SUPPLEMENTARY MATERIAL

Specific ion effects for polyelectrolytes in aqueous and non-aqueous media: the importance of the ion solvation behavior

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I. DERIVATIVES OF CHEMICAL ACTIVITY FOR DIFFERENT SALTS IN METHANOL AND DMAC

In order to determine the derivatives of the chemical activity for distinct ion combinations, we ran independent simulations for simple salts (NPT ensemble: Parrinello-Rahman barostat and Nose-Hoover thermostat with $T = 300$ K and $p = 1$ bar, initial box volume $V = (4\times4\times4)$ nm^3) at 1 mol/L concentration in solvents DMAc and methanol. The derivative of the chemical activity for ions within the indistinguishable ion approach can be evaluated by[1–7]

$$a_{II} = \frac{1}{1+\rho_I(G_{II}+G_{IS})} \tag{1}$$

where ρ_I denotes the salt number density, and G_{IS} and G_{SS} the corresponding Kirkwood-Buff integrals

$$G_{ij} = 4\pi\rho_j \int_0^\infty r^2 \left[g_{ij}-1\right] \mathrm{d}r \tag{2}$$

for indistinguishable ions (I) and solvent molecules (S). More information on the Kirkwood-Buff theory and on the derivative of the chemical activity can be found in the above mentioned references. The corresponding results for alkali metal cations in combination with chloride ions and halide anions in combination with sodium ions for methanol and DMAc are shown in Fig. 1. As it was discussed in Ref. 1, the values of a_{II} are directly related to the solubility of the salt, and thus in qualitative agreement with solubility data for LiCl, NaCl and KCl in methanol[8].

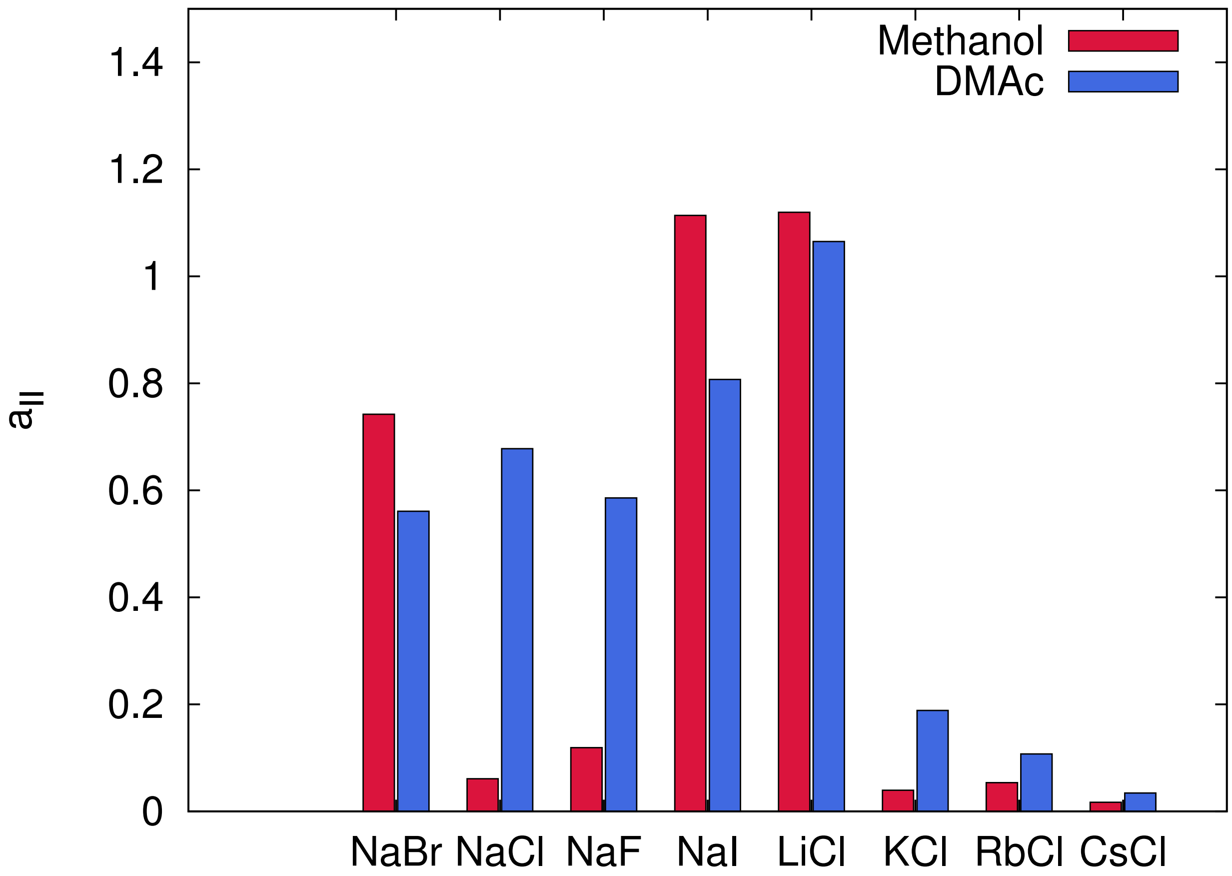


Figure 1: Derivative of the chemical activity a_{II} for different salts in methanol and DMAc.

II. FRACTION OF CONDENSED COUNTERIONS AT BJERRUM LENGTH AND AT MANNING RADIUS

Table I: Fraction of condensed counterions at Bjerrum length $Q^{\mathrm{M}}(\lambda_B)$ and at the Manning radius $Q^{\mathrm{M}}(R_{\mathrm{M}})$ in water. The Manning radius was calculated in accordance with Ref. 9.

