The role of counterions in constant-pH MD simulations of PAMAM dendrimers

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Supporting Information

Results

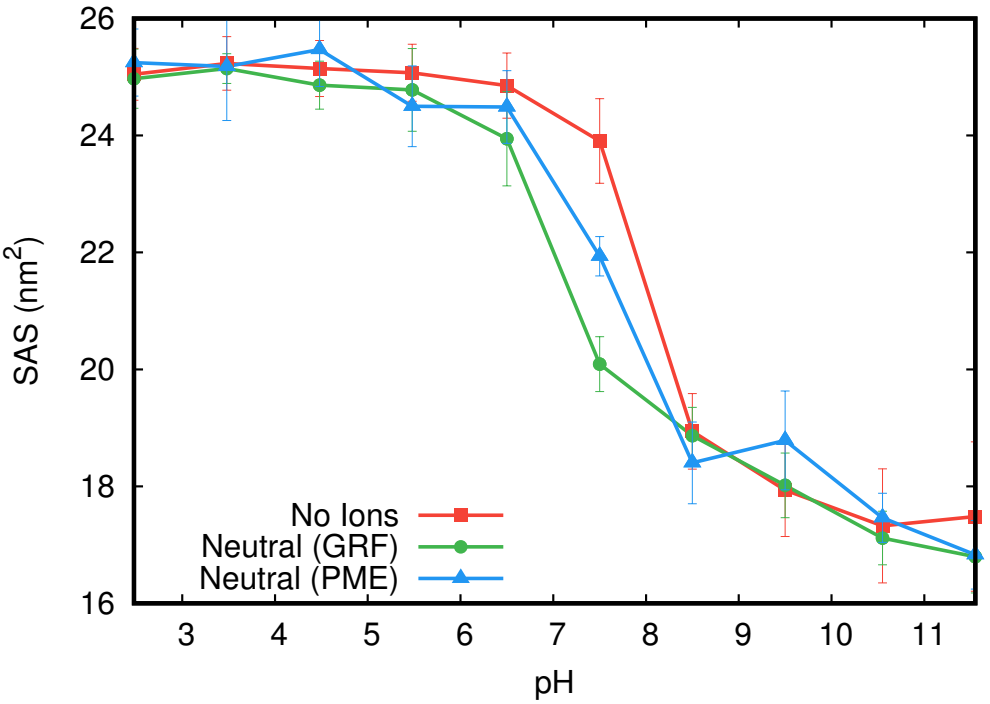

Figure S1: Average solvent accessible surface area of PAMAM at different pH values

