

Electronic Supplementary Information for

Ion association in aqueous and non-aqueous solutions probed by diffusion and electrophoretic NMR

*Marianne Giesecke^a, Guillaume Mériguet^{b,c},
Fredrik Hallberg^a, Yuan Fang^a, Peter Stilbs^a, and István Furo^{a*}*

^aDivision of Applied Physical Chemistry, Department of Chemistry, KTH Royal Institute of
Technology, SE-10044 Stockholm, Sweden

^bSorbonne Universités, UPMC Université Pierre et Marie Curie Paris 06, UMR 8234
PHENIX, F-75005, Paris, France and ^cCNRS, UMR 8234,
PHENIX, F-75005, Paris, France

*Corresponding author, E-mail: furo@kth.se

eNMR measurements with varied water concentration

Additional eNMR experiments were performed in order to investigate the effect of the added water in all samples. The samples consisted of 2 mM tetramethylammonium bromide dissolved in either d₆-DMSO, d₃-acetonitrile, and d₆-ethanol.

The water concentration in the solutions prepared without added water was estimated from ¹H NMR spectral integrals of the TMA⁺ and solvent signals as well as HDO signal. The deuterated solvent did not contain any D₂O, as was verified by the ²H NMR spectra of the solvents. The salt was vacuum-dried overnight to keep the initial water content as low as possible. The effective charge of the TMA⁺ ion was measured by eNMR and diffusion NMR as detailed in the main text. Then, the experiments were repeated but this time after having adjusted the water concentration to 120 ± 20 mM as used in all experiments. The obtained differences between nominal and effective charges are summarized in Table S1 below; corresponding more extensive data for d₄-methanol are in the main text, see Fig. 5. As is

clear, the effect of the added water on the obtained charge difference is small, within the experimental error.

Solvent name	p of TMA ⁺ without added water (solvent as purchased, water concentration indicated in parenthesis)	p of TMA ⁺ with added water (120 ± 20 mM)
d6-dimethylsulfoxide	0 (55 mM)	0.01
d3-acetonitrile	0.08 (21 mM)	0.08
d6-ethanol	0.13 (1.2 mM)	0.15

Table S1.

The obtained diffusion coefficients and electrophoretic mobilities for the TMA cation, TMA⁺, in the studied samples

Solvent	Anion	D ($10^{-11} \text{ m}^2 \text{ s}^{-1}$) ¹	μ ($10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$) ²
D ₂ O (2 mM)	SO ₄ ²⁻	100.8	3.90
	F ⁻	100.0	3.86
	Ac ⁻	101.9	4.10
	Cl ⁻	102.7±1.42	3.96±0.065
	Br ⁻	103.2	3.92
	NO ₃ ⁻	100.9	3.95
	I ⁻	102.7	3.88
	ClO ₄ ⁻	101.8	3.85
d6-dimethylsulfoxide	Ac ⁻	43.2	1.76
	Cl ⁻	43.8±0.23	1.68±0.036
	Br ⁻	44.4	1.71
	NO ₃ ⁻	42.9	1.63
	I ⁻	43.9	1.73
d3-acetonitrile	F ⁻	228.0	8.32
	Ac ⁻	226.4	8.30
	Cl ⁻	229.0±0.00	8.23±0.024
	Br ⁻	231.6	8.29
	NO ₃ ⁻	234.4	8.55
	I ⁻	234.6	8.54
	ClO ₄ ⁻	230.7	8.70
d4-methanol	SO ₄ ²⁻	145.3	4.74
	F ⁻	159.4	6.36
	Ac ⁻	166.3	6.30
	Cl ⁻	156.8±2.71	6.15±0.078
	Br ⁻	162.2	6.06
	NO ₃ ⁻	161.4	6.14
	I ⁻	157.3	6.18
	ClO ₄ ⁻	160.0	6.09
	SO ₄ ²⁻	54.5	1.13

d6-ethanol	F ⁻	67.4	2.41
	Ac ⁻	66.9	2.35
	Cl ⁻	66.3±0.16	2.21±0.02
	Br ⁻	67.8	2.25
	NO ₃ ⁻	66.5	2.27
D ₂ O (10 mM)	SO ₄ ²⁻	100.4	3.53
	F ⁻	98.3	3.66
	Ac ⁻	95.2	3.60
	Cl ⁻	97.7	3.68
	Br ⁻	99.5	3.59
	NO ₃ ⁻	97.8	3.72
	I ⁻	98.9	3.58
	ClO ₄ ⁻	97.8	3.64

Table S2.

¹The diffusion experiments were measured at 298.95 K.

²The eNMR measurement was performed at 299.05 K. As previously mentioned, in the calculation of p (see Fig. 1), the measured diffusion coefficients were adjusted to 299.05 K using the known dependences of viscosity of the solvents. Note also that this dependence can be used to calculate the diffusion coefficient at 298.15 in order to compare it to the predicted value using Eq. (4).