SUPPORTING INFORMATION:

Counting condensed ions around DNA with ASAXS

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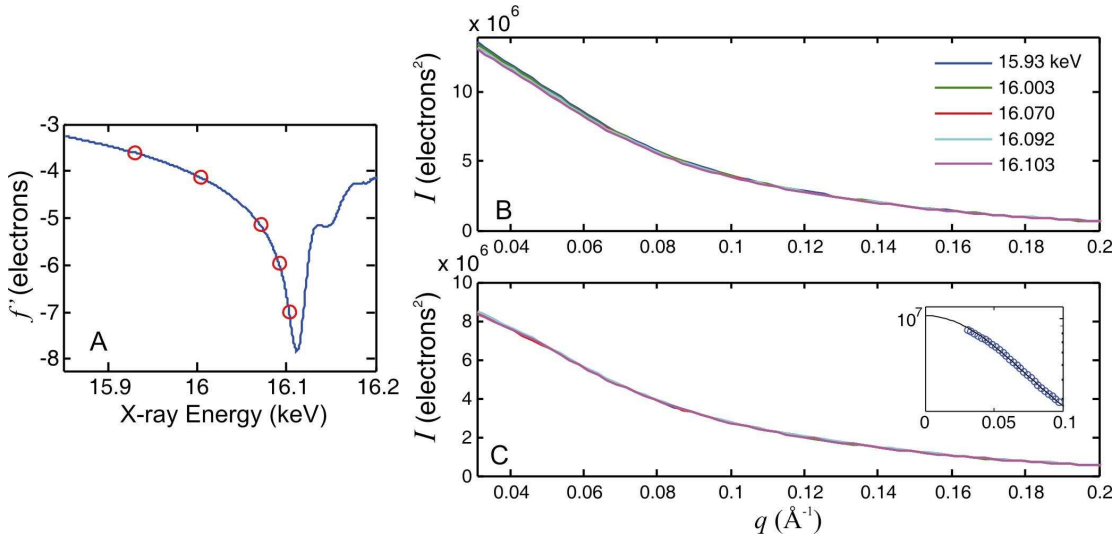

Figure S1: (A) Anomalous scattering factors for Sr^{2+} ions determined from CHOOCH. SAXS profiles of 0.2 mM DNA acquired at 5 energies just below the Sr edge (circled) are shown in (B) for 10 mM SrAcetate and (C) for 100 mM NaAcetate solutions. Only the Sr^{2+} containing solutions display an energy dependence. DNA in Rb^{+} exhibits the same behavior when probed at energies close to the Rb edge (not shown). Buffer-subtraction and correction for x-ray fluorescence and energy-dependent beamline component variations were performed as described previously[1]. SAXS data are normalized by scaling the scattering intensity at the zero-angle, $I(0)$, to the number of electrons squared (n_e^2) measured for the control samples using water as an intensity calibrant[2]. $I(0)$ is determined by extrapolation of I(q) to $q = 0$ using the program GNOM[3] (inset). Alternatively, a Guinier fit can be used to find $I(0)$.

The use of water as a calibration standard is described in detail in ref. 2. In brief, we measure the SAXS scattering profile of pure water (SAXS scattering profile of water subtracted by the scattering from the same sample holder, thoroughly air dried), extrapolate to $q = 0$, and compare with the DNA samples using the equation below:

$$I_{DNA}(q) = \frac{c_{H_2O}}{c_{DNA}} \cdot \frac{P_{H_2O}(0) \cdot S_{H_2O}(0)}{I^{Xn}_{H_2O}(0)} I^{Xn}_{DNA}(q)$$