Value	Li^+	Na^+	K^+	Rb^+	Cs^+	F^-	Cl^-	Br^-	I^-
$Q^{\mathrm{M}}(\lambda_B)$	0.72	0.91	0.83	0.82	0.76	0.48	0.39	0.35	0.28
$Q^{\mathrm{M}}(R_{\mathrm{M}})$	0.72	0.91	0.84	0.83	0.76	0.60	0.46	0.46	0.41

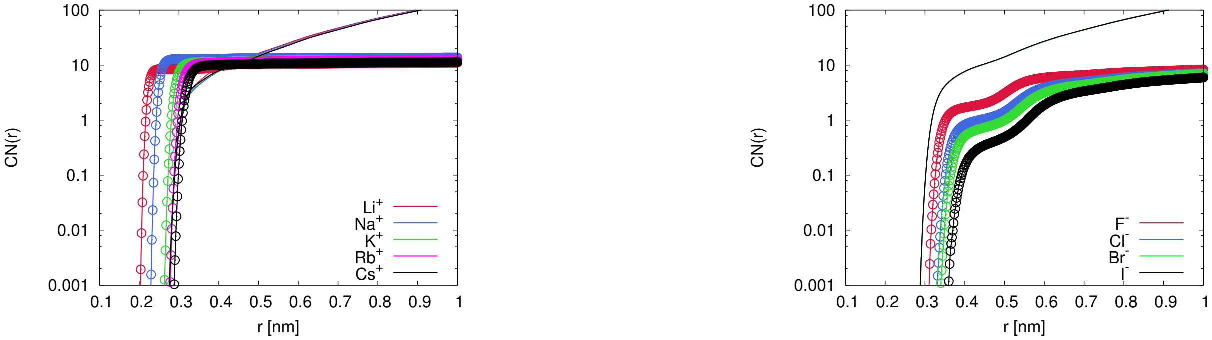
Table II: Fraction of condensed counterions at Bjerrum length $Q^{\mathrm{M}}(\lambda_B)$ and at the Manning radius $Q^{\mathrm{M}}(R_{\mathrm{M}})$ in methanol. The Manning radius was calculated in accordance with Ref. 9.

Value	Li^+	Na^+	K^+	Rb^+	Cs^+	F^-	Cl^-	Br^-	I^-
$Q^{\mathrm{M}}(\lambda_B)$	0.98	0.95	0.98	0.98	0.98	0.87	0.88	0.83	0.81
$Q^{\mathrm{M}}(R_{\mathrm{M}})$	0.99	0.96	0.98	0.98	0.99	0.89	0.90	0.86	0.84

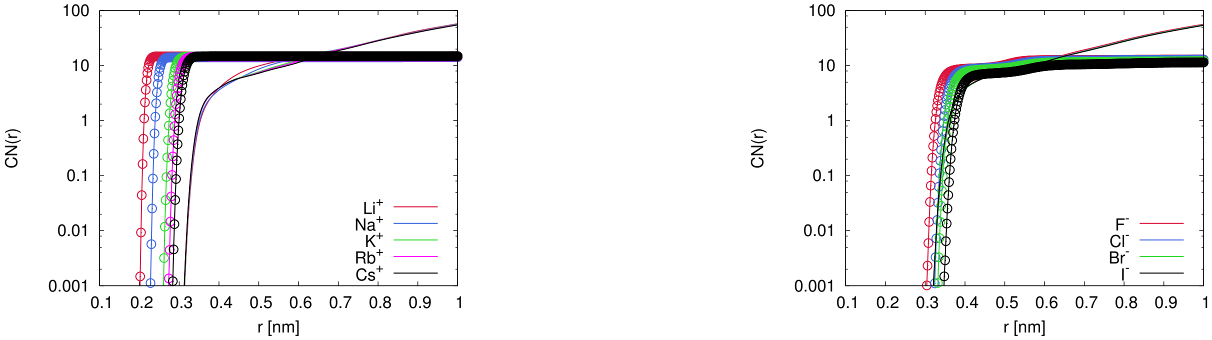
Table III: Fraction of condensed counterions at Bjerrum length $Q^{\mathrm{M}}(\lambda_B)$ and at the Manning radius $Q^{\mathrm{M}}(R_{\mathrm{M}})$ in DMAc. The Manning radius was calculated in accordance with Ref. 9.

Value	Li^+	Na^+	K^+	Rb^+	Cs^+	F^-	Cl^-	Br^-	I^-
$Q^{\mathrm{M}}(\lambda_B)$	0.65	0.59	0.62	0.59	0.67	0.90	0.83	0.82	0.73
$Q^{\mathrm{M}}(R_{\mathrm{M}})$	0.72	0.66	0.69	0.64	0.71	0.90	0.83	0.82	0.72

