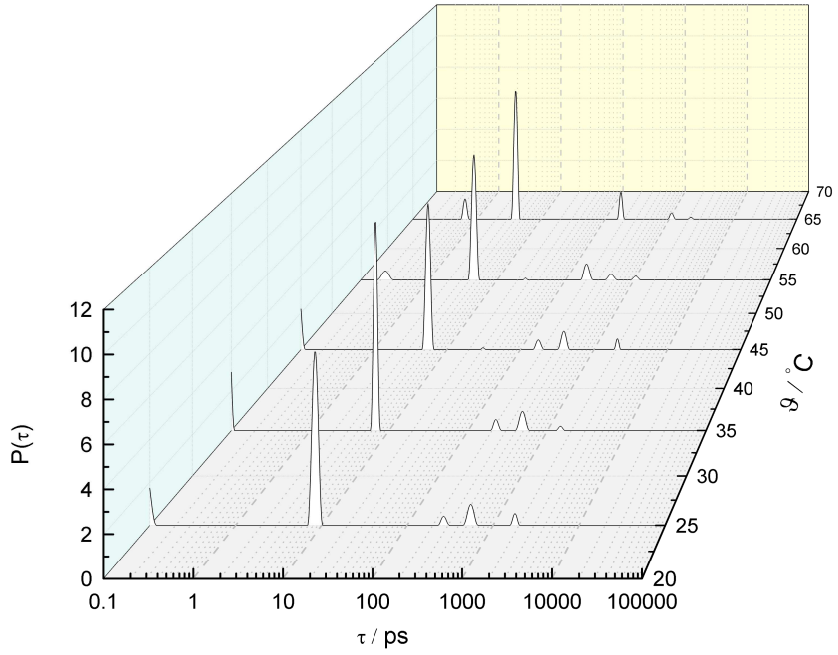

Figure S6: Zasetsky plots[S1] of the relaxation-time distribution functions, $P(\tau)$, for the dielectric spectra of 0.1033 mol/kg $[C_{12}MIM]Br$(aq) in the temperature range 25 - 65 °C.

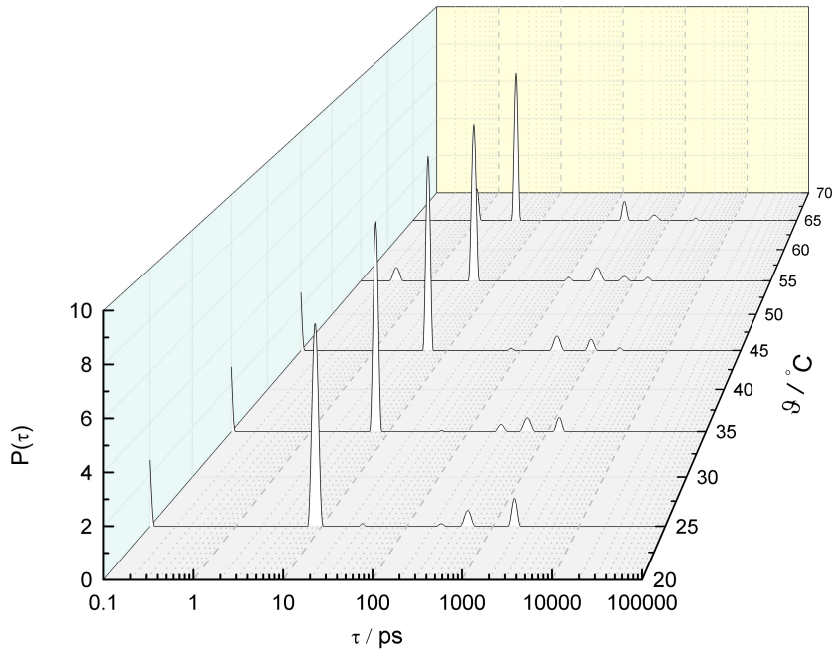

Figure S7: Zasetsky plots[S1] of the relaxation-time distribution functions, $P(\tau)$, for the dielectric spectra of 0.1033 mol/kg $[C_{12}MIM]I$(aq) in the temperature range 25 - 65 °C.