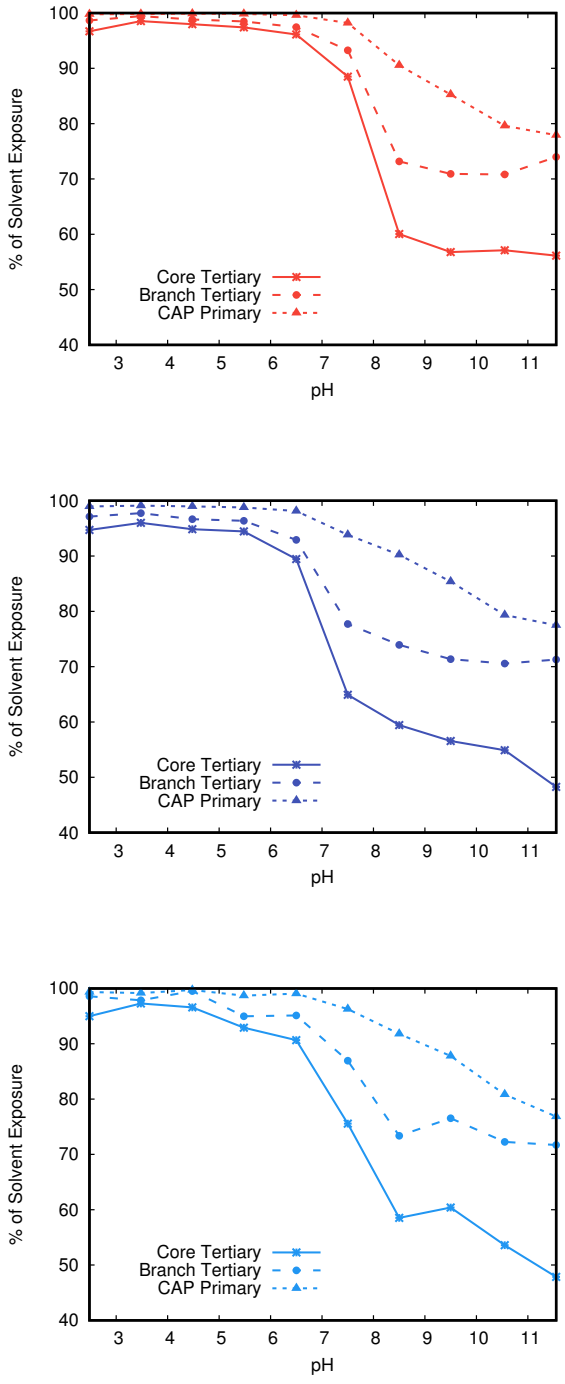

Figure S2: Fraction of solvent exposure per amine type of PAMAM over pH values for: GRF without ions (top); neutral GRF (middle); and neutral PME (bottom).

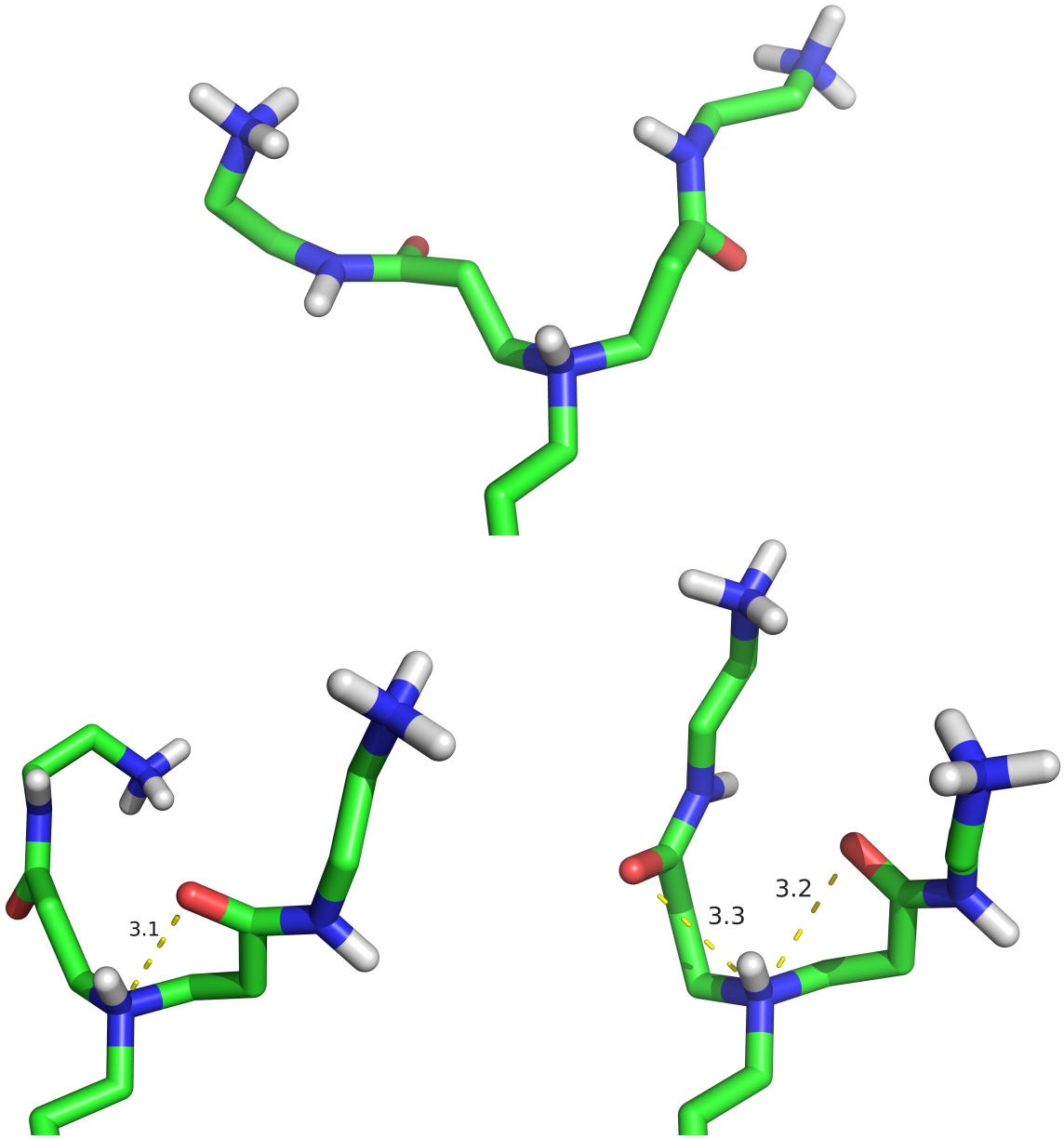

Figure S3: Interaction between the tertiary amines and the carbonyl of the adjacent amide groups. On top, we show the most stretched conformation which unfavors this interactions. On the bottom, we have direct interactions with one (left) or two (right) carbonyl groups, which are only possible by bending the following dendrimer branch.

