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The Charge Reduction Rate for Multiply Charged Polymer Ions via Ion-Ion Recombination at Atmospheric Pressure

Tomoya Tamadate[1], Hidenori Higashi[1,2], Christopher J. Hogan Jr.[3*], & Takafumi Seto[1,2*]

[1]Faculty of Natural System, Graduate School of Natural Science and Technology, Kanazawa University, Kanazawa, Japan
[2]Faculty of Frontier Engineering, Institute of Science and Engineering, Kanazawa University, Kanazawa, Japan
[3]Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN, USA

Supporting Information

[*]To whom correspondence should be address: Takafumi Seto: seto@t.kanazawa-u.ac.jp, Christopher J. Hogan: hogan108@umn.edu

Determination of the Limiting Sphere Radius

As noted in the main text, the limiting sphere radius needs to be sufficiently large to have no bearing on calculation results. Using Fuchs's formula[1] for the limiting sphere radius, we arrived at δ_{Fuchs}=352.2 Å for PEG_{4600}^{z+} and NO_2^- collisions. In previously studying recombination of singly charged ions, we found that use of δ_{Fuchs} as the limiting sphere radius was sufficient. However, as shown in Figure S1, $\delta > \delta_{Fuchs}$ was required in the present study. We obtain similar results for the $z = 2 - 7$ ions, and hence utilize $\delta = 5.0\delta_{Fuchs}$ for these charge states, while for $z = 1$ we utilize $\delta = 3.0\delta_{Fuchs}$

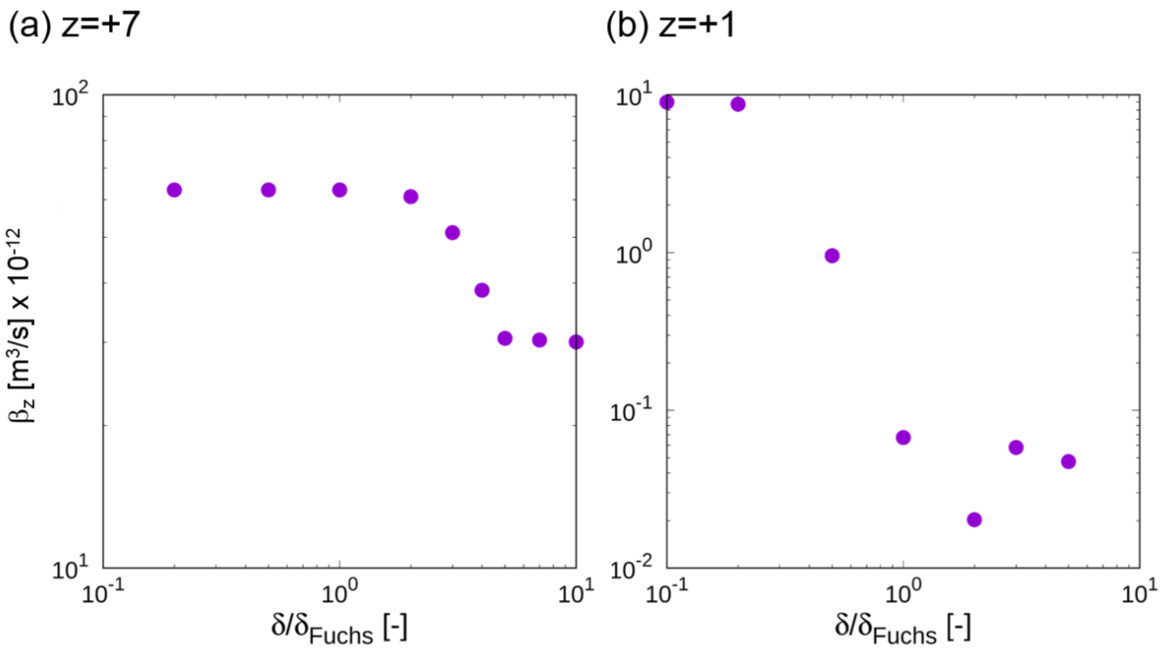

Figure S1. The recombination rate for **(a)** $z = 7$ and **(b)** $z = 1$ PEG_{4600}^{z+} ions as a function of the limiting sphere radius utilized in simulations.

Partial charges of atoms in PEG_{4600}^{z+} and NO_2^-

Table S1. Partial charges on atoms used in MD simulations.