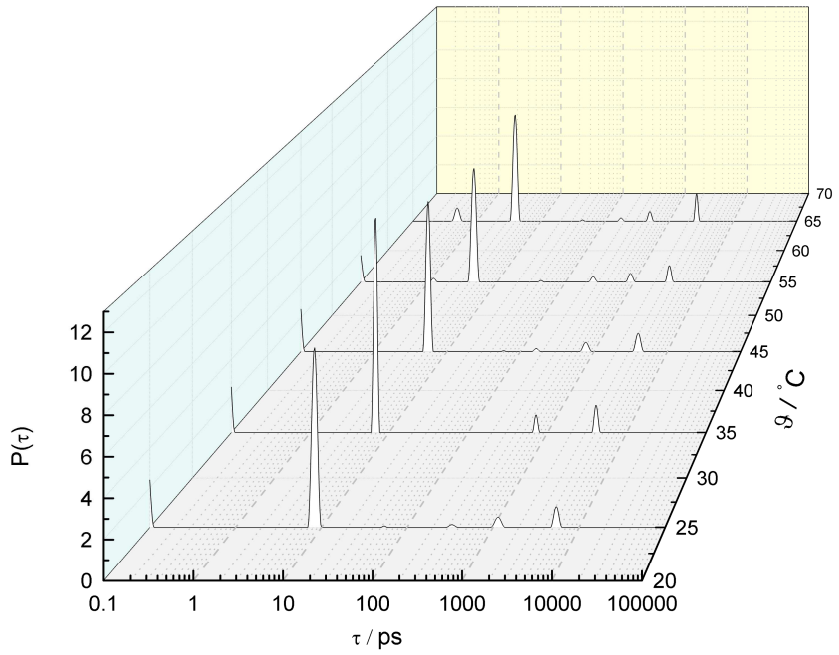

Figure S8: Zasetsky plots[S1] of the relaxation-time distribution functions, $P(\tau)$, for the dielectric spectra of 0.1033 mol/kg $[C_{12}MIM]OTf$(aq) in the temperature range 25 - 65 °C.

Relaxation Parameters of the D+D+D+D Model

Table S7: Parameters of the D+D+D+D model fitting the DR spectra of aqueous $[C_{12}MIM]Br$ solutions at 45 °C and solute concentration, c: static permittivity, ε, amplitudes, S_j, and relaxation times, τ_j, of the resolved modes $j = 1 \ldots 4$, and high-frequency permittivity, ε_∞.[a]

c / M	ε	S_1	τ_1 / ns	S_2	τ_2 / ps	S_3	τ_3 / ps	S_4	τ_4 / ps	ε_∞
0.0106 [b]	72.13	0.47	2.28	0.34	171			65.91	5.39	5.41
0.0199	74.27	1.59	1.70	1.52	254	0.23	30F	65.08	5.45	5.86
0.0494	78.88	3.14	1.33	5.29	282	0.75	30F	64.05	5.42	5.66
0.0747	81.10	3.55	1.21	7.95	271	1.08	23.4	62.80	5.40	5.72
0.0992	81.94	3.13	0.985	9.64	287	1.06	80.7	62.22	5.52	5.89
0.1250	82.98	3.53	0.877	11.26	257	1.70	30F	61.07	5.35	5.43
0.1738	83.50	3.92	0.650	13.10	238	1.66	30F	59.37	5.37	5.45
0.1996	83.71	3.95	0.680	13.93	225	1.59	30F	58.53	5.43	5.70
0.2421	83.30	3.96	0.635	14.92	213	1.19	33.2	57.24	5.54	5.99

[a] Parameter values followed by "F" were fixed; [b] Data not used in further processing, see text.

Table S8: Parameters of the D+D+D+D model fitting the DR spectra of aqueous $[C_{12}MIM]I$ solutions at 45 °C and solute concentration, c: static permittivity, ε, amplitudes, S_j, and relaxation times, τ_j, of the resolved modes $j = 1 \ldots 4$, and high-frequency permittivity, ε_∞.[a]

c / M	ε	S_1	τ_1 / ns	S_2	τ_2 / ps	S_3	τ_3 / ps	S_4	τ_4 / ps	ε_∞
0.0073 [b]	72.26	0.55	2.51	0.20	222			66.04	5.40	5.46
0.0199	74.70	1.75	2.20	1.90	385	0.22	40F	65.60	5.37	5.27
0.0498	78.33	2.79	1.66	5.20	378	0.41	40F	64.37	5.41	5.56
0.0745	79.85	2.81	1.78	7.46	370	0.56	40F	63.41	5.42	5.61
0.0995	80.75	4.68	1.09	7.28	312	0.77	34.5	62.37	5.43	5.64
0.1242	82.43	5.19	1.03	9.28	310	1.23	22.6	60.94	5.39	5.79
0.1739	83.94	6.19	1.01	11.12	309	1.31	33.6	59.28	5.47	6.05
0.1988	84.23	7.40	0.911	10.96	290	1.37	35.8	58.47	5.50	6.03
0.2301	84.12	7.57	0.901	11.57	282	1.49	41.3	57.36	5.52	6.20

[a] Parameter values followed by "F" were fixed; [b] Data not used in further processing, see text.

