


Entropy gain from counterion release

Driving force and pathway in polyelectrolyte complex coacervation

Authors: Shensheng Chen and Zhen-Gang Wang
PNAS, v. **119**, n. 36, p. e2209975119, 2022

*Recommended with a Commentary by Alexander Y. Grosberg ,
Department of Physics and Center for Soft Matter Research, New
York University, 726 Broadway, New York, NY 10003*

We teach in the introductory physics courses that interaction between two point charges in a medium is described by the Coulomb law: in the obvious notations, and using Gauss units, it is

$$E = \frac{q_1 q_2}{\epsilon r} . \quad (1)$$

As in most things we teach, this is true - but not quite true. First of all, things do not look quite that simple at short distances of molecular scale, where dielectric properties of the medium are strongly scale-dependent. Second, E above is, strictly speaking, not energy, but free energy; it is the potential of *mean* force, properly averaged over all microconfigurations of particles in the medium, and that determines dielectric permittivity ϵ . The former circumstance was the subject of many works over the years (see, e.g., a recent installment [1]). The latter fact is, of course, also very well known - but deserves a reminder, as S.Chen and Z.-G. Wang demonstrate in the recommended paper (see also other closely related papers from the same group [2, 3]).

Consider, as an example, the formation of an inter-polyelectrolyte complex: two long flexible polymer chains of polyelectrolytes of opposite signs, one charged positively and one negatively. Alternatively, and equally well, we can consider one flexible chain of a polyampholyte, composed of positive and negative blocks, with overall balanced charge [4, 5]. In both cases, an overall neutral globule is formed. It was understood a long time ago, and popularized by the influential article [6], that the driving force of globule formation in both cases is the entropy due to the release of counterions. Indeed, positive and negative polymer chains, or positive and negative blocks of the same chain, are of course surrounded by the screening clouds of small (usually singly charged) counterions. When complex forms and globule collapses, these counterions are set free to go away and to move freely through the solution, thus increasing entropy and making the process thermodynamically favorable.

There are many other examples of a similar nature, but I do not list them, because I am not writing a review, but just a comment.

The idea of counterion release, and corresponding entropy gain, is nice and intuitively appealing. The trouble is - it does not quite work when compared to experiments. In fact,

some experiments (see, for example, the nice work [7]) demonstrate the release of counterions quite directly. Nevertheless, in terms of standard thermodynamics, when quantitative measurements are performed, ends do not quite meet: entropy associated with counterion release does not completely account for the free energy change in the formation of complexes.

What could be wrong?

Authors of the recommended paper make an observation which I found both very simple and quite profound. Essentially what they do is they remind us of the fact that formula (1) is the free energy, not energy; Coulomb interaction in a medium (1) involves both energetic and entropic parts. Of course, when complex formation of polyelectrolytes happens in a solvent at constant temperature, we should realize that dielectric permittivity is dependent on entropy. That entropy inevitably changes when macroions form complexes. In general terms, the entropy dependence of ε has to do with entropy of orientations of dipoles in the solvent. The specific properties of ε are not easy to understand, especially when the solvent is as complex as water.

Indeed, dielectric permittivity of water is the subject of many studies. As an example of subtleties involved there I just mention the very recent PRL [8]; the subject remains an active and challenging field of research.

But whatever exciting physics might be hidden there, S.Chen and Z.-G. Wang note that one can use experimentally measured (and measured relatively easily and, therefore, reliably) temperature dependence $\varepsilon(T)$. By the usual manipulations, which amount basically to the Legendre transform, they show how temperature dependence $\varepsilon(T)$ indicates that entropy measured by the standard thermodynamic protocol includes not only counterion release, but also rearrangements of water dipoles when screening by counterions gets replaced by mutual screening of positive and negative chains. And this entropy turns out to be a quantitatively significant contribution.

An interesting corollary to this idea concerns a typical “implicit solvent” computer simulation. In such a simulation permittivity ε masquerades itself as just an innocuous parameter. Thus, we should realize, that temperature dependence of this “parameter” hides a significant part of the relevant physics.

I found this observation quite profound, as it starts from essentially the point from the elementary physics textbook and then explains something that kept puzzling people for a long while.

References

- [1] Zachary Goodwin and Alexei Kornyshev. Cracking ion pairs in the electrical double layer of ionic liquids. *Electrochimica Acta*, 434:1 – 9, 2022.
- [2] S Varner, C Balzer, and ZG. Wang. Entropic origin of ionic interactions in polar solvents. *J Phys Chem B.*, 127:4328–4337, 2023.
- [3] Shensheng Chen and Zhen-Gang Wang. Charge asymmetry suppresses coarsening dynamics in polyelectrolyte complex coacervation. *Phys. Rev. Lett.*, 131:218201, 2023.

- [4] Paul G. Higgs and Jean-François Joanny. Theory of polyampholyte solutions. *The Journal of Chemical Physics*, 94(2):1543–1554, 1991.
- [5] Yacov Kantor, Hao Li, and Mehran Kardar. Conformations of polyampholytes. *Phys. Rev. Lett.*, 69:61–64, 1992.
- [6] William M. Gelbart, Robijn F. Bruinsma, Philip A. Pincus, and V. Adrian Parsegian. DNA inspired electrostatics. *Physics Today*, 53(9):38–44, 2000.
- [7] Jérémie Gummel, Fabrice Cousin, and François Boué. Counterions release from electrostatic complexes of polyelectrolytes and proteins of opposite charge: A direct measurement. *Journal of the American Chemical Society*, 129(18):5806–5807, 2007.
- [8] Chunyi Zhang, Shuwen Yue, Athanassios Z. Panagiotopoulos, Michael L. Klein, and Xifan Wu. Why dissolving salt in water decreases its dielectric permittivity. *Phys. Rev. Lett.*, 131:076801, 2023.