The Lyotropic Sequence in the Stability of Hydrophobic Colloids

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The nature of the counterion, among other parameters, has a pronounced influence on the flocculation values for hydrophobic sols. A discussion of the lyotropic sequence, *i. e.* of the increase of the flocculation values for a typical, negatively charged silver iodide sol, in the series Rb^+, K^+, Na^+, and Li^+, is given in terms of the Deryagin-Landau-Verwey-Overbeek theory of colloidal stability. More recent data on adsorption of alkali metal ions on the surface of α-hematite indicate a reversal of the lyotropic series. Interpretation is sought in the predominance of steric factors.

1) *Colloidal Stability*

Hydrophobic colloids are thermodynamically unstable. Due to the relatively large interfacial area, the Gibbs free energy of a sol is higher than the Gibbs free energy of one big crystal of the colloidally dissolved matter in the solution. However, it is not difficult to prepare colloidal solutions that can be kept for years without marked aggregation between the particles. It follows, that in these systems there must be a kind of barrier preventing the particles from agglomeration. Or, saying the same thing in other words, the activation energy of the aggregation process is so high that the rate by which thermodynamical equilibrium is reached is negligibly low.

In the majority of the cases, the barrier against agglomeration is of electrical origin. The other possibility, protection against flocculation by polymers is not considered here, although it has considerable practical importance. The electrostatic repulsion between the particles is due to the fact that the particles are charged, either by adsorption of potential determining ions or due to dissociation of surface groups. However, this is not yet the whole story. Colloidal solutions are electroneutral. If, say, a silver iodide sol has particles with a negative charge on their surfaces, (due to adsorption of the potential determining I^--ions) there must be an equal but opposite charge in the solution around the particles, the so-called countercharge. In electrostatics, a system consisting of such an array of negative ions and a parallel array of positive ions is called an *electrical double layer*. Thus, we can say that it is apparently the repulsion between the electrical double layers around the colloidal particles that ensures stability. As double layers *as a whole* are electroneutral, we conclude that it is not as much the actual charge that counts, as well as the way in which the charge is *distributed*. Indeed, systems of high surface charge are known that are unstable and there exist also systems of relatively low charge that are stable, although in complete absence of charge (*i. e.* in the absence of an electrical double layer) stability is impossible.

This is a basic fact of hydrophobic colloidal stability. All stability theories are based on some ideas concerning the structure of the electrical double layer, relating it to the interaction between colloidal particles. It is also against this background that the discussion of lyotropic effects must be seen.

To that order let us first consider the lyotropic sequence from the experimental side and then discuss stability theory to find out how the experiments fit in the general picture.

2) *Flocculation by Salts*

Hydrophobic sols are very sensitive to salt: addition of relatively small amounts can cause them to flocculate. The concentration of salt required to flocculate the sol is called the *flocculation value* (c_{fl}) or critical concentration of flocculation, it is one of the classical measuring sticks for the stability of a sol*.

Flocculation values depend on a number of things, among which the way in which they are measured, the nature of the sol, the surface charge and double layer composition of the sol particles, the valence of the counter ions and the nature of the counterions. It is in the last mentioned item that we are now interested, but let us first digress into a short discussion of some of the other variables.

The procedures of measuring flocculation values can roughly be divided into three groups: (1) the classical method, (2) the rate of coagulation method and (3) the *in statu nascendi* method. In the classical method, mainly developed in Kruyt's school[1] a series of glass tubes with sol is prepared, containing increasing amounts of salt, and coagulation is visually observed after a certain preset programme of shaking and waiting.

This method has the drawback that the stability criterium is somewhat arbitrary but the advantage that, if properly done, a time scale is used enabling particles and liquid to attain adsorption equilibrium, so that we are pretty sure about the surface charge under flocculation conditions. In the rate of coagulation method, developed by Reerink and Overbeek[2] on the basis of older ideas of Smoluchowski and Fuchs the rate of coagulation is measured extinctiometrically as a function of c_{salt} and the salt concentration at which further increase produces no further speeding up of the coagulation process is identified as c_{fl}. As compared with the classical method, this procedure has the advantage of offering a less ambiguous criterium, but there is no equilibrium between sol and solution. Moreover, the absolute rate of coagulation, as calculated by Reerink and Overbeek's theory does not agree with the experimentally observed one, showing that at least in this respect there is something wrong. Thirdly, in the *in statu nascens* method, developed mainly in the Yugoslavian school[3] the sol is made at the same time as it flocculates. Following the process turbidimetrically at varying salt concentrations enables a coagulation concentration to be established. This procedure has the advantage that no contamination on the growing particles occurs, but the disadvantage that the sol material has no constant and well defined properties during the flocculation process.

