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Coagulation by simple multivalent counterions

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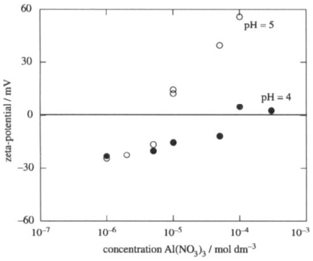
HIGHLIGHTS

- In practice of colloid stability and interaction DLVOE theory works well.
- Overcharging by ion correlations deserves more dedicated experiments.

GRAPHICAL ABSTRACT



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ABSTRACT

The origin of the strong screening power of multivalent counterions in electric double layers is reconsidered. Even for simple multivalent ions like La^{3+} and Th^{4+} more than one mechanism may be held responsible. The most critical alternatives are adsorption by specific non-electrostatic forces and enrichment by ion correlations. Many multivalent ions tend to hydrolyse in water, thereby producing highly absorbable hydrolysis products. This leads to a pH dependence of overcharging by specific adsorption, but as ion correlations are virtually independent of pH, this influence helps to discriminate between the two mechanisms. Some critical literature illustrations show that the number of publications that prove the effect of ion correlations unambiguously is very limited.

1. Introduction

It is a long established experimental fact that multivalent counterions strongly promote the coagulation of hydrophobic colloids. For a variety of colloids this feature has already been established before the beginning of the 20th century and this qualitative feature is generally known as the Schulze-Hardy rule, after their originators [1–4]. Remarkably enough, the quantification of this rule and the underlying mechanism are still subject to interesting developments. This paper intends to present the status quo of this issue.

Strong suppression of the electrostatic repulsion between two charged colloidal particles by multivalent ions must be caused by their relatively strong screening. In electrolyte solutions, electrostatic screening can be accounted for by the Debye-Hückel (DH) theory, according to which the screening between two charged ions is in first approximation proportional to $\sqrt{cz^2}$ where c is the electrolyte concentration and z the valence. If something like this would be the reason for the strong screening activity of multivalent ions, one would expect tetravalent ions to be twice as effective as bivalent ones. In reality the difference is dramatically higher. Experimentally, rather a factor of hundred is found, depending on the nature of the colloid. Obviously, there is more at hand than simple DH-type screening. It seems that multivalent ions feel a stronger specific attraction to the surface than ions of low valency. The existence of such strong specific adsorption is also testified by the propensity of many multivalent ions of inducing overcharging (also called charge reversal), that is the phenomenon that there is more countercharge in the double layer than necessary to compensate

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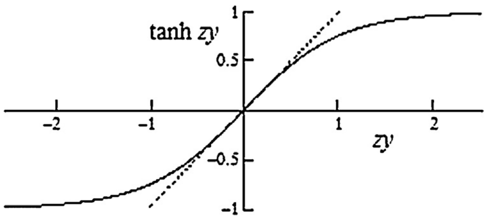

Fig. 1. Sketch of hyperbolic tangent. It starts linear then converges to unity.

the surface charge. The question then arises by what type of forces multivalent ions adsorb so strongly and what the consequences are for the interaction between colloidal particles.

The present paper focuses on this question. In order to approach the basic issue as well as possible, we shall only consider simple multivalent ions, i.e. ions without attached organic groups (like amino, cyanide or substituents with longer chains) that might have a certain non-electrostatic affinity for the surface. Polyelectrolytes will also be ignored. They easily produce overcharging because of their propensity of adsorbing tenaciously on many surfaces, often by non-electrostatic forces. A specific adsorption energy of a few tenths of a kT per segment suffices to render the adsorbed molecule virtually undesorbable by dilution [5]. This is the reason for the term “simple” in the title of this paper.

2. Coagulation by multivalent ions in the DLVO theory

The well-known theory for the stability of lyophobic colloids by Derjaguin and Landau [6] and, independently, by Verwey and Overbeek [7] was the first successful attempt to quantify colloid particle interaction on the basis of a balance between Van der Waals attraction and electrostatic repulsion. We shall use that theory as the starting point of our discussion. The most straightforward way to proceed is by writing down their equation for the coagulation concentration c_{cr} for z–z valent electrolytes. According to [7],

$$c_{cr}=\left(\frac{\text{const.}\,(\tanh zy/4)^4}{A^2\,z^6}\right) \tag{1}$$

In [6] something similar can be found. Here, $y = F\psi/RT$ is the dimensionless potential and A the Hamaker constant. The const. in (1) is known; it contains natural constants and parameters like the temperature T and dielectric permittivity ε. The proportionality to z^6 in the denominator has led many scientists to interpret this law as the quantitative Schulze-Hardy rule. This sloppy habit persists till today. In fact, scrutiny is needed because the hyperbolic tangent in (1) also contains the valency and it depends on the value of y how this works out on the overall z-dependence. See Fig. 1.