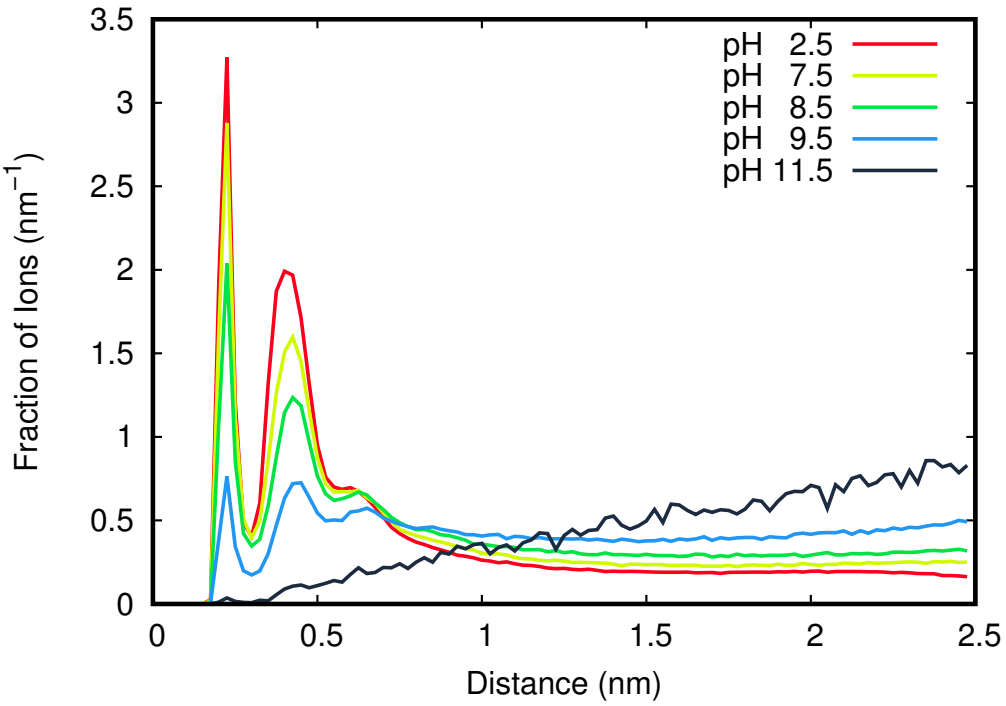

Figure S4: Minimum distance density distribution between Cl^- ions and all PAMAM atoms in PME system. The dendrimer has an average total charge of 29.9, 20.4, 14.8, 10.0, and 0.6, at pH values 2.5, 7.5, 8.5, 9.5, and 11.5, respectively.

Methods

Table S1: Charge sets for the three amino groups obtained from the RESP protocol.

	Ethylamine		Diethylamine		Triethylamine	
Atoms	Charged	Neutral	Charged	Neutral	Charged	Neutral
N	-0.46	-0.98	-0.10	-0.75	-0.19	-0.54
H1	0.35	0.35	0.27	0.33	0.32	0.00
H2	0.35	0.35	0.27	0.00	-	-
H3	0.35	0.00	-	-	-	-
Methylene	0.41	0.28	0.28	0.21	0.29	0.18
Methyl	0.00	0.00	0.00	0.00	0.00	0.00
Total	1.00	0.00	1.00	0.00	1.00	0.00

Table S2: Summary of the pK^{mod} values obtained that reproduce the experimental pK_{a} values in the primary, secondary and tertiary amino groups

Amine Type	pK^{mod}	Experimental[a]
Primary	11.404	10.65
Secondary	11.819	10.84
Terciary	11.989	10.75

[a] Values from Ref.1 for ethylamine, diethylamine and triethylamine.

(1) Albert, A.; Serjeant, E. P. The Determination of Ionization Constants, 3rd ed.; Chapman and Hall: 733 Third Avenue, New York, 1984; p 151.