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* Throughout this paper, the notions »flocculation« and »coagulation« are considered as synonymous.

Do these methods produce the same c_{fl}-values? No, they do not. In fact, by these three approaches something different is measured, so that agreement can not a priori be expected. The trend is that the observed c_{fl} values increase in the order in which they are discussed above. On one and the same preformed sol c_{fl}, measured by the rate of coagulation method tends to be 30—40% higher than the corresponding classical value.

However, luckily enough the three methods do produce the same trends with respect to the nature and valence of the counterion. These trends then, are experimentally fairly well established and hence it has sense to try and interpret them on the basis of double layer structure.

As said before, c_{fl} depends also on the nature of the sol. The explanation is, that colloidal particles attract each other by the ubiquitous van der Waals forces. This attraction competes with double layer repulsion. Hence we must expect that at given double layer charge and composition a metal sol (strong van der Waals attraction) is less stable than a polystyrene latex (weak van der Waals attraction). There are also influences of shape and surface irregularities, the natures of which are not yet properly understood, but if we compare various salts with one and the same sol, these last-mentioned effects are probably irrelevant for our case.

3) The Schulze-Hardy Rule and the Lyotropic Series

On closer inspection the effectivity of salts to flocculate sols can be roughly condensed into three rules.

a) The influence of the co-ion (that is the ion with the same charge as the surface) is usually negligible. For example, for a negative As_2S_3-sol, the classical flocculation concentrations of KNO_3 and KCl differ by no more than 1% (although K_2SO_4 is about 30% higher). This is not surprising because co-ions are repelled by the surface (or negatively adsorbed).

b) There is a strong influence of the valency z of the counterion. Bivalent counterions have, depending on the conditions, flocculation values that are usually a factor of 30—80 lower than monovalent counterions, and trivalent ions flocculate still more effectively. This qualitative rule was already observed long ago by Schulze and Hardy[4] and since then bears their names. More recently, the DLVO-theory of colloidal stability, to be discussed below, predicted that in the limiting case of high surface potential c_{fl} be proportional to z^{-6}, yielding for monovalent to divalent counterions the ratio $2^6 = 64$ which seemed to be supported by the experimental observations of Schulze and Hardy. Since this theoretical prediction was made, the name »Schulze-Hardy rule« has sometimes erroneously been used to indicate the sixth power law and the quality of the theory was then judged by investigating how closely the experiments followed this rule[5]. Doing so is not only historically incorrect, but also scientifically, because the limiting case of high surface potential is not usually encountered in practice. The rather fortuitous agreement of many stability data with the sixth power law is the result of a combination of two effects, operating simultaneously as we shall set forth more quantitatively below.

c) At given counterion valency, the flocculation value still depends on the nature of the counterion. It depends on the system how pronounced this effect is. For negative AgI sols, one of the best studied model systems, c_{fl} increases

from $RbNO_3$ to $LiNO_3$, the latter being about 35⁰/₀ higher than the first. This sequence is known as *the lyotropic series* and a discussion of this sequence is the main theme of this article.

Quantitatively speaking, the lyotropic sequence is a less pronounced effect than the valency effect, but it is still very important because it is of a different character. The valence-effect can be explained in electrostatic terms only, but when specific ionic effects occur they must have to do with more subtle things like adsorbability, effect on structure, extent of hydration etc. We shall call them collectively »chemical« effects (although it is realized that they are also basically of electrostatic origin). In these terms the study of lyotropic sequences is useful to outline chemical and electrostatical contributions to double layer interaction. Besides, as lyotropic series occur also in many biological systems their study is also worth while *per se*.

For sake of argument, let us give in Table I some classical flocculation values for silver iodide sols[6].

<div align="center">TABLE I</div>

Flocculation Values in mmoles/l for Negatively Charged AgI-Sols Determined by the Classical Method

Monovalent cations		Bivalent cations		Trivalent cations	
$LiNO_3$	165	$Mg(NO_3)_2$	2.60	$Al(NO_3)_3$	0.067
$NaNO_3$	140	$Ca(NO_3)_2$	2.40	$La(NO_3)_3$	0.069
KNO_3	136	$Sr(NO_3)_2$	2.38	$Ce(NO_3)_3$	0.069
$RbNO_3$	126	$Ba(NO_3)_2$	2.26		

These old results have since been amplified, but it appears that the quoted data are still good enough to serve as an example. The lyotropic sequence for the monovalent counterions is very pronounced. It must be remarked that the AgI-system is one of the best studied systems in this respect.