Molecular type	Atom	Charge [-]
PEG (At chain end)	H on O	0.435
	O	-0.7
	C	0.145
	H on C	0.06
PEG (At middle of chain)	O	-0.4
	C	0.14
	H on C	0.03
NH_4^+	N	-0.8
	H	0.45
NO_2^-	N	0.046
	O	-0.523

Ion induced dipole potential

The ion-induced dipole potential (U_{ind}) between a unit charge and the center of an induced dipole is given by the equation:

$$U_{ind} = -\frac{\alpha e^2}{8\pi\varepsilon_0 r^4} \quad \text{(S1)}$$

where α is background gas molecule's polarizability (1.7 $Å^3$ for N_2), r is the distance between the gas molecule center and the charge, and the other parameters are defined in the main text. To implement this potential in MD simulations, the ion-gas molecule distance *r* was calculated from N_2 gas molecule and NH_4^+ (or NO_2^-) ion centers of mass ($r=r_{gas}-r_{ion,center}$). Then, the calculated potential, U_{ind}, was directly added to potential working on the N_2 molecule, while the product of the potential and mass ratio, $U_{ind}\frac{m_{atom}}{m_{ion}}$, was imparted to each atom within NH_4^+ and NO_2^- ions. While partial charges were applied to all atoms in PEG_{4600}^{z+}, partial charges where not considered in induced dipole calculations.

Measurement of the ion concentration generated from radioactive source

Ion concentration measurements in the mixing chamber were approximated using the experimental setup depicted in Figure S2. The experimental setup is similar to that depicted in Figure 2b, but with the electrospray ion source removed. At variable bipolar ion source flow rates (Q_{Am}) with constant total system flow rates, the concentration of ions upstream and downstream of the mixing chamber, $N_{ion,in}$ and $N_{ion,out}$, respectively were measured by an ion counter, similar in design to the ion trap described by Adachi et al.[2] Unsurprisingly, we observed that the concentration of ions decreased through the chamber due to deposition of ions on the chamber walls. Therefore, in comparing measurements to models, we utilized the logarithmic average of two ion concentrations ($N_{ion,in}$ and $N_{ion,out}$), with the formula used provided in Figure S2. The resulting mean ion concentrations, along with the inlet and outlet ion concentrations, are shown in lower left panel of Figure S2. The ion concentration increased with increasing flow rate through the ^{241}Am chamber, Q_{Am}.

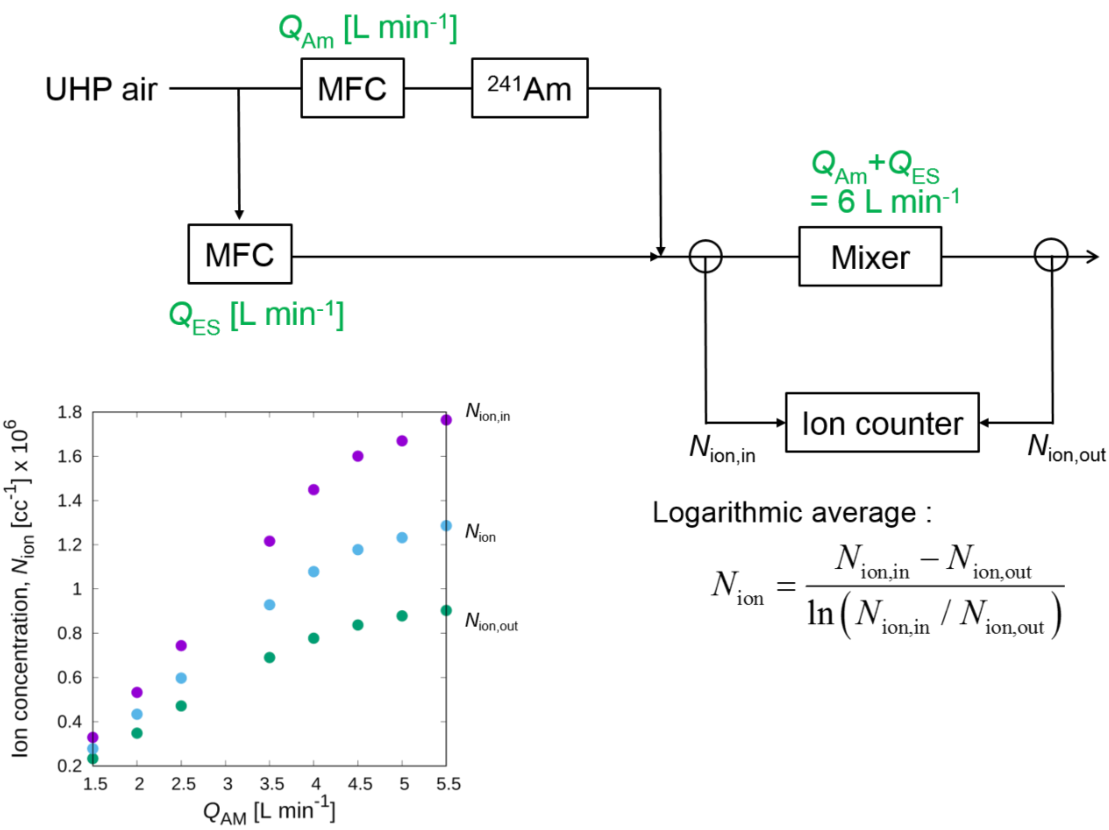

Figure S2. A schematic diagram of the experimental setup used in measurement of mean ion concentration in the mixing chamber. Measurement results are provided in the lower left.