Table S9: Parameters of the D+D+D+D model fitting the DR spectra of aqueous $[C_{12}MIM]OTf$ solutions at 45 °C and solute concentration, c: static permittivity, ε, amplitudes, S_j, and relaxation times, τ_j, of the resolved modes $j = 1 \ldots 4$, and high-frequency permittivity, ε_∞.[a]

c / M	ε	S_1	τ_1 / ns	S_2	τ_2 / ps	S_3	τ_3 / ps	S_4	τ_4 / ps	ε_∞
0.0043 [b]	72.51	0.85	9.05	0.18	1380			67.17	5.21	4.31
0.0149	75.21	2.58	5.16	1.41	915	0.20	89F	65.80	5.35	5.22
0.0299	78.55	5.19	4.57	2.47	814	0.46	89F	65.21	5.33	5.23
0.0498	81.59	7.63	4.39	3.58	707	0.61	79.2	64.16	5.40	5.60
0.0744	83.08	8.39	3.94	4.62	723	1.08	109	63.19	5.47	5.80
0.0995	84.19	8.64	3.83	6.15	712	1.33	115	62.12	5.47	5.95
0.1245	85.41	9.56	3.83	7.62	624	1.48	61.2	61.10	5.42	5.65
0.1739	86.65	10.17	3.63	9.52	611	1.77	81.7	59.22	5.56	5.97
0.2305	86.84	10.63	3.50	11.00	572	2.59	89F	56.83	5.56	5.78

[a] Parameter values followed by "F" were fixed; [b] Data not used in further processing, see text.

Table S10: Parameters of the D+D+D+D model fitting the DR spectra of aqueous solutions of $[C_{12}MIM]Br$ at $m = 0.1033\,\mathrm{mol\,kg^{-1}}$ and temperature T: static permittivity, ε, amplitudes, S_j, and relaxation times, τ_j, of the resolved modes $j = 1 \ldots 4$, and high-frequency permittivity, ε_∞.[a]

T / K	ε	S_1	τ_1 / ns	S_2	τ_2 / ps	S_3	τ_3 / ps	S_4	τ_4 / ps	ε_∞
298.15	89.74	3.26	1.88	9.14	532	2.28	323	69.28	8.40	5.78
308.15	85.08	2.74	1.04	9.70	381	1.3F	150	65.70	6.67	5.65
318.15	81.94	3.13	0.985	9.64	287	1.06	80.7	62.22	5.52	5.89
328.15	78.73	3.42	0.745	9.55	214	1.22	14.8	59.02	4.45	5.51
338.15	75.10	2.92	1.28	9.43	178	0.61	12.6	56.81	3.82	5.33

[a] Parameter values followed by "F" were fixed.

Table S11: Parameters of the D+D+D+D model fitting the DR spectra of aqueous solutions of $[C_{12}MIM]I$ at $m = 0.1038\,\mathrm{mol\,kg^{-1}}$ and temperature T: static permittivity, ε, amplitudes, S_j, and relaxation times, τ_j, of the resolved modes $j = 1 \ldots 4$, and high-frequency permittivity, ε_∞.[a]

T / K	ε	S_1	τ_1 / ns	S_2	τ_2 / ps	S_3	τ_3 / ps	S_4	τ_4 / ps	ε_∞
298.15	88.88	7.96	1.74	5.72	465	0.69	32.3	68.41	8.41	6.10
308.15	84.86	6.10	1.23	6.58	389	0.49	42.7	65.73	6.71	5.96
318.15	80.75	4.68	1.09	7.28	312	0.77	34.5	62.37	5.43	5.64
328.15	78.09	3.28	1.08	8.77	270	0.94	25F	59.58	4.42	5.53
338.15	74.49	2.92	0.908	8.82	210	0.08	20F	57.17	3.85	5.51

[a] Parameter values followed by "F" were fixed.

Table S12: Parameters of the D+D+D+D model fitting the DR spectra of aqueous solutions of $[C_{12}MIM]OTf$ at $m = 0.0749\,\mathrm{mol\,kg^{-1}}$ and temperature T: static permittivity, ε, amplitudes, S_j, and relaxation times, τ_j, of the resolved modes $j = 1 \ldots 4$, and high-frequency permittivity, ε_∞.[a]

T / K	ε	S_1	τ_1 / ns	S_2	τ_2 / ps	S_3	τ_3 / ps	S_4	τ_4 / ps	ε_∞
298.15	87.96	7.15	5.29	4.59	998	0.76	147	69.85	8.28	5.62
308.15	85.38	6.97	4.88	5.18	998	0.8F	120F	67.12	6.66	5.31
318.15	83.08	8.39	3.94	4.62	723	1.08	109	63.19	5.47	5.80
328.15	79.34	7.61	2.95	4.59	527	1.08	70.5	60.84	4.46	5.23
338.15	76.34	7.30	2.42	4.56	465	1.06	77.3	57.67	3.85	5.73

[a] Parameter values followed by "F" were fixed.