4) *The D.L.V.O.-Theory*

Let us now turn to a discussion of the classical theory of colloidal stability. The theory is named after Deryagin and Landau, two Russians and Verwey and Overbeek, two Dutchmen, who developed this theory independently during the second world war[7,8]. In this theory, the increase in free energy of the system is calculated when two double layers overlap. Hence, it is a theory which combines electrostatics and thermodynamics.

The electrostatics is based upon the Gouy-Chapman picture of the electrical double layer[9,10] which means that the distribution of ions around colloidal particles is described with the Poisson-Boltzmann equation. This idea was not new because it had already been extensively studied by Debye and Hückel in their famous theory of activity coefficients[11]. The difference between the two approaches lies in the fact that in the D. H. approximation only the linear terms of the series expansion of the exponentials are retained, whereas in the Gouy-Chapman picture the full series is used, at least if the particles are big. In this respect the double layer theory of the D.L.V.O.-theory is an improvement over the D. H.-model.

In passing, one would wonder why Debye and Hückel, working more recently than Gouy and Chapman, did not use the full Poisson-Boltzmann equation. The reason is that the complete analytical solution is only possible for flat double layers. This may be a good model for a colloidal system as long as the particle radii are large as compared with the interparticle distance, but it is certainly no good model for ions. Modern extensions of the D. H.-theory, retaining more terms indeed show some improvement in the obtained theoretical activity coefficients. Verwey and Overbeek, in their monography, give also equations for spherical double layers, these are necessarily more approximative.

As a consequence of the relatively more sophisticated double layer model, the potential (ψ) — distance (x) relation is also more complex than the corresponding equation of the D. H.-theory. It can conveniently be written in terms of hyperbolic functions and reads for a symmetrical electrolyte

$$\tanh \left(\frac{ze\,\psi(x)}{4\,kT} \right) = \tanh \left(\frac{ze\,\psi_0}{4\,kT} \right) e^{-\varkappa x} \tag{1}$$

where e is the elementary charge, k the Boltzmann constant, T the absolute temperature, ψ_0 the surface potential and $\varkappa$ the well known reciprocal Debye length, defined through

$$\varkappa = \left(\frac{4\,\pi e^2\,\Sigma n_i\,z_i^2}{\varepsilon\,kT} \right)^{1/2} \tag{2}$$

in which n_i is the number of ions i per unit volume and ε represents the dielectric constant. It is through this parameter that the influence of indifferent salts is explained: increase of salt concentration and/or increase in valency leads to a higher value of $\varkappa$ and consequently to a compression of the electrical double layer as schematically shown in Fig. 1. This compression provides the physical basis for the interpretation of the influence of salts on the stability of colloids as well as on activity coefficients.

When two particles approach each other, for example by Brownian motion, the two double layers overlap. This leads to an increase in the free energy of the system which is tantamount to saying that the two double layers repel
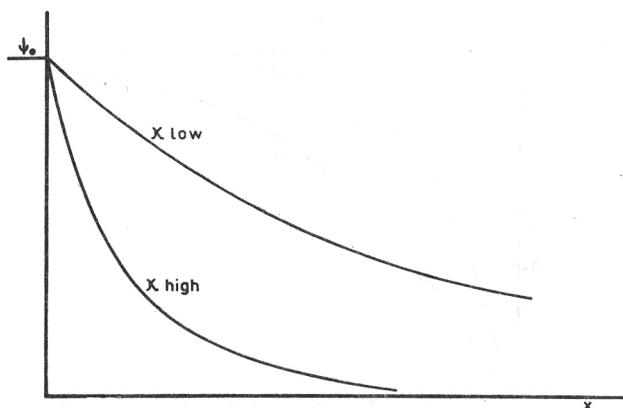

Fig. 1. Potential distribution around colloidal particle according to the Gouy-Chapman picture. 1) c_{salt} and/or z low; 2) c_{salt} and/or z high.