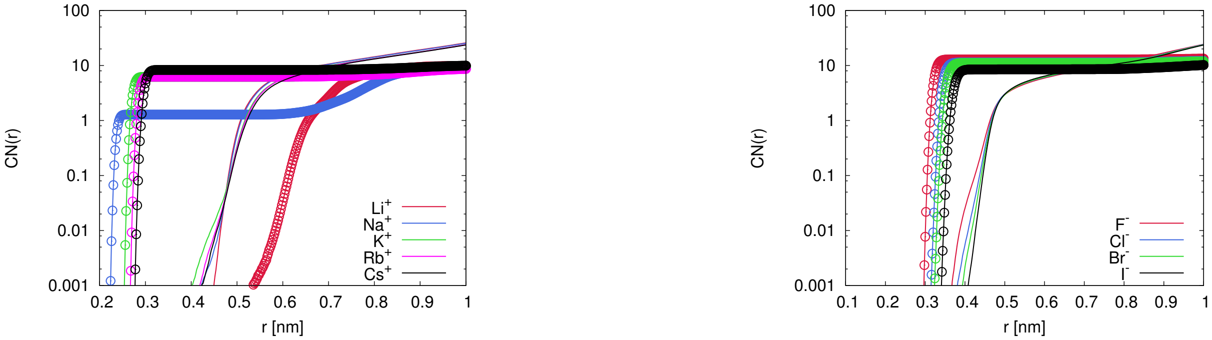
III. POLYION-SOLVENT AND POLYION-COUNTERION COORDINATION NUMBERS



(a) Water



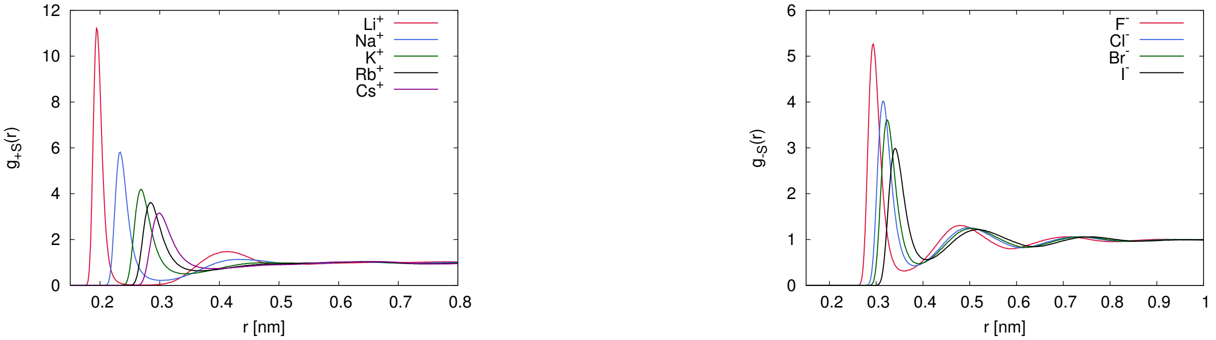
(b) Methanol



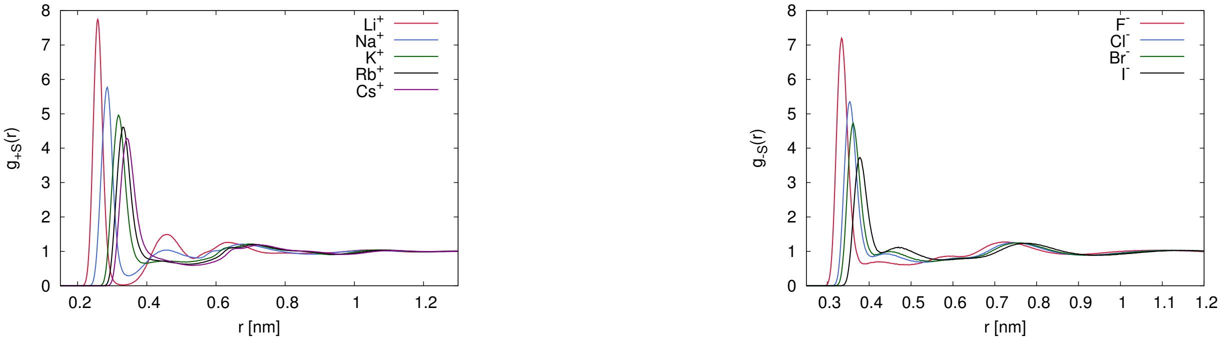
(c) DMAc

Figure 2: Coordination numbers CN(r) between polyion and solvents (solid lines) and between polyion and counterions (lines with datapoints). The left side shows the results for the cations and on the right side the results for the anions are presented. The results for water are shown in the top, methanol in the middle and DMAc in the bottom.