The SAXS intensities, I^{Xn}, are normalized using the transmitted signal from the direct beam reflected by an amorphous beam stop to an X-flash counter (see ref. 1). $P_{H2O}(0)$ is the scattering form factor of water, $P_{H2O}(0) = 100$ electrons squared. $S_{H2O}(0)$ is the structure factor of water at $q = 0$ which is 0.062 at temperature of 23.4°C[2,4]. Concentrations of the water and DNA samples are indicated by c. Errors in the water calibration come from 2 major sources: (1) determination of nucleic acid concentrations using UV-VIS spectroscopy and (2) complications from semidilute interacting solutions of nucleic acids where the structure factor $S(q)$ is not equal to 1. In this case $I(q) = P(q) \cdot S(q)$ where $P(q)$, the scattering form factor of non-interacting dilute DNA solution, and the structure factor, $S(q)$, can both be determined experimentally[5]. For the case of DNA in 100 mM RbAcetate, we measure a structure factor of $S(0) = 0.89$. For DNA in 10 mM SrAcetate, $S(0) = 1$.

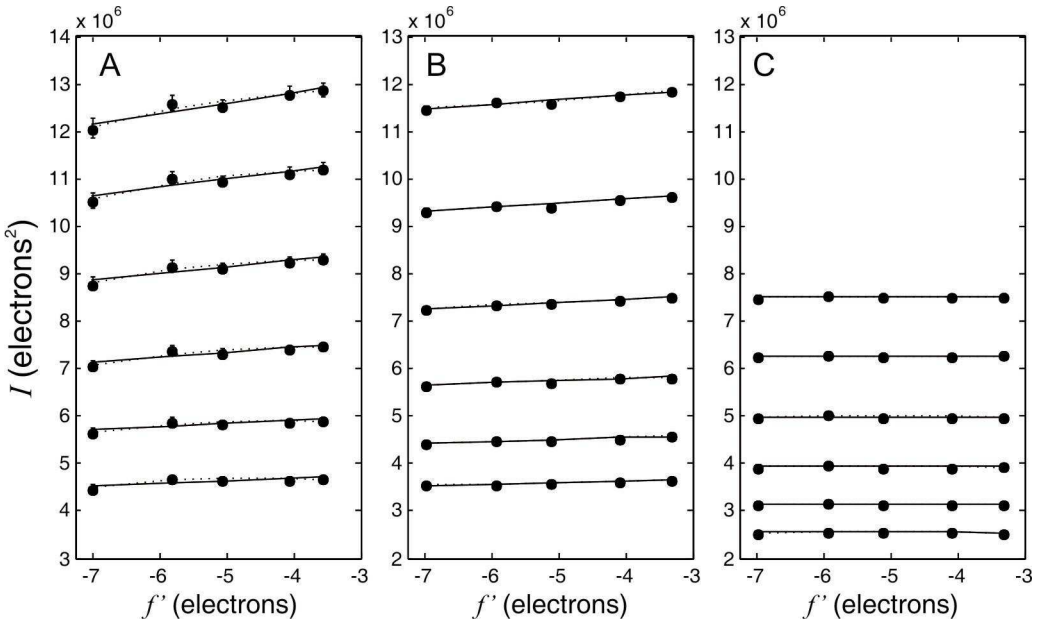

Figure S2: $I(f'(E))$ with respect to f' at different representative values of q for (A) DNA in 100 mM RbAcetate, with q = 0.031, 0.043, 0.055, 0.066, 0.078 and 0.090 Å^{-1} from top to bottom (B) DNA in 10 mM SrAcetate, (C) DNA in 100 mM NaAcetate. For (B) and (C), q = 0.041, 0.054, 0.066, 0.079, 0.092 and 0.105 Å^{-1} from top to bottom

Figure S2 shows that both linear (solid lines) and quadratic (dotted lines) functions fit the data well, with essentially the same χ-square values. For a nucleic acid-ion system, the linear fit using $I(q,f'(E)) = b(q)\cdot f' + c(q)$ best represent the data and a quadratic fit with 3 free parameters overfits the data and leads to non-physical $a(q)$ and $b(q)$ values. The interesting case of a light (less electron dense) polymer with heavy counterions has been previously considered by Ballauf and coworkers[6] use a similar energy-dependent decomposition to study ions around polyelectrolytes. Because of the relative magnitude of their scattering factors, they find a non-negligible $a(q)$ term.

References:

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