

Foreword

At a symposium celebrating the 100th anniversary of the Nobel Prizes in Chemistry, Aaron Klug, Nobel Laureate of 1982, made the remark that it was well known to biologists that the Debye–Hückel theory, and by implication its extensions, was limited to slightly contaminated water. This remark on the relevance of physical chemistry to biology is widely held. Biologists and biochemists, long familiar with specific ion effects, have quite reasonably been bemused by the failure of physical chemistry to deal with effects they know are universal. Another biochemist participant remarked that mechanisms of enzyme action were all understood. There was no need for further work.

This was news to physical chemists.

Klugg's view is fair enough, at one level. After all Hofmeister was a pharmacologist, and the biologists could claim him as their own. Hofmeister's work on specific ion effects goes back to the 1870s. It predates Arrhenius and van 't Hoff. It predates pH and buffers. It was put to one side by colloid scientists and physical chemists and only came back to centre stage again a decade or so ago.

Theorists have been uneasily well aware that Hofmeister effects are as important in the scheme of things as Mendel's work was to genetics. And that they were not accommodated by the classical theories of colloid and physical chemistry. But they could not explain the results.

At another level the Kluggian view is absurdly limited. It admits no role for physical chemistry in biology, or for that matter in chemical engineering. Chemistry is specific, and that is that. This view is pre-Mendeleev.

But biologists and biochemists do use the tools and concepts of physical chemistry. These have their roots in the 'slightly contaminated' water of Debye–Hückel theory and its extensions to include 'ion size' and double layers. This is so for concepts like pH, buffers, pKa's, ion binding, interactions of ions with surfaces, membrane and zeta potentials, colloidal interactions that are deeply embedded in our collective psyche. The foundations of these have only been questioned over the last decade. The theories used

to interpret these things all involve Debye–Hückel theory and its decorations. Indeed the dictum of the IUPAC commission on best practice in pH measurement — that relies on the validity of extended Debye–Hückel theory and the equivalent Poisson Boltzman distribution for charged surfaces — has the unhelpful advice that it is better to restrict pH measurements to pH somewhat less than 0.1 molar. The interpretation of standard measurements generally depends on classical theory. So if the theory is flawed, so is the meaning of the measurement. Various unknown ion-specific mechanisms, words like hydrophobic, hydrophilic, ‘hydration’, ‘secondary hydration’, Stern layers, site binding models, ‘water structure’, have perforce substituted for ‘explanation’ of ‘non-DLVO’ forces and disguise our ignorance.

We have had huge frustration with the muddle and mishmash of unexplained phenomena and the lack of systemisation associated with specific ion effects.

The availability of powerful experimental techniques and advances in computation and computer simulation over the last few decades have changed matters. Add to the situation the fact that Klugg’s real dirty water contains dissolved atmospheric gas and other solutes that strongly affect everything else, like hydrophobic interactions in a way that is itself ion specific. Then we have new beginning.

Some real progress has been made. New insights have emerged. There are opposing views that are coming together. These problems of physical chemistry we can hope are now well on the way to solution and a new synthesis.

From the truly vast confusing literature, this book has distilled a timely, fair, clear and useful statement and summary on the central problem of ion specificity, and of progress in understanding from the viewpoint of physical chemists proper. It is also appropriate as Pavel Jungwirth’s laboratory is a stone’s throw from Hofmeister’s in Prague and that of Werner Kunz in Regensburg is a few hours’ drive away.

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