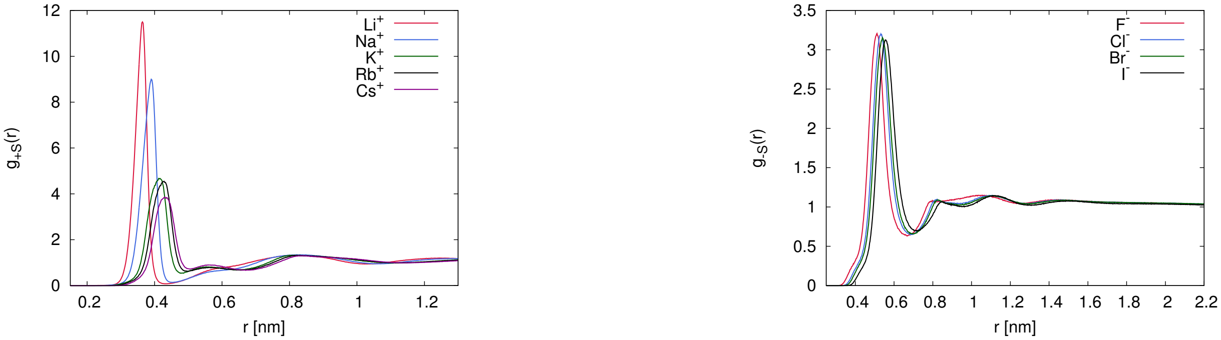
IV. RADIAL DISTRIBUTION FUNCTIONS BETWEEN IONS AND SOLVENT MOLECULES



(a) Water



(b) Methanol

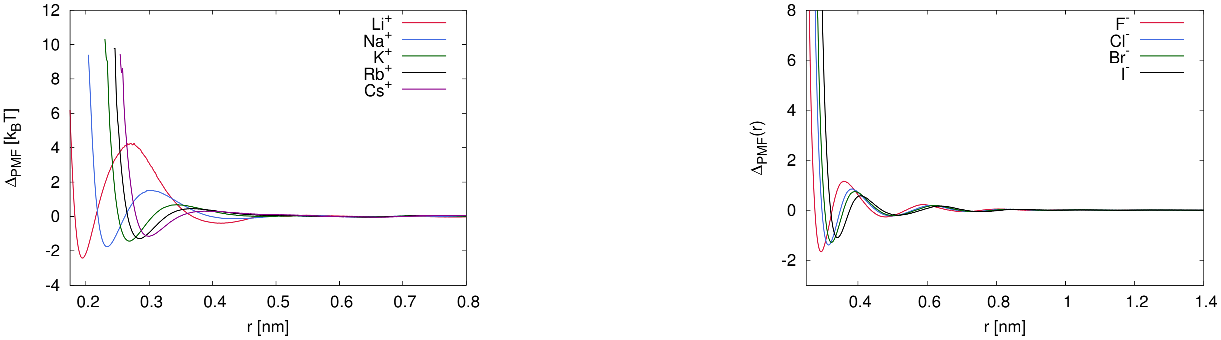


(c) DMAc

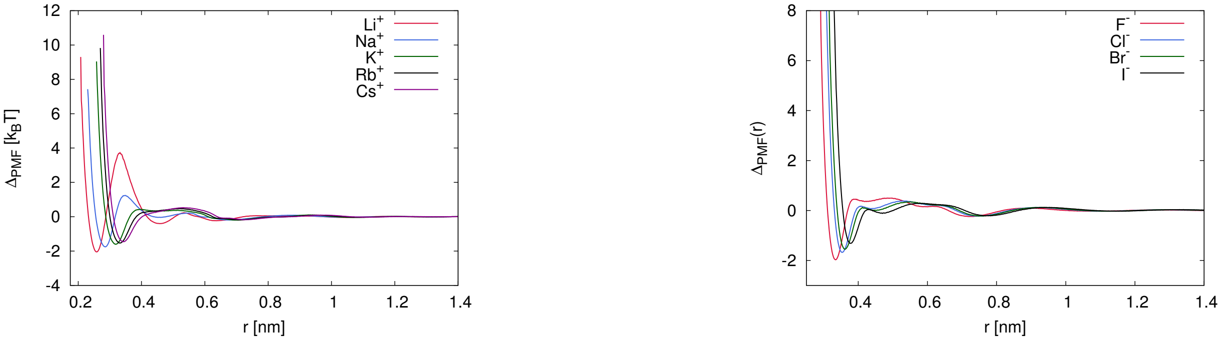
Figure 3: Radial distribution function $g_{\pm s}(r)$ between cations (left side) or anions (right side) and water molecules (top), methanol molecules (middle) and DMAc molecules (bottom).

V. POTENTIALS OF MEAN FORCE BETWEEN IONS AND SOLVENT MOLECULES

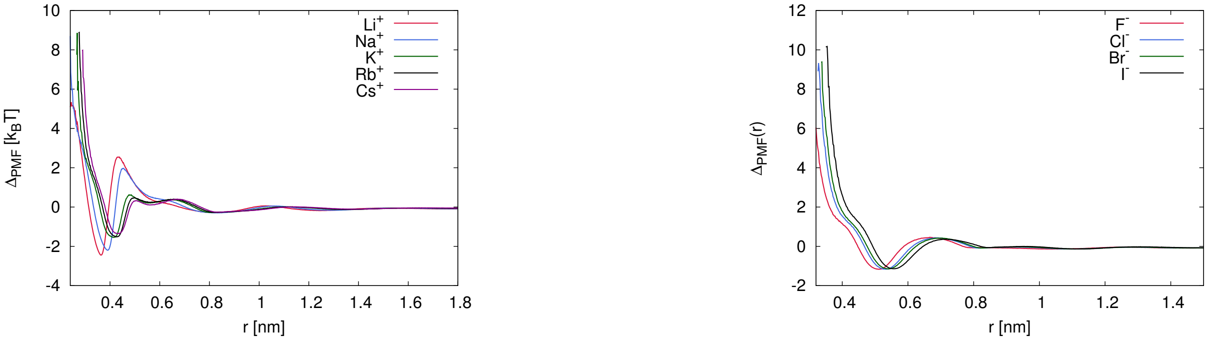
The potentials of mean force[10] are calculated by $\Delta_{\mathrm{PMF}}(r) = -k_B T \ln(g_{\pm s}(r)/g_{\pm s}(\infty))$ where $g_{\pm s}$ denotes the radial distribution function between ions and solvent molecules.



(a) Water



(b) Methanol



(c) DMAc

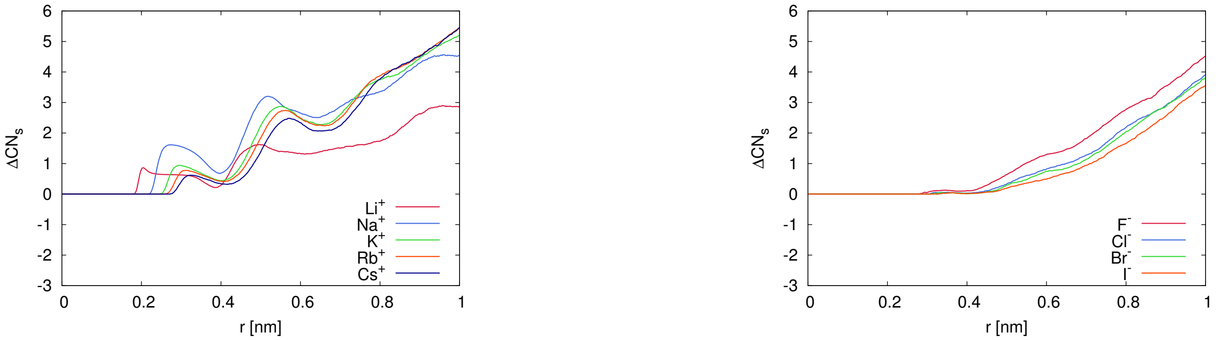
Figure 4: Potential of mean force $\Delta_{\mathrm{PMF}}(r)$ between cations (left side) or anions (right side) and water molecules (top), methanol molecules (middle) and DMAc molecules (bottom).