The tanh y function starts linear from the origin with $\tanh zy = zy$ as the first term of its series expansion, then converges rapidly to unity: $\tanh zy \rightarrow 1$ for positive zy. So, only at high potential does the z^{-6} law apply. For monovalent counterions this limit is attained above about 100 mV, but for tetravalent ions this is already the case for potentials of about 25 mV. All four authors of the DLVO quartet emphasized the z^{-6} proportionality and claimed this as a success of their theory. But all of them were also conscious of the fact that the z^{-6} law was only applicable if y is high enough to allow the tanh function to be replaced by unity. Deryagin and Landau simply stated that the double layers should be strong, but Verwey and Overbeek gave a detailed analysis of the underlying problem. The question of the magnitude of y is related to the physical question of which potential has to be substituted into the equation: what is the double layer potential governing particle interaction? At the time DLVO theory was published, not so much insight into double layer potentials was available: they only had surface potentials for the silver iodide system and electrokinetic potentials for a diversity of materials available. Electrokinetic potentials were then too poorly established and the meaning of the ζ potential was too unclear to act as bases for rigorous theories. So, it was no surprise that the surface potential of silver iodide particles was chosen as their paradigm. This value was well-established and amounted to several hundreds of mV at the pAg of the sols where coagulation was usually investigated. Such values are high enough to substitute $y^\circ = F\psi^\circ/RT$ for y which is plenty to reach the limit of 1 for the hyperbolic tangent. This was their justification for the z^{-6} law.

Against this interpretation two types of objection can be raised. One is of a fundamental nature and will be addressed in Section 4. The other is of a more quantitative nature and will be discussed now. The point is that under coagulation conditions the potentials to be substituted in (1) are much lower than as estimated by Verwey and Overbeek, basically because the double layer is then very much compressed, especially so when the counterions are multivalent. This can be inferred from electrokinetic measurements, but AFM experiments also point into this direction. For the purpose of the present study there is no need to review the extensive available data but the conclusions can be concisely condensed into the following three points:

(1) The operative potential is not the potential at the particle surface, y° but the potential of the diffuse part of the double layer, y^d.
(2) In Eq. (1) for y not y° must be substituted but y^d.
(3) y^d is generally so low that the linear term of the expansion of the hyperbolic tangent suffices. For details see [8]. The immediate consequence is that Eq. (1) has to be replaced by

$$c_{cr}=\frac{\text{const.}'\,(y^d)^4}{A^2\,z^2} \tag{2}$$

The dependence on z is now sensitive to the amount of ions adsorbing in the inner, or Stern layer: the stronger this binding, the lower y^d. As a trend, counterions of higher valency adsorb more strongly than monovalent ones, hence the dependence on z is much stronger than just the square in Eq. (2), and it depends on the nature of the ion. This is in line with experiment, see for example Overbeek’s own collection of coagulation concentrations for various sols in ref. [9]. Among other things he reports c_{cr} values for $Th(NO_3)_4$ that are 16, 3.7 and 9% of the corresponding data for monovalent counterions for colloidal As_2S_3, Au and AgI sols, respectively. This is not as strong as 4^{-6} or 0.39% but dependent on the system. It may be noted that because the potential has a 4th power in Eq. (2) the stability becomes very sensitive to the nature of the counterion, which is the origin of lyotropic, or Hofmeister, series.

3. Present position of DLVOE theory

As is apparent from the previous section, classical stability theory is flexible enough to account for many experimental observations, provided the model is not limited to purely diffuse double layers, but supplemented by an inner (Stern) layer. We call this amended version DLVOE theory, with the E for extended. See [8]. The theory is most rewarding when, besides measurements of the surface charge σ°, also the diffuse charge σ^d is available because then the Stern charge σ^i can immediately be found from the electroneutrality condition.

$$\sigma^o+\sigma^d+\sigma^i=0 \tag{3}$$

The $\sigma^i(\sigma^\circ)$ relationships, obtained this way are kinds of adsorption isotherms and lend themselves easily to modelling. If the parameters needed for this are reasonable one may consider the analysis completed. For practical purposes the power of

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