THE RULE OF SCHULZE AND HARDY

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Abstract - In a brief historical survey various attempts to explain the
rule of Schulze and Hardy are mentioned. It is argued that the inverse
proportionality between the coagulation concentration and the sixth power
of the charge number of the counterion, as it has been derived from the
DLVO theory, cannot be the complete explanation, since as a rule potentials
in the Gouy layer are not high enough. It is shown that a combination of
van der Waals attraction and electrostatic repulsion can explain the rule
of Schulze and Hardy, if adsorption of counterions in the Stern layer is
taken into account. The adsorption potential must then increase fairly
strongly with the charge of the counterion. Structural forces (due to the
molecular structure of the solvent) may be important, but the quantitative
theory of these forces has not yet been sufficiently developed to
incorporate them in the theory of coagulation.

INTRODUCTION

In 1882 Schulze (1) pointed out that the coagulating power (on As_2S_3 and other sols) of salts
increased very strongly with the charge number of the cations. Somewhat later Hardy (2)
widened the statement to include positively charged sol particles for which the coagulation
is sensitive to the charge of the anions. He also gave a quantitative formulation of what
later would be called the rule of Schulze and Hardy. According to Hardy the coagulation
concentrations (*c.c*) of mono-, di- and tervalent coagulating ions are in the ratio of 1 to x
to x^2 where x is about 1/30 to 1/40 or, with z as the absolute value of the charge number,

$$\log c.c.(z) = a - bz \tag{1}$$

where b is a positive constant.
With Whetham (3) he also gave a theoretical interpretation of this relation, which nowadays
does not sound very convincing.
Hardy knew that colloid stability is lost when the particles are brought to the isoelectric
point. Based on more precise data Ellis (4) and Powis (5) found that a critical electrokine-
tic potential (ζ_{crit}) exists below which lyophobic sols are unstable. ζ_{crit} varies around
25-30 mV, but often monovalent coagulating ions form an exception with coagulation occurring
at higher values of ζ (50 mV or more).
Freundlich (6) combined the idea that coagulation requires discharge of the sol particles to
the same extent with the assumption, that the adsorption isotherms of the coagulating ions
are about identical if expressed on a *molar* scale. Since the discharge requires adsorption
of the same number of *equivalents*, and since the adsorption isotherm is curved, coagulation
occurs at a lower concentration, the higher the charge of the ions. Quantitatively the use
of Freundlich's adsorption isotherm leads to:

$$\log ads \text{ (in moles/area)} = p + \frac{1}{n} \log c \text{ (in moles/vol)}$$

or

$$\log \frac{ads \text{ (in equiv/area)}}{z} = p + \frac{1}{n} \log c \text{ (moles/vol)}$$

or $\qquad \log c.c.(z) = const. - n \log z \tag{2}$

In the late thirties and early forties other interpretations of the Schulze Hardy rule
(S.H. rule) were given.
Wo. Ostwald (7) postulated constancy of the activity coefficient of the counterion at the
coagulation concentration.

$$\log f_z = - Bz^2\kappa = - Dz^3(c.c.)^{\frac{1}{2}} = constant \tag{3}$$

where κ is the inverse Debye length and B and D are constants.
Težak (8) derived an equation

$$\log c.c.(z) = \text{const} - bz \tag{4}$$

using the concept of Bjerrum's critical distance $(z_+z_-e^2/8\pi\epsilon\epsilon_0 kT)$ for the formation of ion pairs.
Eilers and Korff (9) suggested that a combination of the Debye length $(1/\kappa)$ and the ζ-potential, having the dimension of an energy, should govern the $c.c.$ and they found:

$$\zeta^2/\kappa = \text{constant at the } c.c. \tag{5}$$

Even if this relation would always be satisfied, it leaves the question open, how ζ depends on c and z, and therefore, how the S.H. rule has to be explained.
All the above mentioned authors have realized that within one charge group (e.g. the alkali ions) small and sometimes not so small variations of the $c.c.$ occurred, and that charge and nature of the co-ions were not without some influence on the $c.c.$ These variations make it more difficult to choose amongst the various equations on the basis of empirical data. Moreover, probably none of these equations reflects the data precisely.