VI. DIFFERENCES IN THE SOLVENT COORDINATION NUMBER: INFLUENCE OF THE POLYELECTROLYTE

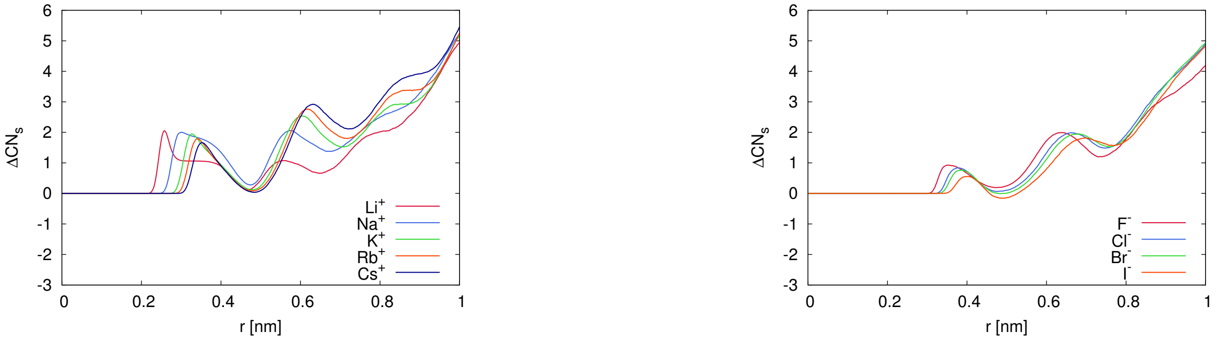
In order to study the influence of the polyelectrolyte on the solvation behavior of the ions, we also simulated all solvents with a single alkali cloride ion pair, and a single sodium halide ion pair, respectively. The position of the ions are fixed, which allows us to estimate the solvent coordination number around the alkali and the halide ions individually. The corresponding free ion-solvent coordination numbers $\mathrm{CN}_s^*(r)$ can be used to estimate the difference in the coordination numbers in accordance with

$$\Delta\mathrm{CN}_s(r) = \mathrm{CN}_s^*(r) - \mathrm{CN}_s(r), \tag{3}$$

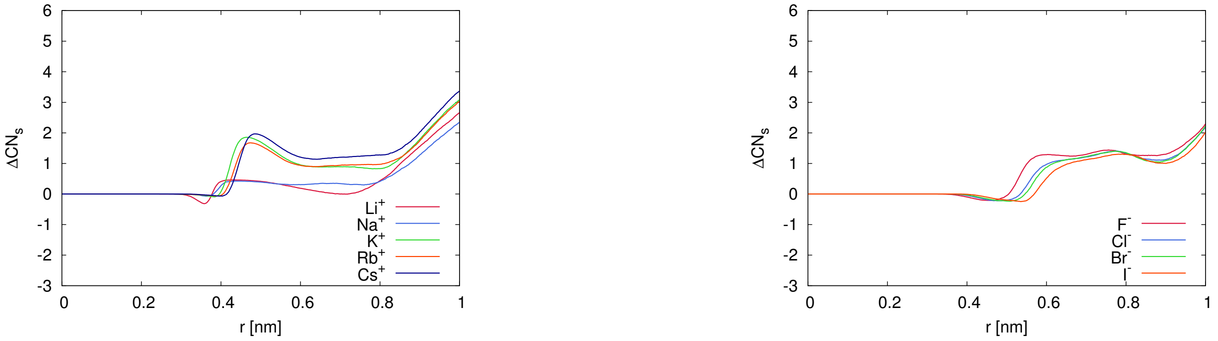
where $\mathrm{CN}_s(r)$ denotes the ion-solvent coordination number in presence of the polyelectrolyte. The corresponding results are shown in Fig. 5.



(a) Water



(b) Methanol



(c) DMAc

Figure 5: Differences in the ion-solvent coordination numbers $\Delta\mathrm{CN}_s(r)$ for cations (left side) or anions (right side) and water molecules (top), methanol molecules (middle) and DMAc molecules (bottom).