Initial charge distribution of electrosprayed PEG_{4600}^{z+} ions

The mass-to-charge ratio distribution of PEG_{4600}^{z+} as electrosprayed is shown Figure S3. To obtain an initial charge distribution from this spectrum, we first estimated the mass distribution of the PEG_{4600} sample by fitting to the electrical mobility distribution of singly charged PEG ions. Fitting to this distribution is shown in Figure S4. Electrical mobility (Z_p) was converted to mass (M_w) using relationship, $Z_p^{-0.5} = 0.0936 M_w^{1/3} + 0.355$, established by Saucy et al.[3] Through fitting a mean $<M_w>$ = 4,339 Da and standard deviation of σ_s = 413 Da was obtained for the mass distribution. Second, using this mass distribution, we fit the mass-to-charge ratio distribution by a least squares method to determine the relative weightings of the distributions for different charge states (each distribution with mean $<M_w>/z$ and standard deviation σ_s/z). This resulted in an initial charge distribution with 0.421 at $z = 7$, 0.437 at $z = 6$, 0.069 at $z = 5$, 0.050 at $z = 4$ and 0.023 at $z = 3$.

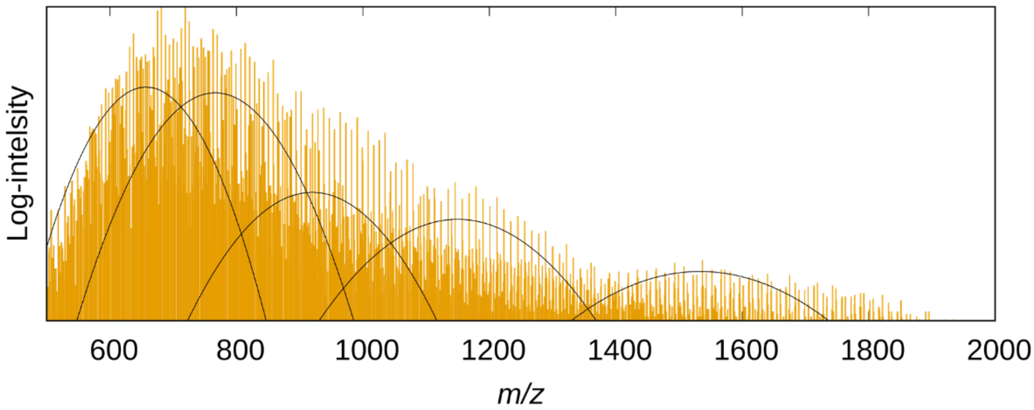

Figure S3. Mass-to-charge ratio distribution for PEG_{4600}^{z+} as electrosprayed. The fit distributions for different charge states are also depicted, with the $z = 7$ distribution occupying the lowest mass-to-charge ratio range.

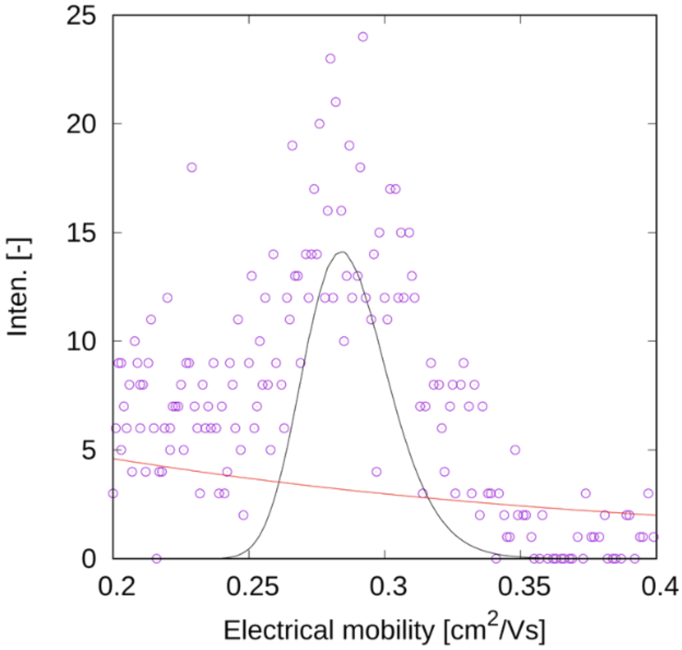

Figure S4. A Gaussian fit of the singly charged PEG ion electrical mobility distribution, measured at $Q_{\mathrm{Am}}/Q_{\mathrm{ES}}$=11. Open circles are measurements, and black and red lines are fit lines for the singly charged monomer and aggregates, respectively.

References

1. N. A. Fuchs, *Geofis. Pura Appl.*, 1963, **51**, 185-193.
2. M. Adachi, Y. Kousaka and K. Okuyama, *J Aerosol Sci*, 1985, **16**, 109-123.
3. D. A. Saucy, S. Ude, I. W. Lenggoro and J. Fernandez de la Mora, *Analytical Chemistry*, 2004, **76**, 1045-1053.