On the Relation between Surface Charge and Sol Stability

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This paper discusses various charges distinguishable in electrical double layers, namely the electrokinetic charge σ_{ek}, the Stern charge σ_m and the surface charge σ_o. The electrokinetic charge can be calculated from the electrokinetic potential ζ. The approximation $\psi_d = \zeta$ appears to work well for the AgI-system. Hence, $\sigma_{ek} \sim \sigma_d$, the diffuse double layer charge. The potential ψ_d is the determining quantity in colloidal stability. Concersely, from stability measurements ψ_d and hence σ_d can be evaluated. The surface charge σ_o can in most cases also be determined experimentally. Its relation to σ_d, and hence to sol stability, is indirect. Because of the balance $\sigma_d + \sigma_m + \sigma_o = 0$, the Stern charge can be found from σ_o and σ_d by subtraction. This is the relatively most informative quantity. Two example are worked out for the AgI-sistem, the lyotropic sequence ($\sigma_m (Li^+) < \sigma_m (K^+) < \sigma_m (Rb^+)$) and the effect of different alcohols on σ_m. In the latter case it is found that butanol tends to desorb cations, whereas ethylene glycol has only a negligible effect on the cation binding.

To ensure the stability of hydrophobic colloids against aggregation, it is necessary that the particles bear an electric charge. However, the *presence* of such a charge in itself is still not enough; the charge around the particle should also be *distributed* in the right way. Good stability requires extended double layers.

The relationship between the thickness of the double layer and sol stability is clearly borne out by the intimate relationship between stability and electrokinetic potential ζ. For instance, addition of indifferent electrolytes, compressing the double layer, reduces both.

The *electrokinetic* potential is related to the electrokinetic charge σ_{ek}. For a flat double layer in a symmetrical (z-z)eletrolyte[1,2]:

$$\sigma_{ek} = (8\varepsilon\varepsilon_o nkT)^{1/2} \sinh\frac{ze\zeta}{2kT} . \tag{1}$$

Here, n is the electrolyte concentration in molecules cm^{-3}, ε the relative dielectric constant, $\varepsilon_o = 8.854 \times 10^{-12} C^2 N^{-1} m^{-2}$, k is the Boltzmann constant, T the absolute temperature and e the elementary charge. For a spherical particle at not too high ζ (the so-called Debye-Hückel approximation),

$$\sigma_{ek} = \frac{\varepsilon \varepsilon_0 \zeta}{a} (1 + \varkappa a), \tag{2}$$

where a is the particle radius (counted from the centre of the sphere to the position where the potential is ζ), and

$$\varkappa = \left(\frac{2e^2 n z^2}{\varepsilon \varepsilon_0 kT} \right)^{1/2} . \tag{3}$$

For spherical particles at high ζ, values for σ_{ek} are tabulated[3].

These relations indicate that the close relationship between sol stability and ζ can also be read as a relationship between sol stability and σ_{ek}. However, there is no such relationship between stability and the *surface* charge σ_0, or, for that matter, such a relation is at best indirect. Surface charge and electrokinetic charge are widely different notions.

The surface charge σ_0 is the charge on the surface proper. It can be due to the adsorption of potential determining ions. For example, for oxidic particles where H^+ and OH^- are potential determining,

$$\sigma_0 = F (\Gamma_{H^+} - \Gamma_{OH^-}). \tag{4}$$

Here, F is the Faraday and Γ_i indicates the surface excess of i. For silver iodide, Ag^+ and I^- are potential determining and

$$\sigma_0 = F (\Gamma_{Ag^+} - \Gamma_{I^-}). \tag{5}$$

In still other cases, σ_0 can be due to dissociation of surface groups (for example with latices) or to isomorphic substitution (clays). In most cases, σ_0 is experimentally accessible.

In the classical picture, ζ is the potential at the slipping plane, that is the boundary between moving and stagnant liquid in any electrokinetic process. Although it is probably more appropriate to think in terms of a slipping *layer* instead of a slipping *plane*[4], for the discussion given below it is not necessary to consider this refinement. Consequently, σ_{ek} is the charge outside the slipping plane (equal to minus the same within the slipping plane because of electroneutrality).

