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Salt-induced overcharging, charge inversion and reentrant condensation in polyelectrolyte solutions[1] PAI-YI HSIAO, Department of Engineering and System Science, National Tsing Hua University — The behavior of highly-charged polyelectrolytes (PE) in multivalent salt solutions is investigated by computer simulations. By studying the charge distribution function around a chain, we show that PE is charge-overcompensated near its surface by condensed multivalent counterions when salt concentration is high. Nonetheless, the effective chain charge, computed by the ratio of the electrophoretic mobility to the diffusive mobility, can be positive or negative, depending sensitively on the ion size. This finding violates our intuitive thinking that an overcharging on the surface of a charged macromolecule leads inevitably the sign inversion of its effective charge. Moreover, the reentrant condensation of PE is studied by calculating the mean distance between chains. Chain aggregation happens only when salt concentration is intermediate and the ion size is comparable to the monomer size. The results demonstrate the importance of ion excluded volume and suggest a disconnection of the salt-induced segregation of PE chains at high salt concentrations with charge inversion.

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Pai-Yi Hsiao
Dept. of Engineering and System Science, National Tsing Hua University

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