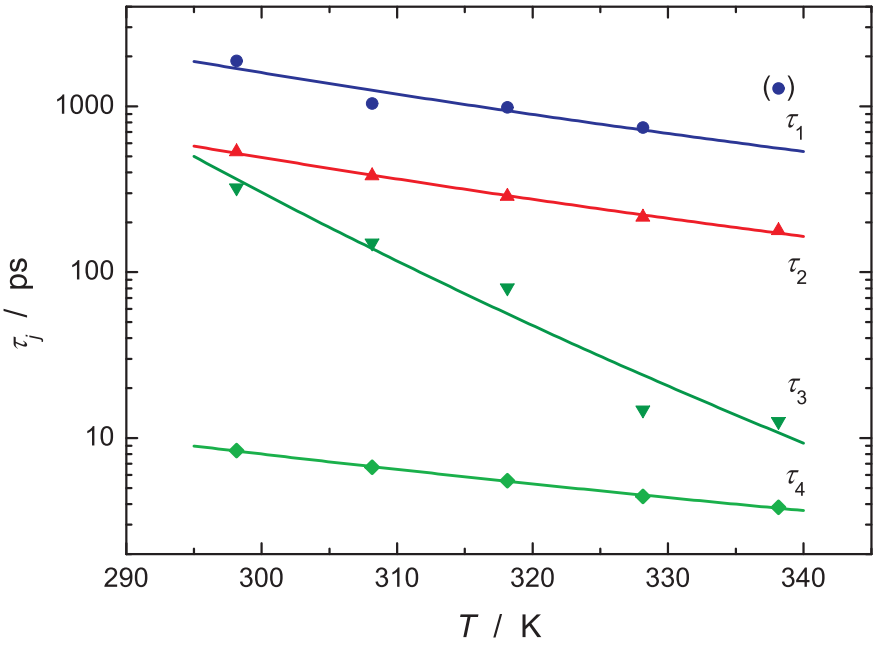

Figure S9: Relaxation times τ_1 (●), τ_2 (▲), τ_3 (▼) and τ_4 (♦) of 0.1033 mol/kg aqueous [C_{12}MIM]Br as a function of temperature, T. The solid lines show Eyring fits, eq 3 of the main paper (bracketed symbol not included in the fit).

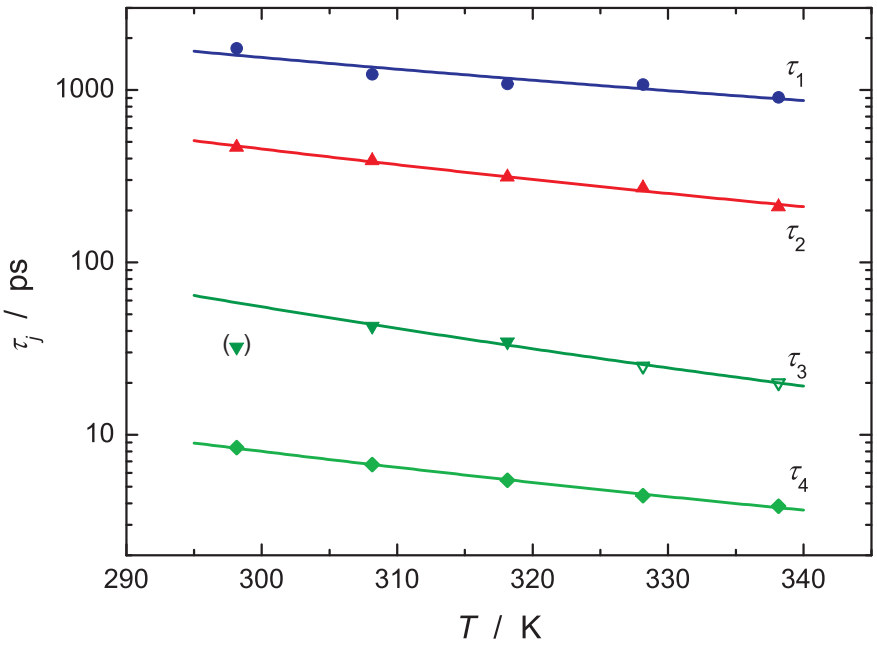

Figure S10: Relaxation times τ_1 (●), τ_2 (▲), τ_3 (▼) and τ_4 (♦) of 0.1038 mol/kg aqueous [C_{12}MIM]I as a function of temperature, T. Open symbols indicate that τ_3 was fixed in the D+D+D+D fit of the dielectric spectrum, the bracketed point was neglected in the Eyring fit. The solid lines show Eyring fits, eq 3 of the main paper, to the relaxation times.

