The effect of the charge per ion on dispersion stability

In 1948 E.J.W. Verwey and J. Th. G. Overbeek from the Netherlands published "Theory of the stability of lyophobic colloids[1]". This work, along with similar work by B. Derjaguin and L. Landau from the USSR, formed the foundation of our modern understanding of the stability of charge-stabilized dispersions and is called DLVO theory.

A triumph of this physics was an explanation of the remarkable, independent, observations of Schulze and Hardy that the concentrations necessary to flocculate an electrocratic dispersion varies with the sixth power of the counterion charge:

$$c_1 : c_2 : c_3 = \frac{1}{1^6} : \frac{1}{2^6} : \frac{1}{3^6} \qquad [1]$$

where c_1, c_2, and c_3 are the flocculating concentrations for monovalent, bivalent, and trivalent counterions.[2] The theoretical explanation of this remarkable dependence of dispersion stability on the charge of the ions follows:[3]

The charge density ρ anywhere position, x, in a dispersion is

$$\rho(x) = \sum_i z_i e n_i(x) \qquad [2]$$

where z_i is the charge on the ith kind of ion, both negative and positive, n_i is the number of those ions per unit volume, and e is the electronic charge. Note that if there are the same number of positive charges as negative charges, the charge density is zero. Far from any

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[1] Verwey, E.J.W.; Overbeek, J. Th. G. Overbeek *Theory of the stability of lyophobic colloids*, Dover Publications: Mineola, NY; 1999, a republicaton of the work originally published by Elsevier Publishing: New York in 1948.

[2] Ibid, *Summary*, pp *vi - viii*.

[3] Morrison, I.D.; Ross, S. *Colloidal Dispersions: Suspensions, Emulsions, and Foams*; John Wiley & Sons: NewYork; 2002; Chapters 19 and 20.

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particles we expect the charge density to be zero, but near the surface of a particle the charge density will not be zero and will have the opposite sign charge as the charge on the particle. The Boltzmann equation gives the number of charges per unit volume as a function of the local electric field:

$$n_i = n_{io} \exp\left(-\frac{z_i e \Phi(x)}{kT}\right)$$
[3]

where n_{i0} is the concentration of the ith kind of ion in the absence of an electric field, i.e. far from any particles, $\Phi(x)$ is the electric field at position x, k is the Boltzmann constant, and T is the temperature. Poisson's equation relates the Laplacean of the local electric field to the local charge density:

$$\nabla^2 \Phi = -\frac{\rho}{D\varepsilon_0}$$
[4]

where D is the liquid dielectric constant and ε_0 is the permittivity of free space. Combining Equations [2], [3], and [4] gives the Poisson-Boltzmann equation:

$$\nabla^2 \Phi(x) = -\frac{e}{D\varepsilon_0} \sum_i z_i n_{i0} \exp\left(-\frac{z_i e \Phi(x)}{kT}\right)$$
[5]

The usual goal is to solve for the electric field anywhere in the dispersion, $\Phi(x)$. What we are interested in is how solutions depend on the charge per ions, z_i. Note that the charge per ion appears in both the pre-exponential factor and the exponential factor. Already we see that the equations are strong functions of the charge per ion. For a planar surface and symmetrical electrolyte ($z_+ = -z_- = z$), the solution to Equation [5] is:

$$\Phi(x) = \frac{2kT}{ze} \ln \frac{1 + \gamma \exp(-\kappa x)}{1 - \gamma \exp(-\kappa x)}$$
[6]

where

$$\kappa = \sqrt{\frac{2n_0 z^2 e^2}{D\varepsilon_0 kT}} \qquad [7]$$

and

$$\gamma = \tanh\frac{ze\Phi_0}{4kT} \qquad [8]$$

Φ_0 is the electric potential at the surface of the particle (practically, the zeta potential). κ has units of inverse distance so that $1/\kappa$ has units of distance and is called the Debye length corresponding to "thickness" of the electrically charged region surrounding each charged particle, called the electrical double layer.[4] A useful approximation is the form of Equation [6] at distances far from the surface of a charged particle:

$$\Phi(x) = \frac{8\gamma kT}{ze}\exp(-\kappa x) \qquad [9]$$

Our purpose here is to watch the dependence of these functions on the charge of the ions, z. In Equation [9] z appears in the function γ, the denominator of the fraction, and in the exponent as part of κ.