The charges σ_0 and σ_{ek} are widely different quantities. It is not uncommon that σ_{ek} is only a fraction of σ_0. For instance, with oxidic materials, σ_{ek} is of the order of $\mu C\ cm^{-2}$, whereas σ_0 is of the order of tens or hundreds of $\mu C\ cm^{-2}$ [5]. In other cases, σ_{ek} and σ_0 even have opposite signs.

To summarize the above, two accessible double layer charges can be distinguished; the surface charge σ_0 and the electrokinetic charge σ_{ek}. The former is a property of the particle proper but it has no direct bearing on stability. The latter is a derived property (its value is also determined by hydrodynamic factors), it is less characteristic for the particle than σ_0, but closely related to sol stability.

The difference between σ_0 and σ_{ek} is essenttially attributable to the charge residing in the thin layer between the surface and slipping plane. This charge is perhaps the most interesting one, since its magnitude reflects processes in a liquid very close to a solid surface. Moreover, it determines the relation between σ_0 and σ_{ek}. However, it is not unambiguously analytically accessible, since measurements of any Γ_i always yield the *total* amount at

an interface, i. e. the sum of the amounts within and outside the slipping plane.

These considerations automatically lead one to search the feasibility of obtaining the inner layer charge by subtraction of σ_{ek} from σ_o. This is an interesting possibility, but before such a subtraction is carried out, two problems must be solved.

The first is that instead of subtracting σ_{ek} from σ_o it is more fundamental to subtract σ_d from σ_o, where σ_d is the total charge in the diffuse part of the double layer. The stability theory describes colloid interaction in terms of the overlap of diffuse double layers. In a real double layer, the diffuse part starts at the Outer Helmholtz Plane (OHP), where the potential is ψ_d. Hence, the stability equations contain ψ_d rather than ζ. The relation between these two potentials is still not settled[4]. Many authors simply equalize ζ and ψ_d. In the author's experience with AgI-sols, this is probably a very good approximation and as the examples to follow concern the AgI-system, we shall adhere to this simplification. Consequently,

$$\sigma_{ek} \simeq \sigma_d \tag{6}$$

if σ_d is the diffuse double layer charge.

The second difficulty is that σ_o and σ_d are derived from entirely different sources and measured with differently processed materials. This issue has been discussed by Lyklema and de Wit[6]. The provisional conclusion is that deriving σ_d from coagulation data is warranted as long as the double layers are sufficiently smooth. In the case of patchwise adsorption, the quantities σ_o, σ_d etc. lose their physical meaning. Below, such smoothing is presupposed.

The basic equation is the electroneutrality balance

$$\sigma_o + \sigma_m + \sigma_d = 0 \tag{7}$$

where σ_m stands for the charge between the surface and the OHP, in short σ_m is the Stern charge[7]. This equation shows that the discrepancy between σ_o and σ_d is determined by σ_m. Some typical examples are:

a) systems with little specific adsorption of counterions (AgI). In this case, σ_m and σ_d have the same sign, and all three charges are of the order of a $\mu C. cm^{-2}$. The balance between σ_m and σ_d shifts in favour of the former with increasing salt concentration.

b) uncharged systems on which strong adsorption of a charged surfactant occurs. In that case, the charge attributable to the surfactants acts as the surface charge σ_o, and σ_m is then that part of the countercharge which is not present in the diffuse part of the double layer.

c) oxides, where both σ_o and σ_m are very high, probably because of the penetration of both potential-determining- and counterions into the solid[5].

Two typical examples of the AgI-system are given below.

The balance (7) is very helpful in interpreting the lyotropic sequence in the coagulation concentrations. This problem has previously been discussed in this journal[8]. For negative AgI-sols at pI ~ 4, for the critical coagulation concentration c_c it has been found that

$$c_c (RbNO_3) < c_c (KNO_3) < c_c (LiNO_3),$$

implying

$$\sigma_d \, RbNO_3) < \sigma_d \, (KNO_3) < \sigma_d \, (LiNO_3).\tag{8}$$

Since at the same time

$$\sigma_o \, (RbNO_3) > \sigma_o \, (KNO_3) > \sigma_o \, (LiNO_3),\tag{9}$$

apparently

$$\sigma_m \, (RbNO_3) > \sigma_m \, (KNO_3) > \sigma_m \, (LiNO_3),\tag{10}$$

because Rb$^+$-ions are more strongly adsorbed in the Stern-layer than Li$^+$-ions. It is particularly noteworthy that the sequence of σ_o is just the reverse of the sequence of c_c, underlining the indirect relationship between σ_o and c_c. The decisive factor is the value of σ_m. If σ_m is high, σ_o is also high (because of better screening), and at the same time σ_d is low.

