Local order due to electrostatic interactions

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Abstract - This lecture surveys ion-dipole and anion-cation interactions such as ion pairing, ionic solvation, counterion binding and condensation around a polyelectrolyte. Results obtained by a variety of methods but predominantly by nuclear magnetic resonance will be discussed. They have been obtained for systems having the symmetry of a cylindrical rod, of a sphere, and of a plane. The following questions are addressed :
(i)   consistency between the timescale of molecular dynamics in solution and a chemical equilibrium description;
(ii) the empirical equivalence between conceptually opposed models, such as mass action law binding and Poisson-Boltzmann condensation; and the few experimental criteria available for a distinction;
(iii) the importance of the fractal dimension (in the sense of the Mandelbrot theory) in determining diffusion rates and reaction kinetics between partners constrained upon an irregular and self-similar surface.

INTRODUCTION

In their collective psyche, chemists usually view electrostatic interactions as just bringing together positively-charged and negatively-charged particles to form ion pairs (also termed, in a different context, that of protein chemistry, salt bridges). The purpose of this lecture is to enlarge upon this viewpoint, to give it more depth as it were, by pointing out other consequences of electrostatic interactions which are important to the understanding of reaction equilibria and dynamics in solution.

These other features are :
- restrictions in reorientational motions of
    - solute
    - solvent
  molecules;
- restricted radial motions of the counterions;
- increased concentration of counterions in volume elements close to a charged surface;
- in biphasic systems, by restricting diffusional random walks at the interface reactive encounters are made much more frequent, hence increased reaction rates can be observed.

This written text is meant to give just the outline of the lecture, together with a glossary for the concepts involved. The lecture itself will enlarge upon work from this group, both experimental and computational.

EQUILIBRIUM BINDING

Consider a surface pocked with potential energy holes, each of which corresponds to the presence of a charged anionic or cationic group. In reality, this molecular (or macromolecular) surface is likely to be studied in solution; and, in order to fulfill electroneutrality, the number of charged groups on the surface is exactly matched by an equal number of counterions in the solution. The location of these counterions, with respect to the charged surface, is the question of interest. The two limiting cases are probably the simplest, if also the least interesting : if the two partners are at an infinite distance (full dissociation), each will surround itself with solvent molecules (ion-dipole interactions, typically) in order to reduce the Gibbs free energy; if the two partners A and C, anion and cation, are nearest neighbors -- let us refer to binding for this electrostatic neutralization --, then one may speak of the formation of an electrostatic bond.

The complex thus formed can be characterized by the dimensionless parameter

$$\phi = \frac{Z_A \, Z_C \, e^2}{4\pi \, \epsilon_0 \epsilon \, kT}$$

If $\phi \gg 1$, the complex is termed stable, if $\phi < 1$ the complex formed is unstable. To give order of magnitude estimates, Coulombic energies of interaction between univalent cations, such as Li^+ or Na^+, and neutral molecules, such as formaldehyde or water, are in the range 50-100 kcal mol^{-1} in the gas phase : which translates into stable complexes being capable of existence in solvents with dielectric constants below 50 or so (water, with $\epsilon = 80$, oftentimes is a borderline case : only weakly stable salt complexes can form in it).

Such an equilibrium electrostatic binding situation obeys mass **action law.** Regarding the dynamic (rather than the thermodynamic) situation, these are some of the consequences of $A^- C^+$ binding :

(i)   during the lifetime of the complex (<u>vide infra</u>), the two particles A^- and C^+ reorient as a single entity, they are constrained to stay in one another's proximity;

(ii)   this local ordering (formation of an electrostatic bond) translates into a modification of the overall molecular <u>shape</u>, which affects in turn the reorientational motion of each ionic partner. Typically, reorientational motion may change from being fully isotropic to strongly anisotropic, at least one diffusional constant being made slower by about one order of magnitude;

(iii)   partial removal (loosening) of solvation molecules from the two partners, A^- and C^+, as the complex forms, is partly compensated by establishment of a new shell of solvent molecules around the complex.

Free ions such as Na^+ surround themselves with clusters of irrotationally bound solvent molecules. For structure-forming sodium cations and with various types of solvents such as water or methanol, ordering of solvent molecules around the ions keeps them bound for a residence time τ_B significantly longer than the correlation time τ_R descriptive of their random reorientation in the pure solvent.
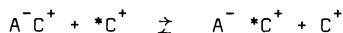
EXISTENCE OF THE COMPLEX

A conceptual trap to be avoided consists in the circular argument, defining the complex from whatever observable is used for its description. Yet, we would like a <u>bona fide</u> complex to be a very real entity, independent of our tools of observation.

A definition which avoids this quite common pitfall consists in calling a complex <u>a complex</u> if and only if its lifetime is vastly superior to its reorientational correlation <u>time as a</u> separate entity. That is to say, the local ordering referred to under (i) above is such that A^- and C^+ are huddled together for a time long with respect to the time required for the $A^- \dots C^+$ axis (internuclear, or center-of-masses axis) to reorient by an angle of one radian. Typically, for small anions and cations, these reorientational correlation times are of the order of 10 ps. Hence, electrostatic complexes are characterized by lifetimes often greater than 0.5-1 ns.