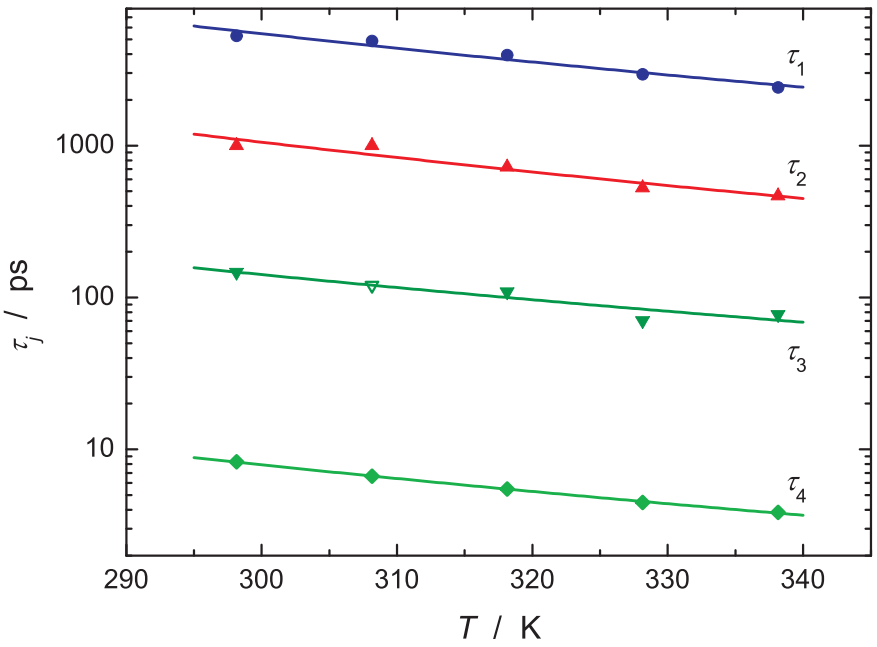

Figure S11: Relaxation times τ_1 (●), τ_2 (▲), τ_3 (▼) and τ_4 (♦) of 0.0749 mol/kg aqueous $[C_{12}MIM]OTf$ as a function of temperature, T. Open symbol indicates that τ_3 was fixed in the D+D+D+D fit of the dielectric spectrum. The solid lines show Eyring fits, eq 3 of the main paper, to the relaxation times.

Simultaneous Fitting of the Micelle-specific Modes

For the simultaneous fitting of the solute-specific relaxation modes with the Grosse model, eqs 11-14 of the main paper, a nonlinear least-squares fitting routine was implemented using software based on MATLAB (Mathworks). In this procedure the error function

$$\chi^2_G = \frac{1}{4m-n} \cdot \sum_{i=1}^{m} \left[\left(\frac{(S_1)_i - (S_1)_{i,calc}}{\frac{c_i}{\mathrm{mol/L^3}} \cdot (\sigma_{S_1})_i} \right)^2 + \left(\frac{(S_2)_i - (S_2)_{i,calc}}{\frac{c_i}{\mathrm{mol/L^3}} \cdot (\sigma_{S_2})_i} \right)^2 + \left(\frac{(\tau_1)_i - (\tau_1)_{i,calc}}{\frac{c_i}{\mathrm{mol/L^3}} \cdot (\sigma_{\tau_1})_i} \right)^2 + \left(\frac{(\tau_2)_i - (\tau_2)_{i,calc}}{\frac{c_i}{\mathrm{mol/L^3}} \cdot (\sigma_{\tau_2})_i} \right)^2 \right] \quad (1)$$

was minimized, where m denotes the number of the individual data points i (equal to the number of solutions of the concentration series), n is the number of fitting parameters, c_i is the IL concentration and σ a weighting parameter. The latter is defined as the deviation of

the respective relaxation parameter, S_j or τ_j (j = 1, 2), from a low-order polynomial fit. The concentration, c_i, serves as an additional weight which accounts for the condition $\phi \ll 1$ of the Grosse theory by giving larger weight to low surfactant concentrations.