each other, and apparently the more so as the double layers are more diffuse. The higher c_{salt} and z, the lesser the repulsive force at given distance and the more likely it is that the van der Waals attraction between the particles can surmount the repulsion thus causing the particles to agglomerate. The salt concentration and valency that just suffice to obtain flocculation can be calculated from theory. In the D.L.V.O.-theory this is done under some simplifying assumptions, (a. o. the assumption that ψ_0 remains constant during the encounter between the particles and the assumption that the overlap is slight enough to consider the potential between two particles as the linear superposition of the potentials of the individual particles). The result for flat double layers is

$$n_{vl} = \frac{107 \, \varepsilon^3 \, (kT)^5}{A_{1\,(2)}^{2} \, (ze)^6} \, \tanh^4 \left(\frac{ze \, \psi_0}{4 \, kT} \right) \tag{3}$$

where $A_{1(2)}$ is the Hamaker — van der Waals constant of particles 1 in medium 2 and n is expressed in molecules/cm³, whereas

$$n_{vl} = \frac{49.5 \, \varepsilon^3 \, (kT)^5}{A_{1\,(2)}^{2} \, (ze)^6} \, \tanh^4 \left(\frac{ze \, \psi_0}{4 \, kT} \right) \tag{4}$$

is found for spherical double layers in the approximation of close approach of the particles. More general equations can be written for spherical particles, they are usually more complex and contain the particle radius as a parameter. The equations (3) and (4) are given to show that the influence of particle radius is not very pronounced: a factor of 2 in the coagulation concentration is also obtained by changing to a different stability criterium or by a variation of $\sqrt{2}$ in the Hamaker constant.

It is instructive to consider the potential dependency of n_{vl} in some more detail. The hyperbolic tangent can be expanded in a series:

$$\tanh y = y - \frac{y^3}{3} + \frac{2y^5}{15} - \dots \tag{5}$$

schematically represented in Fig. 2. If ψ_0 is high, the hyperbolic tangent approaches unity. In that case, n_{vl} is inversely proportional to z^6, as discussed
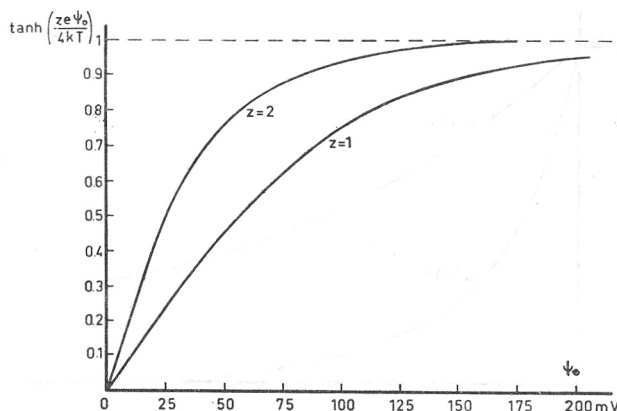

Fig. 2. The relation between the hyperbolic function in the stability equation and the surface potential.

above in section 3. However, in actual cases, under flocculation conditions the effective potential to be inserted in the equation is not ψ_0 but the potential ψ_δ of the diffuse part of the double layer. This will be discussed at length in section 5 but for the moment it suffices to state that ψ_δ is usually so low that the low-potential linear relation is a better approximation whence

$$n_{vl} = \frac{0.418 \, \varepsilon^3 \, kT \, \psi_\delta^4}{A_{1\,(2)}^2 \, (ze)^2} \tag{6}$$

predicting a z^{-2} dependence rather than the z^{-6} relationship mentioned before.

5) *Specific Ionic Effects*

The Gouy Chapman theory is better than the Debye — Hückel approximation but it is still not yet good enough for colloidal stability. The main objection is, that on the basis of this picture lyotropic sequences can not be explained. In equations (1) and (3) the only occurring ionic property is the valency z, but distinction between, say lithium and rubidium can not be made.

The physical reason behind this lack of discrimination is that in the Poisson-Boltzmann picture ions are considered as point-charges, adsorbed through electrostatic forces only. This may be a good approximation if the ionic concentrations are low, (that is in the region far from the particle, especially when c_{salt} is low), but it does certainly not hold close to the surface where potentials are high. Besides this, there are a number of other defects having to do with the electrostatic fundamentals of the model. There are two ways to correct for them.