VII. TOTAL ENERGIES: ION-SOLVENT AND ION-POLYELECTROLYTE INTERACTIONS

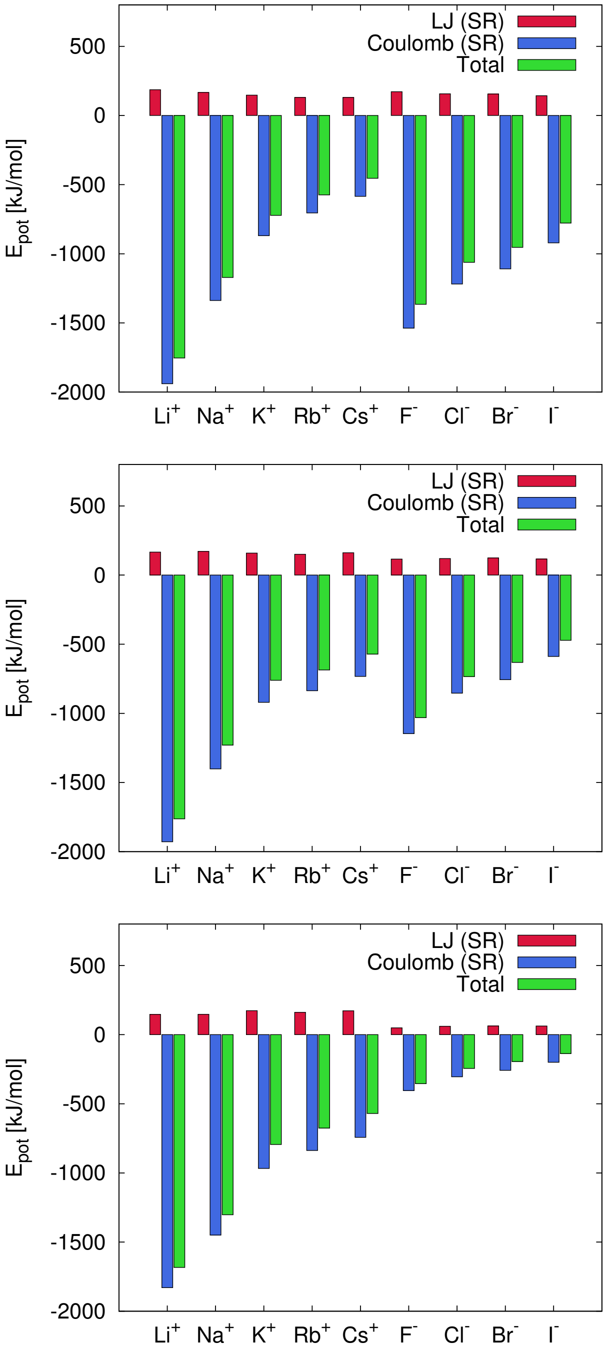


Figure 6: Sum of Lennard-Jones short-range (LJ (SR)) and Coulomb short-range (Coulomb (SR)) energies between ions and polyelectrolyte and ions and solvent in water (top), in methanol (middle) and in DMAc (bottom).

VIII. INTERACTION ENERGIES BETWEEN IONS

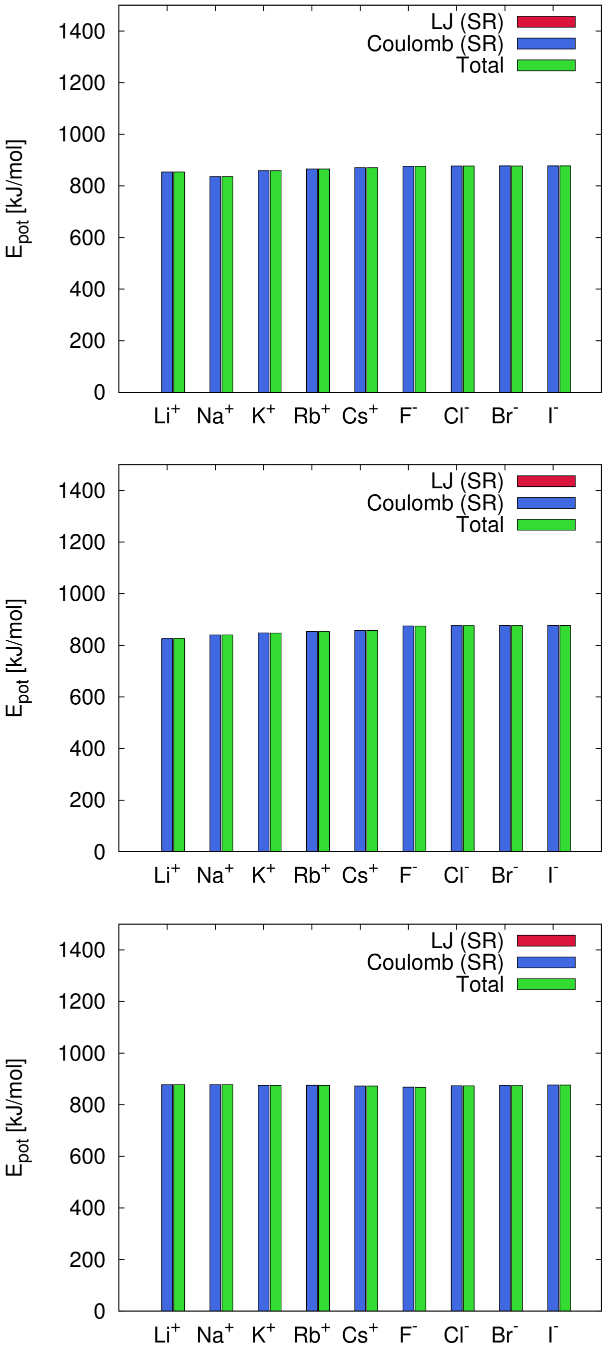


Figure 7: Lennard-Jones short-range (LJ (SR)) and Coulomb short-range (Coulomb (SR)) energies between ions in water (top), in methanol (middle) and in DMAc (bottom).