STABILITY OF COLLOIDS BASED ON FORCES BETWEEN PARTICLES

Great progress in the understanding of colloid stability became possible after Kallmann and Willstätter (10) drew attention to the long range character of the van der Waals attraction between colloid particles and especially after de Boer (11) and Hamaker (12) gave explicit equations for the attraction between two plates and between two spheres.
Combining this long range attraction with the long range repulsion caused by the overlap of electric double layers, Derjaguin and Landau (13) and Verwey and Overbeek (14) worked out a theory of colloid stability. The key notions in this theory are the facts that the van der Waals force decays as an inverse power of the distance, H, between the particles, whereas the electrostatic repulsion decays exponentially as $\exp(-\kappa H)$, in which κ is proportional to $z\sqrt{c}$. The free energy of interaction, V, between two particles, when plotted against the distance between their surfaces gives curves as shown in Fig. 1. When V_{max} is high enough the
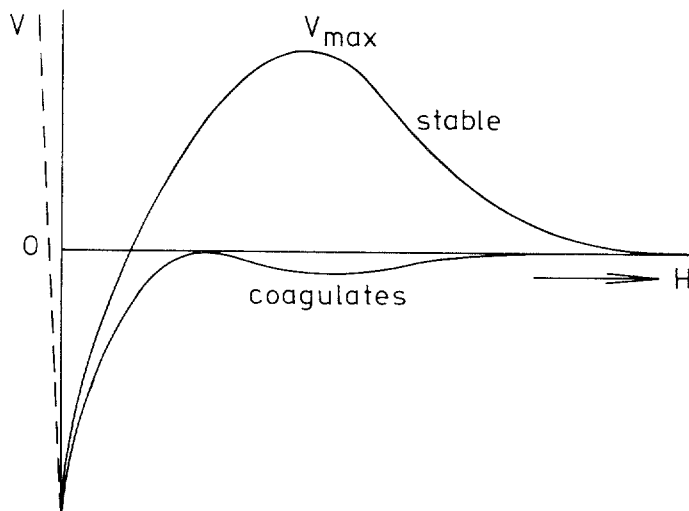

Fig. 1.   Schematic picture of the free energy of interaction between two particles.

curve represents a stable system. Increasing the concentration and/or the charge number of the counterions shortens the range of the repulsion and decreases V_{max}. The system coagulates when V_{max} is small compared to kT and the coagulation concentration can in principle be found from the condition $V = dV/dH = 0$.
Using the relations for the interactions of two parallel thick plates separated by a gap H, coagulation conditions are easily derived. For the attraction energy per unit area we have:

$$V_A = -\frac{A}{12\pi H^2} \tag{6}$$

where A, the Hamaker constant is proportional to the London constant λ and the square of the number density of molecules q $(A = \pi^2 q^2 \lambda)$. The influence of the medium between the plates can be taken into account (12).

If we describe the electric double layers as pure Gouy-Chapman double layers with a surface potential, ϕ_0, the repulsion energy per unit area is:

$$V_R = 2\kappa\varepsilon\varepsilon_0 \ \left(\frac{4RT}{zF} \gamma\right)^2 \ e^{-\kappa H} \tag{7}$$

where for symmetrical electrolytes

$$\kappa^2 = 2z^2 F^2 c / \varepsilon\varepsilon_0 RT \tag{8}$$

$$\gamma = \tanh(zF\phi_0/4RT) \tag{9}$$

with ε = dielectric constant of the medium, ε_0 = permittivity of the vacuum = 8.854×10^{-12} $CV^{-1}m^{-1}$, and R, T and F have their usual meaning.

Applying the condition $V = dV/dH = 0$ to the total free energy of interaction

$$V = V_R + V_A \tag{10}$$

we find easily that

$$\kappa H = 2 \tag{11}$$

and

$$c = \frac{3^2 2^{11} (4\pi\varepsilon\varepsilon_0)^3 (RT)^5 \exp(-4)}{\pi F^6} \frac{\gamma^4}{A^2 z^6} \tag{12}$$

When this relation had been found the explanation of the S.H. rule seemed obvious. γ, being a tanh, could be considered a constant at high ϕ_0 and thus cz^6 = constant. This agreed with Freundlich's equation (2) for $n = 6$, with Ostwald's equation (3) and moreover when ϕ_0 is not high, but so low that $\tanh(zF\phi_0/4RT) \approx zF\phi_0/4RT$ eq. (12) reduces to the Eilers and Korff relation (5) if we identify ϕ_0 with ζ. This all was made easy by the fact that the Hamaker constant, A, could justifiably be considered as an adaptable parameter. Values of A calculated from c.c.'s were of a reasonable order of magnitude, although somewhat on the high side.

However, in the course of the years it became obvious that the theory required several refinements and then the interpretation of the S.H. rule was not so obvious any more. After the publications by Lifshitz and his coworkers (15) on the dispersion forces in condensed matter, and after Parsegian, Ninham (16) and others (17,18) showed how numerical values for A could be derived from Lifshitz' complicated equations with the help of limited optical data, the Hamaker constant ceased to be a widely adaptable parameter. Furthermore realistic models of the double layer had to include ion size, as was done in the Stern (19) theory. This theory indicated that, at least in coagulation conditions, ϕ_0 in γ was rather low than high, and then eq. (12) brought us back to the Eilers and Korff relation with the vexing question how ζ or ϕ_0 in γ depends on c and z. Before we dive more deeply into this problem, we first have to mention a recent development of another nature.