The other example concerns the effect of organic additives on σ_o and c_c. Butanol (BuOH) and ethylene glycol (EG) have been extensively studied with respect to their effect on the stability of AgI-sols and on the double layer on that substance[9–12]. At fixed pI, in both cases σ_o decreases continually upon addition of the alcohol. With BuOH, the reduction is more pronounced. However, the effect on c_c is strikingly different. With increasing concentration of EG, c_c decreases continually, whereas with BuOH c_c passes through a maximum. Figure 1. illustrates this observation. In this Figure, the two horizontal axes have been reduced to a comparable scale, in order to facilitate comparison (BuOH is moderately soluble in water, while EG mixes in all
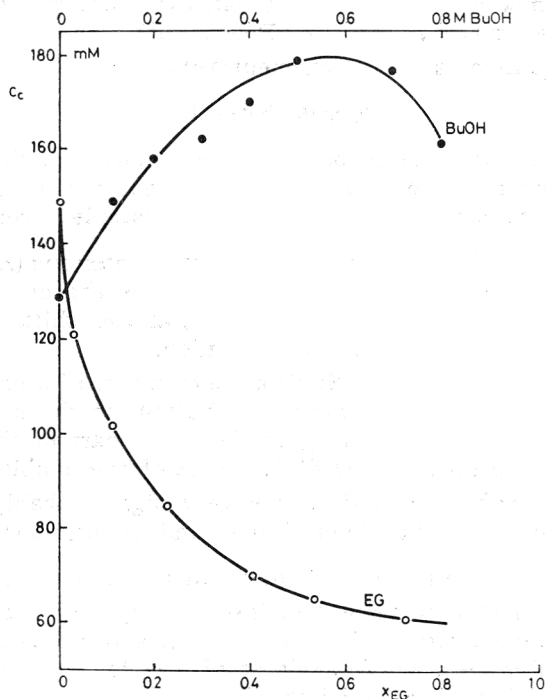

Figure 1. Critical coagulation concentrations of negatively charged silver iodide sols in the presence of butanol or ethylene glycol.

proportions). The discrepancy at x = 0 is due to the fact that the experiments have been done with different sols and different techniques. The evaluation of ψ_d has been done with the following pair of equations:

$$V_R = 64\pi\varepsilon_o\varepsilon \left(\frac{kT}{ze}\right)^2 \frac{a+\Delta}{s} \left[\; \tanh\left(\frac{ze\psi_d}{4kT}\right)\right]^2 \exp\left[\; -\varkappa\,(a+\Delta)\,(s'-2)\right] \qquad (11)$$

$$V_A = -\;\frac{A_{1(2)}}{6}\left[\frac{2}{s^2-4}+\frac{2}{s^2}+\ln\frac{s^2-4}{s^2}\right], \qquad (12)$$

where V_R is the electrostatic repulsion energy, V_A the attractive energy Δ is the thickness of the inner layer, $A_{1(2)}$ the Hamaker constant for silver iodide in the liquid medium, whereas s and s′ are dimensionless distance parameters, defined through $S = R/a$ and $s' = R/(a+\Delta)$ respectively, where R is the distance between the particle centres. A discussion of the underlying model and of the values selected for the parameters $A_{1(2)}$ and Δ is given in[6]. Here, we note that for Δ choices have been made first in the absence of the organic adsorbate and upon saturation; for intermediate coverages, Δ was then varied in proportion to the amount adsorbed. In the EG case, the rate of coagulation was measured, in the BuOH case the critical coagulation concentration was analysed. Both analyses led to a value for ψ_d and hence for σ_d. Finally, subtraction from σ_o yielded σ_m. The result is given in Figure 2 in terms of the fraction $\Theta = \sigma_m/\sigma_o$ of the surface charge that is compensated by counterion adsorption in the Stern layer.