IX. INTERACTION ENERGIES BETWEEN SOLVENT MOLECULES

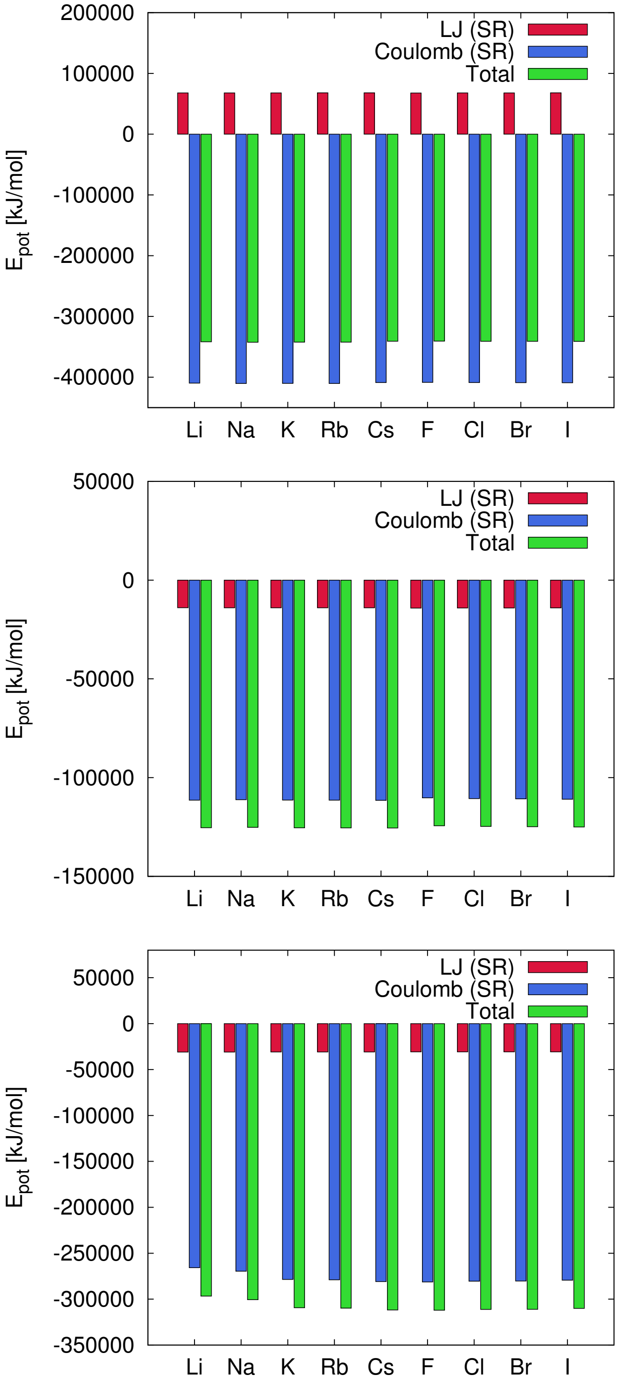


Figure 8: Lennard-Jones short-range (LJ (SR)) and Coulomb short-range (Coulomb (SR)) energies between water molecules (top), between methanol molecules (middle), and between DMAc molecules (bottom) in presence of the polyelectrolyte and the individual ions.

X. RATIO BETWEEN LJ AND ELECTROSTATIC ENERGIES INCLUDING ION-POLYELECTROLYTE AND ION-SOLVENT INTERACTIONS

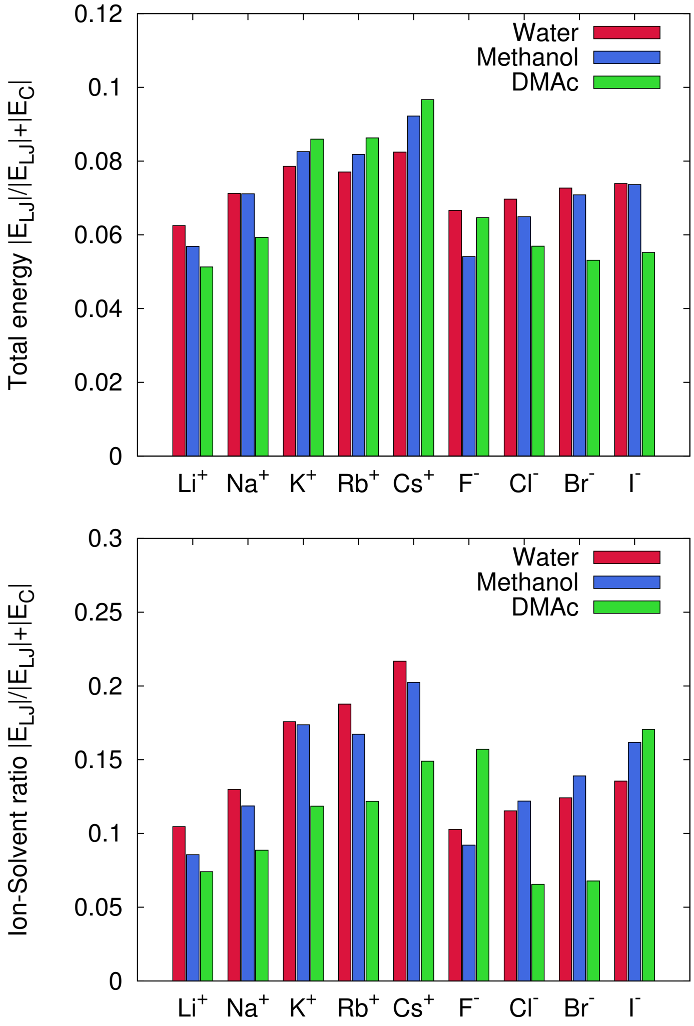


Figure 9: Ratio of Lennard-Jones to electrostatic interactions concerning the total interaction energy of the ions, including ion-solvent, and ion-polyelectrolyte interactions (top), and between the ions and the solvent molecules (bottom).

XI. ION DIAMETERS

Table IV: Diameters (taken from Ref. 2) for all ion species.

Ion	d_0 [nm]
Li^+	0.182
Na^+	0.245
K^+	0.334
Rb^+	0.362
Cs^+	0.413
F^-	0.370
Cl^-	0.440
Br^-	0.476
I^-	0.535