STRUCTURAL FORCES

The notion that near an interface the solvent has a structure differing from that in the bulk and that this solvation might influence the interaction between particles at short distances is not new. In recent years, however, it has been set on a new footing by Ninham and coworkers (20) and by van Megen and Snook (21). They argue that the disturbance of the packing of a liquid near a "wall" stretches out over several (5-10) molecular diameters and that the overlap of two such disturbances leads to a force, which at short distances is large compared with the van der Waals force, especially if the Hamaker constant is low, as in lipid-water systems. Modern theories of liquids can in principle be applied to these structural effects. Unfortunately, there is still a good deal of argument about the size and range of these structural forces. It is even not certain whether they decay monotonously or with pronounced oscillations. Especially for water, for which it still is impossible to derive bulk properties from a priori models, the structural forces can only be dealt with qualitatively. It is too early to try to incorporate them in a theory of colloid stability, but one may hope that since stability is governed mainly by the interaction at fairly large distances (eq. (11), $\kappa H = 2$), structural forces may be neglected in a first approximation, unless A is very small. Pending further developments in this field, we shall therefore now attempt to analyze the van der Waals-electrostatic theory of colloid stability, taking care to include the necessary refinements.

FURTHER ANALYSIS OF THE RELATION BETWEEN COLLOID STABILITY AND
ELECTROSTATIC AND VAN DER WAALS FORCES

The rule of Schulze and Hardy is found very generally for hydrophobic colloids. Lyotropic
influences and effects of co-ions lead only to minor quantitative changes. Therefore we shall
neglect all these specific effects and only invoke the charge number of the counterions in
our analysis. This does not mean that we may forget adsorption of these ions in the Stern
layer, only that the extent of this adsorption should be determined by z and c. We must take
the fact that ions have a finite size into account and this leads us to the choice of the
Gouy-Stern double layer as our model. As Fig. 2 shows, this model implies that the van der
Waals attraction acts over a distance H and the repulsion over a distance $H - 2\Delta$, with ϕ_d,
the potential at the transition between Gouy and Stern layers acting as the surface potential
in eqs. (7) and (9). It can be proved (Ref. 14, p.126) that the distribution of charge
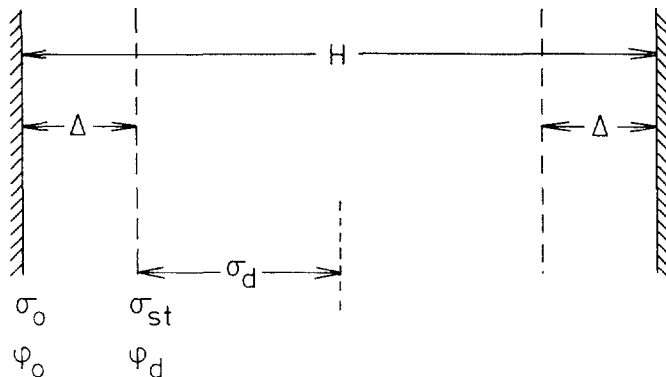between the two layers changes very little during the approach of two particles.

Fig. 2. Notation for distances, surface charge densities and potentials
in the interacting double layers of two particles. For spherical particles
H is the shortest distance between the surfaces. The potential, ϕ, is zero
in the bulk of the liquid far away from any particle.

The coagulation condition (eq. 12) has to be modified by introducing the distance Δ into it
and by replacing ϕ_o in eq. (9) for γ by ϕ_d. Furthermore we shall use equations for spherical
particles rather than for flat plates, since this allows us to discuss where the particle
size enters into the picture.
We must now realize that $c.c.$'s are in the order of 10-200 mM for $z = 1$, 0.2-2 mM for $z = 2$
and 0.1 mM or less for $z = 3$ (see Ref. 22).
Furthermore, Hamaker constants across water as the dispersion medium are in the range
$A = 0.5 - 5 \times 10^{-20}$ J for salts and oxides, $A = 5 - 30 \times 10^{-20}$ J for metals (18), and
$A = 0.3 - 1 \times 10^{-20}$ J for hydrocarbons. In this latter case A is not strictly constant, but
varies with H even for non-retarded forces (see Ref. 16). When we use these figures in the
coagulation relation (eq. 12) and its modifications, we find that $z\phi_d$ is in the range of
10-90 mV, which leads to values of σ_{Gouy} of 2-20 μ C cm^{-2} for $z = 1$, 0.1-1 μ C cm^{-2} for
$z = 2$, and < 0.2 μ C cm^{-2} for $z = 3$.
Combining these values with the knowledge that analytical surface charge densities, σ_o, vary
from a few to perhaps 50 μ C cm^{-2} (AgI in water has $\sigma_o = 4-5$ μ C cm^{-2}, and this is a low
value, when compared with other substances), it is clear that, certainly for multivalent
counterions, a substantial part of the charge must be in the Stern layer, in which also a
substantial fraction of the total potential drop, ϕ_o, occurs. Since the potential drop in
the Stern layer (strictly, between the interface and the inner Helmholtz plane) is
proportional to σ_o, it makes little difference whether we assume σ_o or ϕ_o to be independent
of the concentration of non-potential determining electrolytes, or make any assumption
between these two extremes. For simplicity we choose σ_o = constant for the rest of our
analysis.