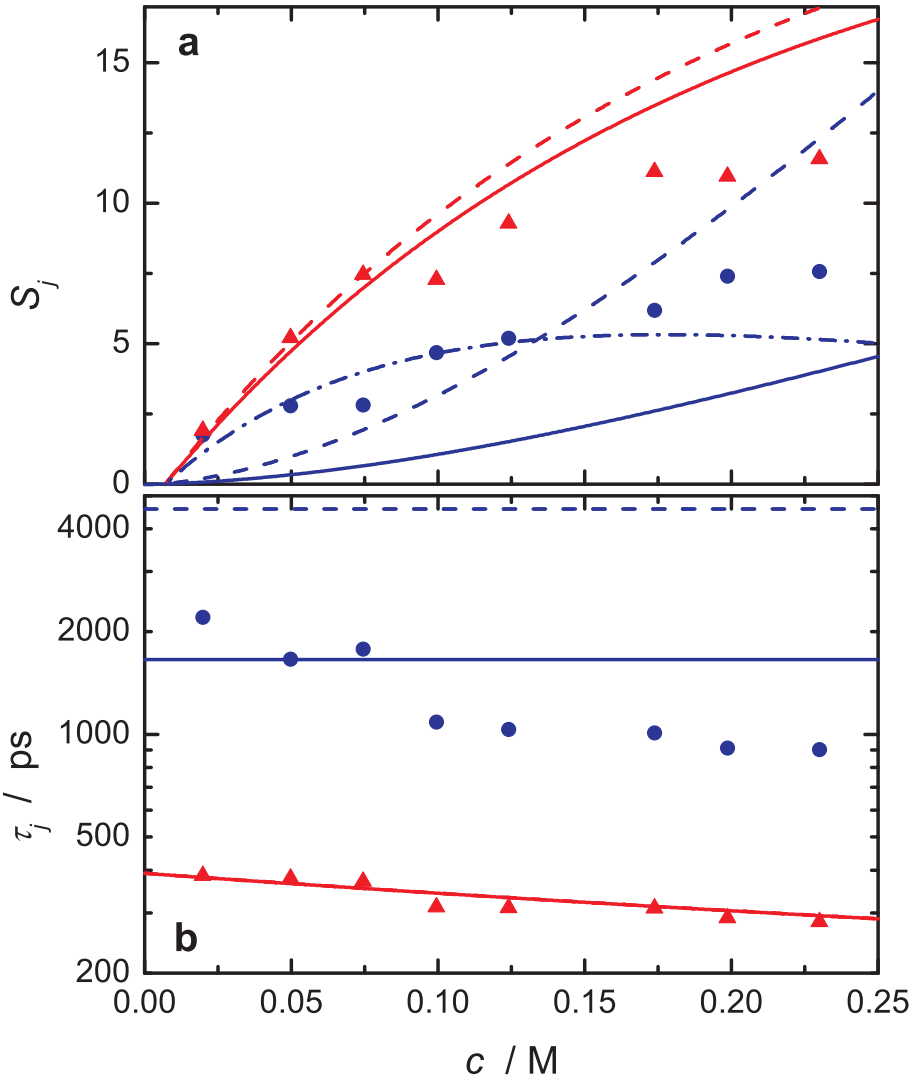

Figure S12: (a) Experimental amplitudes, S_j, and (b) relaxation times, τ_j, of the micellar relaxation processes j = 1 (●) and j = 2 (▲) of [C_{12}MIM]I at 45 °C. The correspondingly colored lines represent the fit of Grosse's model with all relaxation times and amplitudes simultaneously fitted (broken lines) and with S_1 omitted in the fit (solid lines). The dash-dotted line gives the fit of S_1 with adjusted Debye length, χ^{-1}_{emp}.