When two charged surfaces approach each other, their electrical double layers overlap. Since the particles have the same sign charge, the electrical double layers have the same sign charge, and the overlap is a repulsive energy. A derivation due to Langmuir gives the following as the repulsive energy, ΔG_R, as a function of the distances between two charged flat plates:

$$\Delta G_R = \frac{64n_0 kT}{\kappa}\gamma^2\exp(-\kappa H) \qquad [10]$$

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[4] The most interesting problems have asymmetric electrolytes, but the mathematics is much more complex and not much more useful for out purposes.

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where H is the distance between the plates.[5] We see that the charge per ion, z, appears in the pre-exponential factor, γ, and in the exponential factor, κ. Equation [10] takes on other forms for other geometries such as spheres, for asymmetric electrolytes where anions and cations do not have the same number of charge per ion, and for asymmetric particles where the surface potentials are not the same.[6]

The total interaction between the two flat plates is the sum of this electrostatic repulsion and the dispersion energies of attraction, ΔG_D, (discussed elsewhere in the short course and in the textbook):

$$\Delta G_T = \Delta G_R + \Delta G_D \qquad [11]$$

or

$$\Delta G_T = \frac{64 n_0 kT \gamma^2}{\kappa} \exp(-\kappa H) - \frac{A_{121}}{12 \pi H^2} \qquad [12]$$

where A_{121} is the Hamaker constant for the attraction between two surfaces of material 1 through a liquid of material 2. If the dispersion is stable, Equation [12] has a positive maximum corresponding to a repulsive barrier preventing two particles from sticking together. As ions are added to the dispersion, the repulsive barrier decreases.

Suppose we ask the question, Under what conditions would Equation [12] not have a positive maximum? That is, under what conditions would the dispersion not be stable? Mathematically this corresponds to the equation and its derivative being zero at the maximum. Let's call the concentration of ions under those conditions, the critical coagulation concentration, CCC. The critical coagulation concentration will be that

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[5] Again, the more interesting problems are for particles, possibly spheres, but the mathematics is much more complex and not much more useful for our purposes.

[6] Hunter, R.J. *Foundations of Colloid Science*, 2nd ed.; Oxford University Press: New York; 2001, Chapter 12.

amount of salt in a dispersion that will flocculate it. This is concentration can be measured experimentally quite easily with a beaker of dispersion and a few pinches of salt. A little algebra produces the following:

$$CCC(\text{ions/liter}) = \frac{(4\pi\varepsilon_0)^3(2^{11}3^2 D^3 k^5 T^5 \gamma^4)}{\pi \exp(4) e^6 A_{121}^2 z^6} \qquad [13]$$

A truly amazing equation! Taking $T = 298$ K and $D = 80$ for water leads to

$$CCC(\text{moles/liter}) = \frac{8.74 \times 10^{-39} \gamma^4}{A_{121}^2 z^6} \qquad [14]$$

where the Hamaker constant is in Joules. When the surface potential is high, γ is near unity and independent of the valency and the surface potential so we have the result:

$$CCC(\text{moles/liter}) \sim \frac{1}{z^6} \qquad [15]$$

which is the Schulze - Hardy rule. The electrostatic stability of a dispersion decreases with increasing concentration of ions as is well known, but, more importantly in most practical applications, it is the concentration of the highest charged ions that are most significant. Rather than careful measurements of zeta potential, a careful analysis of the ions in the dispersion may be more fruitful.