Supporting information

for

Binding of Monovalent and Multivalent Metal Cations to Polyethylene Oxide in Methanol Probed by Electrophoretic and Diffusion NMR

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The obtained diffusion coefficients and electrophoretic mobilities

From repeated experiments, we can estimate that the error of the obtained self-diffusion coefficients D at 2 mM PEO concentration was better than ±1 %. Since the diffusion coefficient is roughly the same irrespective of the added salt, this figure is invariant over the samples. On the other hand, the error of the electrophoretic mobilities μ was *ca* ±0.8×10^{-9} m^2 V^{-1} s^{-1}. Hence, even at the highest observed electrophoretic mobilities, the relative contribution of error (*ca* ± 5%) in the derived effective charges z_{PEO} (see Fig. 2 in the main text) is dominantly from the eNMR measurements. Hence, the error of z_{PEO} is approximately ±0.25 (that is, in units of elementary charge). The binding constant K was calculated as given by Eq. (5) in the main text.

Table S1. The obtained diffusion coefficients, electrophoretic mobilities and binding constants (see Eq. 5) at equimolar 2 mM concentrations of EO units and salt.

Anion	Cation	D_{PEO} (10^{-11} m^2 s^{-1})	μ_{PEO} (10^{-9} m^2 V^{-1} s^{-1})	K (M^{-1})
	Li$^+$	8.81	-0.1	-
	Na$^+$	8.72	8.0	14
	K$^+$	7.89	16.8	35
	Rb$^+$	7.87	17.0	35
	Cs$^+$	8.06	14.3	29
	Mg^{2+}	9.03	1.1	0.8

ClO_4^-	Zn^{2+}	8.48	1.0	0.8
	Cd^{2+}	8.46	0.4	0.4
	Ca^{2+}	9.02	-0.3	-
	Ba^{2+}	8.63	22.8	21
	Al^{3+}	8.79	2.5	1
	Sc^{3+}	8.57	1.3	0.7
I^-	Li^+	8.53	1.0	2
	K^+	7.67	18.4	40
	Cs^+	7.76	16.9	36
	Ca^{2+}	8.34	0.3	0.2
	Ba^{2+}	7.47	21.4	23
CH_3COO^-	Li^+	8.33	0.8	2
	K^+	7.53	16.5	36
	Cs^+	7.53	17.5	38
	Ca^{2+}	8.39	0.3	0.3
	Ba^{2+}	7.69	18.4	19

Table S2. The obtained diffusion coefficients, electrophoretic mobilities and binding constants at c_{PEO} = 0.5 mM and c_{PEO} = 2 mM concentrations and at different salt concentrations c_{salt}. The anion was ClO_4^-.

c_{PEO}	Cation	D_{PEO} $(10^{-11}\,m^2\,s^{-1})$	μ_{PEO} $(10^{-9}\,m^2\,V^{-1}\,s^{-1})$	z_{PEO}	$K\,(M^{-1})$
0.5 mM	K^+ 0.5 mM	8.19	16.7	5.2	135
	K^+ 2 mM	7.82	20.9	6.8	45
	K^+ 6 mM	8.26	22.4	6.5	14
	Ca^{2+} 0.5 mM	8.68	0.7	0.2	3
	Ba^{2+} 0.5 mM	7.75	18.5	6.1	77
	Ba^{2+} 2 mM	7.44	20.7	7.1	22
	Ba^{2+} 6 mM	16.2	19.7	3.1	3
	Al^{3+} 0.5 mM	8.37	0.7	0.2	2
2 mM	K^+ 0.5 mM	8.30	16.8	5.2	139
	K^+ 2 mM	7.89	16.8	6.8	34
	K^+ 6 mM	8.23	20.7	6.5	14
	Ba^{2+} 0.5 mM	8.13	19.5	6.1	78
	Ba^{2+} 2 mM	8.63	22.8	6.7	21
	Ba^{2+} 6 mM	17.4	19.0	2.8	3

eNMR measurements with and without a small amount of added water

Additional eNMR experiments were performed in order to investigate the effect of the added water in all samples. Specifically, we investigated if the presence of a small amount of water has any detectable influence on the derived effective charges. The samples studied had the following composition: 100 mM mc PEO with 2 mM salt where the salt was either lithium perchlorate ($LiClO_4$), potassium perchlorate ($KClO_4$) and barium perchlorate ($Ba(ClO_4)_2$) in d4-MeOH. The concentration of 100 mM mc PEO was chosen in order to have a more comparable PEO (mc) to water concentration, making the experiment more sensitive to any possible water effect. The water concentration was measured in a ^1H 1D NMR experiment using the integrals of the PEO, methyl group of MeOH as well as HDO signals. The deuterated solvent did not contain any D_2O, as was verified by a ^2H NMR 1D spectrum of the solvent.

The salts and PEO were dried under vacuum for at least 48 hours to keep the initial water content as low as possible. The effective charge of PEO was measured by eNMR. Then, the experiments were repeated but this time adjusting the water concentration to 120 ± 20 mM. The results are summarized below in Table S3 and show that the minute amount of water in our samples has no significant influence on the observed effective charge and thereby on the ion binding.

Table S3. The effective charge obtained at different water contents.

Salt name	z_{PEO} (without added water, the estimated water concentration in parenthesis)	z_{PEO} (with added water, water concentration at 120 ± 20 mM)
$LiClO_4$	0.1 (22 mM)	0.0
$KClO_4$	3.6 (9 mM)	3.7
$Ba(ClO_4)_2$	4.5 (19 mM)	4.8

Solution parameters and results of fits of theoretical expressions

Table S4. The Bjerrum length l_B and the Debye screening length κ^{-1} in methanol[1] at various local and bulk salt concentrations and the rate constant λ of exponential decays fitted to the concentration-dependent binding-constant data.

	l_B (nm)	κ^{-1} (nm)[a]	κ^{-1} (nm)[b]	λ (nm)[c]
monovalent	1.72	1.87	4.39	9.2
divalent	6.86	1.66	2.53	6.2
trivalent	15.4	1.42	1.79	-

[a]calculated for local concentration of 20 mM anion and 2 mM cation.

[b]calculated for concentration of 2 mM cation and electroneutral amount of anions.

[c]The exponent obtained by fitting the equation[2-3] $K = K_0 \exp(-\lambda\kappa)$ to the binding-constant data presented in Fig. 3, see Eq. 6.

1.   Hunter, R. J. *Foundations of Colloid Science*; Oxford Univ. Press: Oxford, 2001.
2.   Hakem, I. F.; Lal, J. Polyelectrolyte-like behaviour of poly(ethylene-oxide) solutions with added monovalent salt. *Europhys. Lett.* **2003,** *64*, 204-210.
3.   Hakem, I. F.; Lal, J.; Bockstaller, M. R. Binding of Monovalent Ions to PEO in Solution: Relevant Parameters and Structural Transitions. *Macromolecules* **2004,** *37*, 8431-8440.