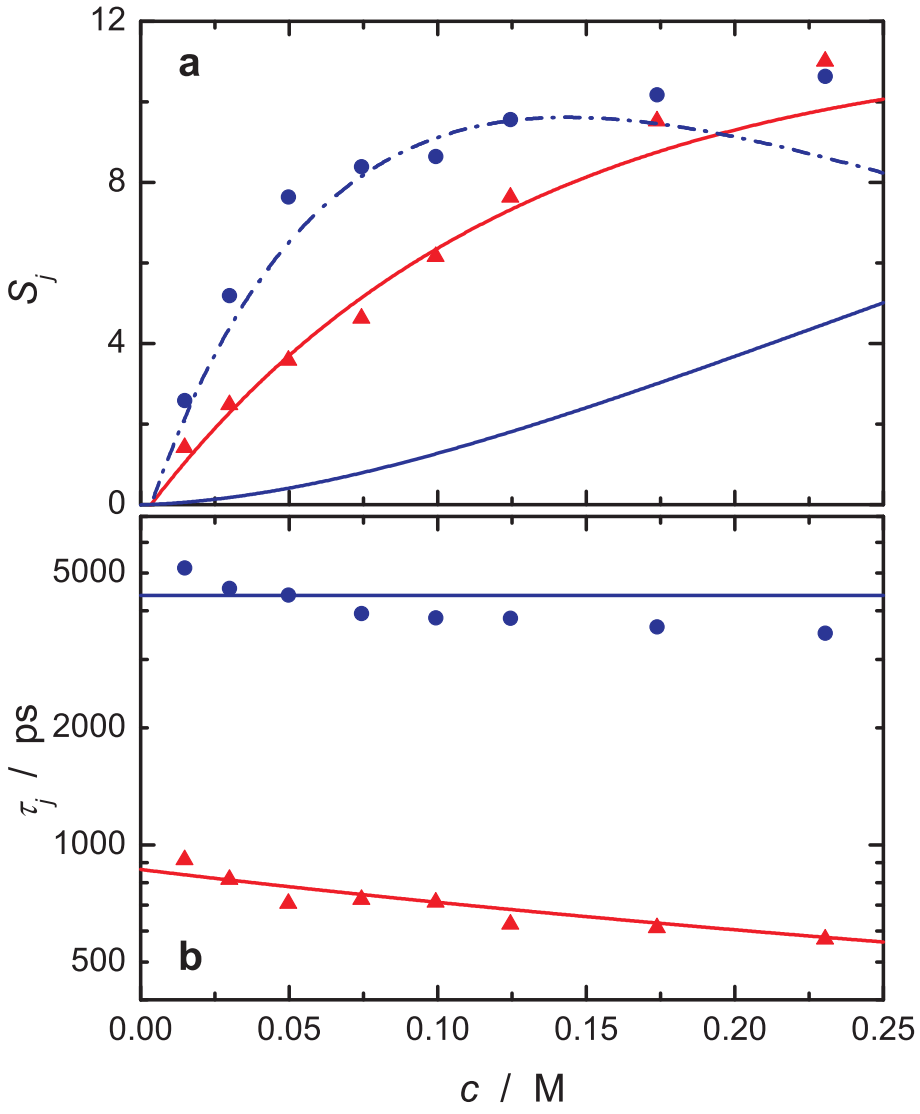

Figure S13: (a) Experimental amplitudes, S_j, and (b) relaxation times, τ_j, of the micellar relaxation processes $j = 1$ (●) and $j = 2$ (▲) of $[C_{12}MIM]OTf$ at 45 °C. The correspondingly colored lines represent the fit of Grosse's model with S_1 omitted in the fit. The dash-dotted line gives the fit of S_1 with adjusted Debye length, χ_{emp}^{-1}.

Table S13: Intercept, a_0, and slope, a_1, of the empirical equation $\chi^{-1}_{\mathrm{emp}} = a_0 + a_1 \times c$ for the effective Debye length of the investigated surfactants at 45 °C.

	a_0 / 10^{-9} m	a_1 / 10^{-12} m^4 mol^{-1}
[C_{12}MIM]Br	0.947	2.01
[C_{12}MIM]I	0.950	2.94
[C_{12}MIM]OTf	0.703	2.48

Micelle Volume Fraction from DRS

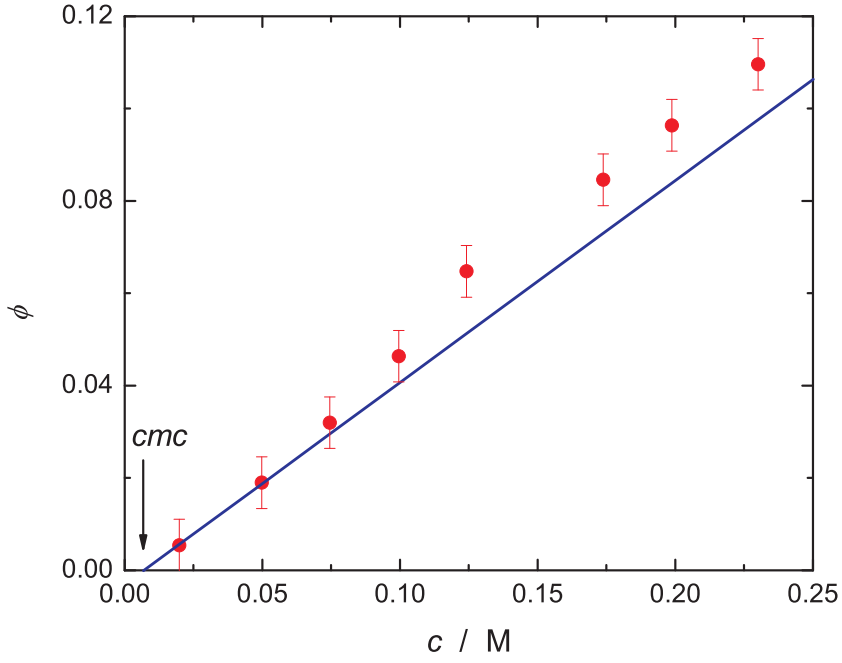

Figure S14: Effective volume fraction, ϕ, of [C_{12}MIM]I micelles in aqueous solution calculated from the Grosse radius, R_G (solid line), and from the bulk water amplitude, S_b (●).