The uncertainty in the values of Θ is 10—20% if measurements with different batches of silver iodide and by different techniques are considered. Moreover, the obtained values of Θ depend also on the choice of the parameters in equations (11) and (12)[6]. Therefore we have ignored the relatively
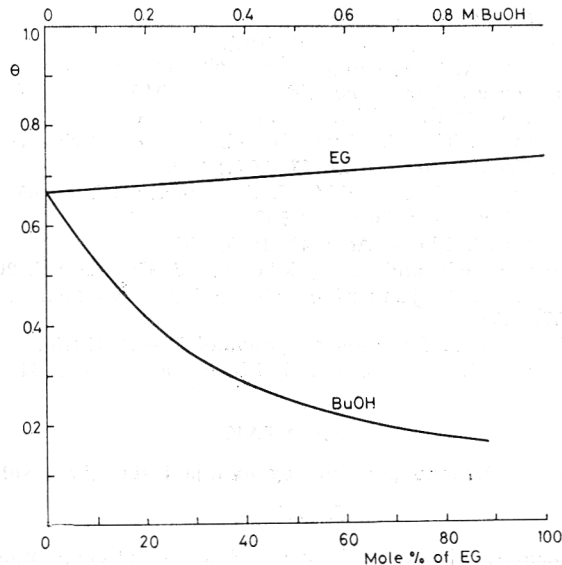

Figure 2. Fraction Θ of the surface charge on silver iodide, compensated by counterions in the Stern layer, in the presence of butanol or ethylene glycol.

small differences between the values of Θ at $x = 0$, obtained in the two series of experiments (Figure 1). However, the trends of the two curves are significant. The Figure reveals that adsorption of butanol strongly reduces the Stern layer charge, whereas ethylene glycol adsorption hardly affects the amount of charge in this layer. This interesting conclusion could only be reached by combining the double layer and stability data.

The widely different trends of the two curves in Figure 2 indicate that the Stern layer structure is quite different with the two adsorbates. In previous work it has been found, that butanol molecules adsorb with their hydrocarbon moiety towards the surface[9]. This mode of sorption apparently renders the immediate surroundings of the silver iodide surface so hydrophobic that cations are expelled. The remaining 15—20⁰/o at saturation are probably placed somewhere close to the OH-groups, i. e. rather distant from the surface. In this case, the Stern layer is thick. In fact, in the computation we used $\Delta = 0.82$ nm in the presence of butanol, gradually decreasing to 0.54 nm in its absence.

For ethylene glycol, the picture is different. Adsorption of these molecules does not create extensive hydrophobic layers and cations can remain close to the surface in a relatively hydrophobic environment. Consideration of the double layer capacitance produces additional information. For example, the reduction of the capacitance with increasing x_{EG} could largely be attributed to a gradual thickening of the Stern layer, probably because ethylene glycol molecules are more bulky than water molecules[12]. Details of this picture still need to be worked out and they do not pertain to the theme of this article. The main point we wished to stress is that surface charge measurements in conjuction with stability studies are conducive to a better understanding of the composition of the most interesting part of an electrical double layer, the Stern layer.

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SAŽETAK

O vezi između površinskog naboja i stabiliteta sola

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Na osnovi razmatranja veza između elektrokinetičkog potencijala ζ, elektrokinetičkog naboja σ_{ek} i površinskog naboja σ_o izvedena je pretpostavka za razlikovanje dviju vrsta naboja dvosloja. Analizom međusobnih relacija električnih ka-

rakteristika dvosloja za solove srebrnog jodida uvodi se aproksimacija $\psi_d \to \zeta$ odnosno $\sigma_{ek} \simeq \sigma_d$ (ψ_d je potencijal a σ_d je ukupni naboj difuznog dijela dvosloja). Uvođenjem naboja između površine i OHP σ_m postavlja se relacija $\sigma_o + \sigma_m + \sigma_d = 0$ iz koje proizlazi značenje σ_m za razliku između σ_o i σ_d. Postavljene razlike se analiziraju na primjeru liotropnih serija za kritične koagulacijske koncentracije c_c, σ_d, σ_o i σ_m. Kao drugi primjer razmatra se utjecaj butanola i etilenglikola na σ_o i c_c i izvodi se zaključak o djelovanju alkohola na debljinu Sternova sloja te razmatra način adsorpcije različitih vrsta alkohola u dvosloju. Veza između površinskog naboja i stabilnosti sola razmatra se u okviru međusobnih veza opisanih veličina.

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