The first approach is to correct the basic Poisson-Boltzmann equation, the second approach boils down to taking specific adsorption and ion size into account only in the first ionic layer, adjacent to the surface. The first method is principally perhaps the most attractive, but mathematically almost untreatable. It has recently been discussed by Levine[12] who showed that if the major correction, specific adsorption, may be neglected, the other corrections tend to cancel each other, as a result of which the Poisson-Boltzmann equation remains a good approximation till moderate potentials and salt concentrations. The second approach, suggested by Stern[13] is theoretically perhaps less attractive, but more effective. Specific adsorption will occur only in the immediate neighbourhood of the particle surface. Also, the finite ion size prevents counterions of approaching the surface more closely than the radius of the (hydrated) ion, thus providing for a charge-free layer in which the potential drops linearly with distance. Due to this ion size effect, either or not in conjunction with specific adsorption, a potential drop close to the surface is attained that is so steep that the remaining potential is low enough to warrant the applicability of the Poisson-Boltzmann equation. In this picture, the double layer is split up into two parts, a thin layer of a few Å-units thick on the surface and an extended diffuse double layer part farther away. These two double layer parts are usually known as the *Stern-layer* and the *Gouy-layer*. The potential drop is schematically shown in Fig. 3.

The Stern-layer is the virtual region for specific ionic effects: any influence of the nature of the solid, physical and structural effects as well as chemical interactions occur in this layer. More to the point, the Stern
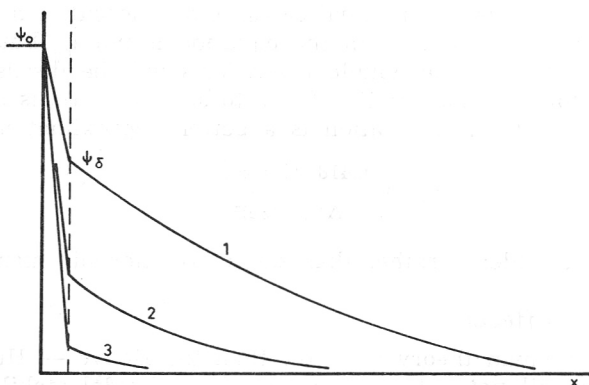
Fig. 3. Potential distribution in Gouy-Stern double layer: (1) low salt concentration, no specific adsorption; (2) high salt concentration, some specific adsorption; (3) high salt concentration, strong specific adsorption.

theory provides a direct interpretation of the observed trends in the stability: the lyotropic sequence and the Schulze-Hardy rule. It should first be realized that the stability equations of section 4 remain valid, but now with ψ_δ instead of ψ_0 because stability is determined by the diffuse part of the double layer only*.

Going from a monovalent to a bivalent counter ion two things occur: z changes from 1 to 2 and ψ_δ decreases because bivalent ions tend to adsorb specifically more strongly than monovalent ones, at least on silver iodide and oxides, belonging to the most extensively studied colloidal systems. Substitution of reasonable values for ψ_δ (instead of ψ_0) in eq. (3) shows that in this way very easily c_{fl} ratios are found that agree with experiment. Consider for example the $KNO_3/Ca(NO_3)_2$ ratio for AgI-sols which according to Table I is $136/2.40 = 57$. According to eq. (3)

$$57 = \left[\frac{\tanh \dfrac{e\psi_\delta \, (Ca)}{2\,kT}}{\tanh \dfrac{e\psi_\delta \, (K)}{4\,kT}} \right]^4 \cdot \left(\frac{2}{1} \right)^6$$

ψ_δ (K) is of the order of -30 mV, which enables ψ_δ (Ca) to be calculated as -14 mV. One might argue that a reduction from 30 to 14 mV is a considerable effect, but that is not the proper way to look at it. It is the potential drop in the Stern-layer, $(\psi_0 - \psi_\delta)$ that is governed by specific adsorption. As $\psi_0 \sim -300$ mV the above calculation says that $\psi_0 - \psi_\delta$ increases by about $6^0/_0$.

The lyotropic sequence is directly explained by Fig. 3, curves 2 and 3. Specific adsorption leads to ψ_δ -values changing with the nature of the cation, which in turn affects n_{vl}.

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* The assumption that ψ_δ remains constant during particle encounter is then implicitly made. This is not correct, but it can be proven that under the conditions we are discussing the »constant potential« and »constant charge« model yield almost identical results.

This discussion shows also that a general bivalent/monovalent ratio must not be expected, because as a rule specific adsorption depends on the specific nature of counterion-surface interaction and this depends on the nature of the dispersed phase. As long as there is a lyotropic sequence, there is specific adsorption and are specific adsorption and valence *simultaneously* responsible for stability against salts. Therefore it is clear that the study of lyotropic effects helps to find the limits of applicability of the non-specific stability theory.