Such a situation, formation of a long-lived electrostatic complex, is also referred to as <u>site-binding</u>. Site-binding involves the restricted radial motion of A^- and C^+ away from one <u>another;</u> and this restriction in translational motion is accompanied by restrictions in rotational motion : there is a partial freeze in the translational <u>and</u> in the rotational motions of A^- and C^+ due to the formation of the electrostatic bond (<u>point</u> (i) above).

One may give an equivalent definition of site-binding, based upon structure rather than upon lifetime : this is the situation where the two partners having opposite charges are nearest neighbors.

Consider one of the two partners, A^- for instance. Its C^+ counterion vies with solvent molecules S for getting or remaining in   contact with A^-. One has to consider also exchange equilibria of the type :

$$A^- C^+ + {}^*C^+ \; \rightleftharpoons \; A^- \, {}^*C^+ + C^+$$

In other words, the thermodynamic description is insufficient. Stability of the complex is a necessary but is not a sufficient condition for its existence. The lability of a complex has also to be considered : which is why, coming back to the first point in this paragraph, site-binding has to be characterized by its duration rather than by its thermodynamic parameters (such as $\Delta H°$ and $\Delta G°$).

For instance, for the univalent sodium cations referred to above, the ratio τ_B/τ_R is in the range 2-5, depending upon the solvent and the type of measurement. In other words, Coulom-

bic attraction by a <u>point</u> charge exerts a geometric constraint, tending to immobilize the counterion to a <u>point</u> in space.

ATMOSPHERIC CONDENSATION

We have just described a mode of interaction, the electrostatic bond, characterized by full electrostatic neutralization during the lifetime of the complex. In structural and thermo-dynamic terms, counterions have prevailed : the minimum of potential energy corresponds to A^- and C^+ being nearest neighbors, solvent molecules remain at a distance.

The converse situation is also of interest. This is when full electrostatic neutralization fails to occur. Only partial neutralization (screening) of the electric charges takes place. A^- and C^+ have solvent molecules as nearest neighbors, as the minimum potential energy situation. Since partial neutralization only has occurred, the counterions continue to be drawn in, in close proximity but not in physical contact, by the electrostatic field. This is the situation known as <u>atmospheric condensation</u>.

Site binding corresponded to the formation of temporary tight ion pairs between A^- and C^+. Atmospheric condensation is the formation of loose, solvent-separated, ion pairs between the anionic and cationic partners, A^- and C^+. Whereas site binding obeys mass action law, atmospheric condensation does not. Atmospheric condensation has to be described by other means, such as solving the so-called Poisson-Boltzmann equation for the system.

Atmospheric condensation is a quite powerful force. It can boost by several orders of magnitude the concentration of counterions in a shell surrounding the polyelectrolyte considered, by comparison to the average concentration in the bulk solution. For instance, with polyelectrolytes of spherical shape such as micelles, this local increase in counter-ion concentration is an important factor in micellar catalysis : faster reaction rates are obtained, simply because local concentrations are increased markedly.

Atmospheric condensation imposes local order. An equivalent statement to that just made about concentrations is the restricted radial (but not tangential) motions of the counter-ions.

Contrast the microdynamics of counterions, in the site binding and in the atmospheric condensation modes, for a linear cylinder bearing equal electric charges at regular inter-vals. In the former mode, the motion (translational and rotational) of the counterions is tightly coupled to the motion of their binding sites. In the latter mode, only their radial translational motion is restricted; they continue to be free to diffuse back and forth over the surface of the polyelectrolyte in the shell to which atmospheric condensation cons-trains them.

In other words, Coulombic attraction by a charge <u>distribution</u> exerts upon the counterions a geometric constraint to a <u>distribution</u> within a <u>given volume</u> in space, whose symmetry is that of the original charge <u>distribution</u> (spherical; cylindrical; or planar).

ELECTROSTATIC INTERACTIONS AND FRACTALS

So far, we have referred to idealized geometries for our surface pocked with potential energy holes : the sphere, the cylinder, the plane. Real systems are characterized, at least at the atomic scale, by rough rather than by smooth surfaces.

A second consideration is of prime importance for reaction kinetics. This is connected to the mathematical problem known as the "drunkard problem" (Polya; Montroll). In three-dimensional space, a drunkard attempting to return to his home by a random walk process has a small (<u>ca.</u> 0.35) probability for doing so successfully. However, if the dimensionality of the problem is reduced from three or two, so that his uncertain gait occurs on a surface, then the probability of his achieving successfully the return to his abode goes back to unity.

Translated into the language of reaction kinetics, this means that a particle will make contact with a target, to which it diffuses, much quicker if its Brownian motion is cons-trained upon a surface.

This, as originally pointed out by Adam and Delbrück, is one of the key factors in the efficiency of enzymatic catalysis.

However, the real, rough surfaces of Nature have an effective dimension greater than two, intermediate between two and three. In cases of self-similar surfaces -- which are very widespread in Nature -- the fractal dimension of Mandelbrot can be either calculated or

determined by experiment.

An important case in practice, because of heterogeneous catalysis and because of the numerous chemical reactions at solid-liquid or solid-gas or liquid-liquid interface, is Brownian motion constrained upon such a "fractal" surface. For instance, the porous solids (such as alumina, silica, silicagel, etc.) often used as reaction supports have fractal dimensions much above two.

Besides the geometric fractal dimension, the energetic fractal dimension should also be considered : there again, it distinguishes usefully between smoothly undulating and more irregular surfaces.