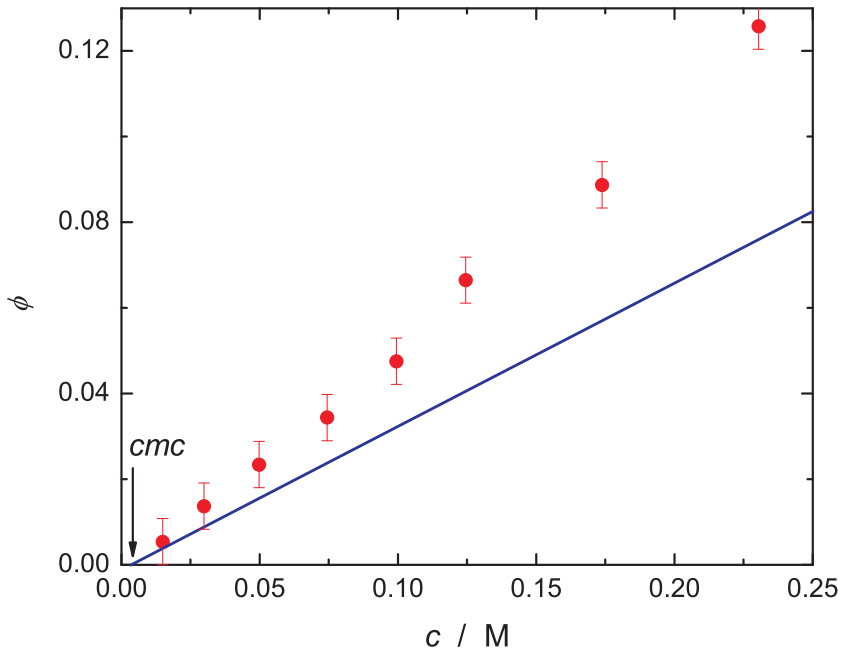

Figure S15: Effective volume fraction, ϕ, of $[C_{12}MIM]OTf$ micelles in aqueous solution calculated from the Grosse radius, R_G (solid line), and from the bulk water amplitude, S_b (●).

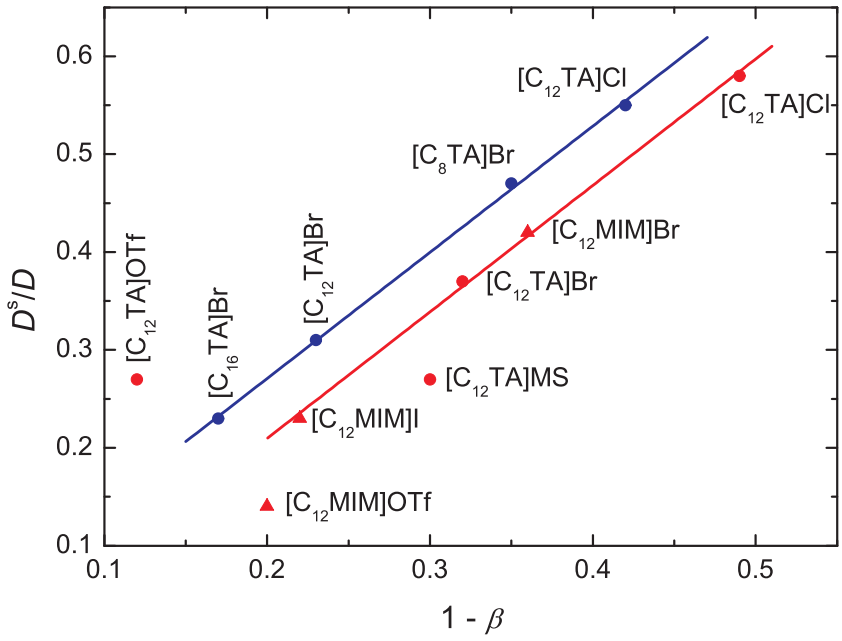

Figure S16: Relative surface diffusion coefficient of condensed counterions, D^S/D, as a function of the degree of counterion dissociation, $1-\beta$, for $[C_nTA]X$ (●)[S2,S3] and $[C_{12}MIM]X$ (▲, this work) surfactants at 25 (blue; $[C_{16}TA]Br$: 28 °C) and 45 °C (red). The lines are a guide to the eye.

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