6) *Quantitative Studies*

The principles, discussed above may be considered as the basic theory for the interpretation of valence influences and lyotropic effects on stability. A number of attempts have been undertaken to study these trends quantitatively. As they have been published or will be published soon we shall in this instance not discuss them at length but give only a rough outline to indicate in which way the problem can be attacked.

One approach involves double layer studies at elevated temperatures[14]. It was found that at 85^0 C the surface charge and the flocculation value for negative AgI-sols are independent of the nature of the cation. This was attributed to desorption of the cations from the Stern-layer due to the increased thermal motion. In that case, the Gouy-Stern theory without specific adsorption may be applied. The surface charge σ_0 equals the charge of the diffuse part of the double layer, σ_d (except for the sign). The Gouy theory relates ψ_δ to σ_d through

$$\sigma_d = \sqrt{\frac{2 \varepsilon \, n \, kT}{\pi}} \, \sinh \left(\frac{e\psi_\delta}{2 \, kT} \right) \qquad (7)$$

from which ψ_δ can be found. Substitution of ψ_δ for ψ_0 in eq. (3) then yields $A_{1(2)}$ at 85^0 C. It was supposed that $A_{1(2)}$ does not depend strongly on T, hence the same value was used at 25^0 C. At 25^0 there is specific adsorption. If the Stern layer charge is σ_m:

$$-\sigma_0 = \sigma_m + \sigma_d \qquad (8)$$

In this equation σ_0 follows from epxeriment and σ_d can be derived from stability using again equation (3) and (7). In this way the specifically adsorbed amount was found. Going one step further, and applying a Langmuir-type adsorption equation, specific adsorption energies for Rb^+, K^+ and Li^+ of 2.9 kT; 2.5 kT and 2.1 kT respectively were found. The specific adsorption energy and the electrostatic adsorption energy in the Stern-layer appeared to be of the same order of magnitude.

Another approach involves the replacement of counterions due to adsorption of neutral molecules like butanol[15]. In this case there is a tendency for the lyotropic effect to decrease with increasing butanol adsorption. This adsorption has its subtleties, like change in point of zero charge and change in reference plane of attraction and repulsion with respect to each other, but if properly done, it is again possible to find the Stern-charge from a combination of stability and surface charge determination. The analysis shows how this charge decreases with increasing butanol concentration and eventually vanishes, thus yielding again a non-specific system in which the

stability is governed by electrostatic effects only. Bivalent cations adsorbing more strongly are much more difficult to replace than monovalent ones.

It is expected that experiments of this kind will contribute to our knowledge of colloidal stability. It is especially interesting to compare specific effects on different systems, because this can give a clue to the understanding of the counterion-surface interaction. For example, it was recently found by Breeuwsma in our laboratory that on negative hematite (α-Fe_2O_3) Li^+ ions adsorb more strongly than K^+ or Rb^+ ions, *i. e.* just the other way round as on AgI. This must have to do with the fact that the radius of the Li^+-ion is almost equal to that of Fe^{3+}. At any rate, the study of specific ion effects in colloidal stability remains an interesting field of investigation.

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IZVOD

Liotropni niz u stabilnosti hidrofobnih koloida

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Pojava liotropne serije, tj. povećavanja flokulacione koncentracije za negativno nabijeni argentum jodid sol u nizu Rb^+, K^+, Na^+, Li^+ tumači se primjenom teorije stabilnosti koloida po Derjagin-Landau-Verwey-Overbeeku. Dok se efekt valencije koagulacionog iona može protumačiti elektrostatskim efektima, liotropni efekti ovise o adsorbabilitetu, strukturi i hidrataciji iona. Stoga se liotropni efekt, iako u osnovi elektrostatički, može ipak kolektivno nazvati *kemijskim* efektom. Model elektrokemijskog dvosloja po Sternu dozvoljava direktnu interpretaciju specifičnih ionskih efekata i Schulze-Hardieva pravila. Eksperimentalni podaci o flokulaciji negativnih AgJ solova kod povišene temperature ili u miješanim otapalima (butanol-voda), gdje dolazi do desorpcije kationa, aproksimacija dvosloja daje na bazi Gouy-Chapmanove teorije jednako zadovoljavajuće rezultate.

Daljnji eksperimentalni podaci, koji će poslužiti saznanjima o teoriji koloidne stabilnosti, dobit će se uspoređivanjem specifičnih ionskih efekata na različitim sistemima, posebno na oksidnim.

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