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

Electronic Supporting Information

Urea hydration from dielectric relaxation spectroscopy: old findings confirmed, new insights gained

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Supporting tables and figures

Table S1. Densities, d, molarities, c, and viscosities, η, of aqueous urea solutions at solute molalities, m, and temperatures of (5, 25 & 45) °C.

m / mol kg^{-1}	d / g cm^{-3}	c / M	$\eta \cdot 10^3$ / Pa s
	5 °C		
1.999	1.03151	1.841	1.600
6.001	1.07834	4.757	1.853
11.995	1.12500	7.844	2.368
	25 °C		
0.100	0.99865	0.099	0.888
0.250	1.00099	0.247	0.897
0.500	1.00482	0.488	0.905
0.998	1.01215	0.953	0.921
1.999	1.02586	1.831	0.957
3.998	1.04963	3.384	1.045
6.001	1.06963	4.718	1.135
9.000	1.09423	6.393	1.287
11.995	1.11408	7.768	1.442
15.006	1.13048	8.923	1.616
17.994	1.14411	9.894	1.794
	45 °C		
1.999	1.01739	1.816	0.653
6.001	1.05920	4.672	0.776
11.995	1.10211	7.684	0.985

Table S2. Amplitudes, S_j, and relaxation times, τ_j / ps, of the resolved modes, j = 1…3; static and high-frequency permittivity limits, ε_s and ε_∞, and reduced error function, χ^2, obtained as a function of solute molality, m, for the dielectric spectra of urea in water at (5, 25 and 45) °C.

m / mol kg^{-1}	S_1	S_2	S_3	τ_1	τ_2	τ_3	ε_s	ε_∞	$\chi^2 \cdot 10^3$
				5 °C					
1.999	21.67	62.90	2.26	31.4	14.1	1.34	91.57	4.74	43
6.001	45.11	46.10	2.09	37.8	13.9	1.29	98.91	5.61	39
11.995	63.37	32.99	3.10	47.3	14.5	1.18	104.78	5.33	42
				25 °C					
0.100	0.54	71.78	4.03	18.9*	8.45	0.54	78.73	2.38	11
0.250	2.16	70.83	3.15	19.1*	8.38	0.29	79.19	3.04	20
0.500	3.63	69.01	1.85	19.3*	8.56	1.78	79.74	5.25	25
0.998	8.06	65.97	5.86	19.7*	8.60	0.56	81.24	1.34	25
1.999	15.52	60.55	2.91	20.4	8.60	0.94	83.51	4.52	39
3.998	26.93	51.40	3.27	22.4	8.91	1.55	86.83	5.23	35
6.001	36.40	46.13	3.71	24.0	9.01	0.90	90.54	4.29	14
9.000	47.33	38.17	4.44	26.4	9.33	0.88	93.94	3.99	18
11.995	55.05	32.49	2.90	29.0	9.74	1.59	96.41	5.98	15
15.006	61.40	27.85	2.37	31.5	9.84	1.72	98.13	6.50	15
17.994	65.46	25.03	4.15	34.1	10.2	0.92	99.34	4.70	20
				45 °C					
1.999	15.94	54.04	2.63*	13.2	5.43	0.17*	76.24	3.63	24
6.001	34.18	41.22	2.63*	15.9	5.92	0.17*	82.51	4.48	58
11.995	45.26	33.75	2.63*	20.3	7.81	0.17*	88.27	6.63	82

* Parameter fixed in fit procedure

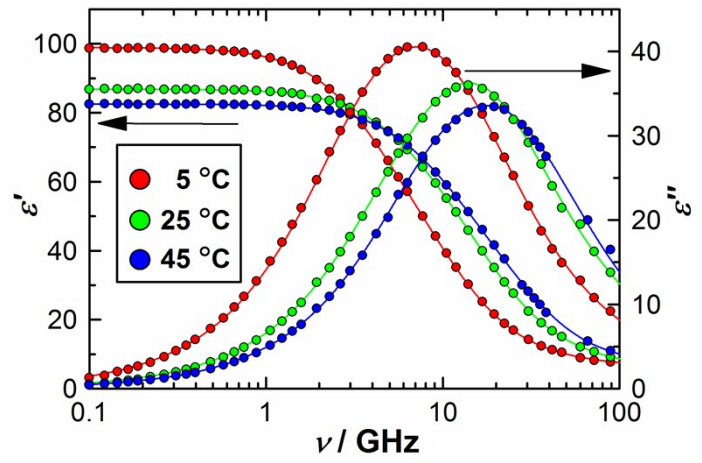

Fig. S1. Relative permittivity, ε', and dielectric loss, ε'', spectra of a solution of 6.0 mol kg^{-1} urea in water at (5, 25 and 45) °C. Symbols correspond to the experimental data, lines show to the fits with the 3D model. The arrows address the curves to appropriate axes.

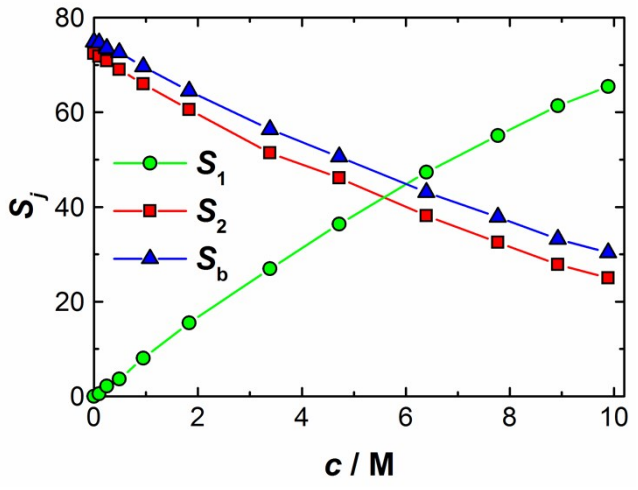

Fig. S2. Amplitudes of the solute mode, S_1, and the α-relaxation of water, S_2, as a function of urea concentration, c, at 25 °C. Also shown is the total amplitude of bulk-like water, $S_b(c) = S_2(c) + S_3(c) + \varepsilon_\infty(c) - \varepsilon_\infty(0)$.

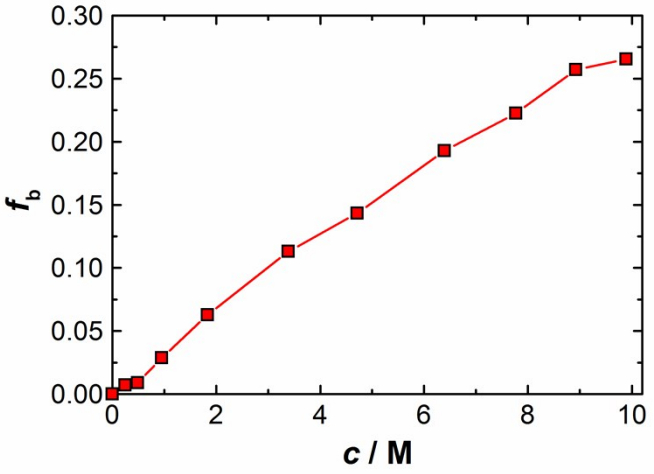

Fig. S3. Fraction, $f_b = c_b / c_w$, of the solvent not contributing to the amplitude of bulk-like water at 25 °C.