XII. CLOSEST CONTACT DISTANCE r_0 BETWEEN IONS AND POLYIONS

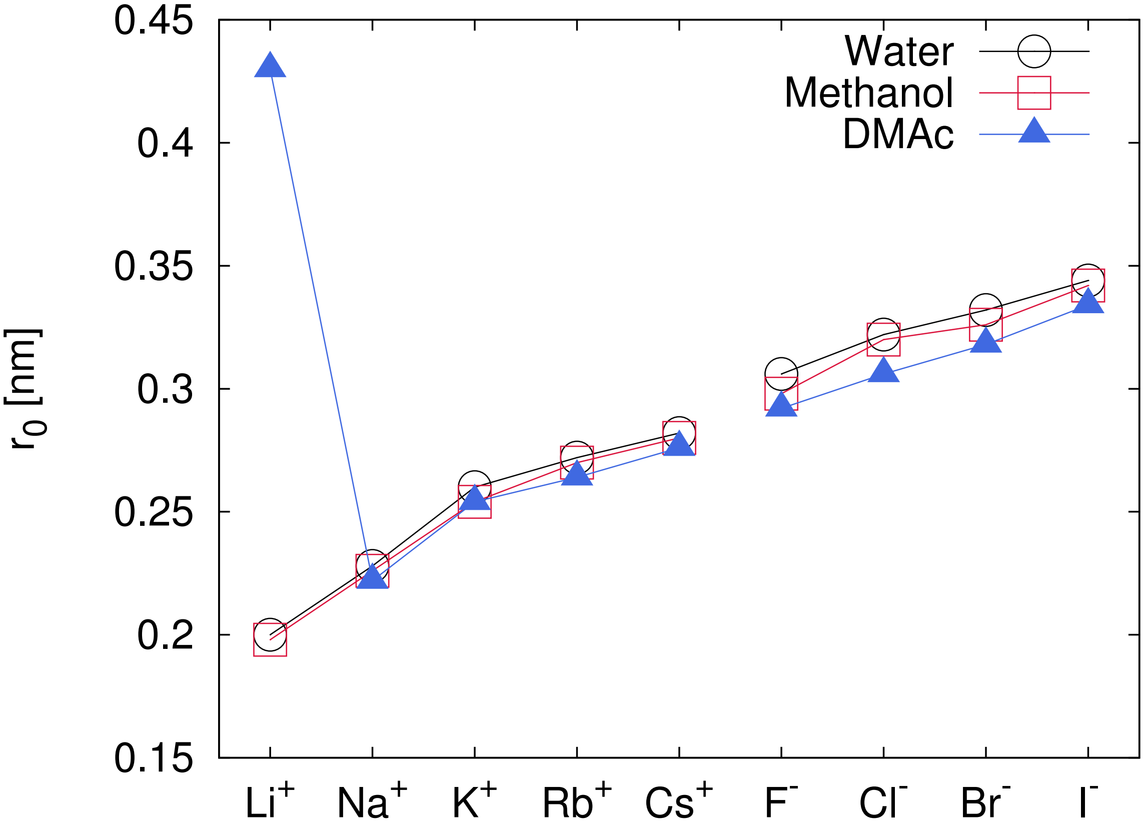


Figure 10: Closest contact distance r_0 (center of mass) between ions and polyions for all solvents and all ion species. The lines are just guides for the eyes.

XIII. CLOSEST CONTACT DISTANCE BETWEEN IONS AND SOLVENT MOLECULES

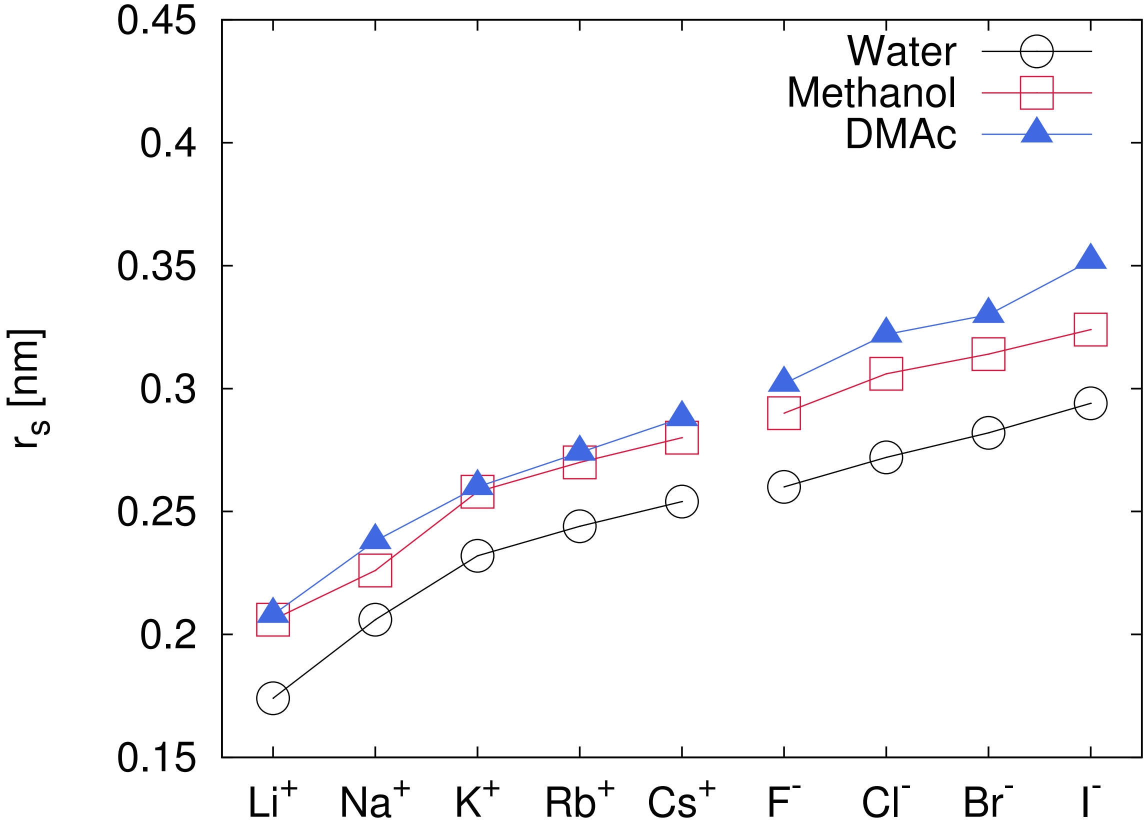


Figure 11: Closest contact distance r_s (center of mass) between ions and solvent molecules for all solvents and all ion species.

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