QUANTITATIVE ASPECTS

A quantitative theory for the S.H. rule for spherical particles contains the following
elements.
1. The free energy of interaction, V, between a pair of spheres of radius a.
2. Derived from it (using $V = dV/dH = 0$) the coagulation relation between c, z and ϕ_d
(modified eq. 12).
3. A relation between σ_o, c, z and ϕ_d based upon the chosen model of the double layer.

These elements give two fairly complicated relations between c, z and ϕ_d. Using numerical work it is not too difficult to eliminate ϕ_d and find the S.H. rule expressed as a non-analytical relation between c and z.

Van der Waals attraction

Hamaker [12] gave the energy of attraction V_A between two equal spheres of radius a at a distance H between their surfaces.

$$V_A = -\frac{A}{6}\left(\frac{2a^2}{H(4a+H)} + \frac{2a^2}{(2a+H)^2} + \ln\frac{H(4a+H)}{(2a+H)^2}\right) \tag{13}$$

For small distances ($H \ll a$) eq. (13) can be approximated as

$$V_A = -\frac{Aa}{12H} \tag{14}$$

but due to the logarithmic term in eq. (13) this is rather a bad approximation. It is already off by 9% at $H = 0.01\,a$ and by 70% at $H = 0.1\,a$. A very much better approximation is:

$$V_A = -\frac{A}{12}\left(\frac{L}{H} + 2\ln\frac{H}{L}\right) \tag{15}$$

where $L = a + \frac{3}{4}H$. It is off by only 1.4% at $H = 0.1\,a$

Electrostatic repulsion

The free energy of repulsion, V_R, between two particles is given by:

$$V_R = 2\pi\varepsilon\varepsilon_o(a+\Delta)\left(\frac{4RT\gamma}{zF}\right)^2 e^{-\kappa(H-2\Delta)} \tag{16}$$

with $\gamma = \tanh(zF\phi_d/4RT)$. When ϕ_d is small ($z\phi_d < 100$ mV), V_R may be approximated by:

$$V_R = 2\pi\varepsilon\varepsilon_o(a+\Delta)\phi_d^2\, e^{-\kappa(H-2\Delta)} \tag{17}$$

These equations are good approximations for $\kappa a \gg 1$ and $\kappa(H-2\Delta) > 1$ and not bad down to $\kappa(H-2\Delta) = 1$.

Coagulation condition

Combining eqs. (15) and (16) to the total free energy of interaction $V = V_A + V_R$ and applying the condition $V = dV/dH = 0$ leads to:

$$\kappa H = 1 - \frac{1}{\kappa a}\left(\frac{11}{4} - 2\ln \kappa a\right) + O\left(\frac{1}{\kappa a}\right)^2 \tag{18}$$

and

$$c = \frac{3^2 2^7 \exp(-2)(4\pi\varepsilon\varepsilon_o)^3 (RT)^5}{\pi F^6} \frac{\gamma^4}{A^2 z^6}\left(1 - \frac{3}{2\kappa a} + \frac{4}{\kappa a}\ln \kappa a\right)\left(1 + \frac{2\Delta}{a}\right)e^{4\Delta\kappa} \tag{19}$$

Apart from the corrections for Δ and for $1/\kappa a$ this equation differs from eq. (12) by a factor $e^2 2^{-4} = 0.46182$.

Surface charge density

The surface charge density, $\sigma_o = $ (charge on sphere)$/4\pi a^2$, is compensated by the charges in the Stern and Gouy layers.

$$-\sigma_o = \sigma_{st} + \sigma_d \tag{20}$$

For the diffuse charge we have:

$$\sigma_d = -\sqrt{8\varepsilon\varepsilon_o RT}\left(1 + \frac{1}{\kappa a}\right)c^{\frac{1}{2}}\sinh\frac{zF\phi_d}{2RT} \tag{21}$$

and for the charge adsorbed in the molecular condenser:

$$\sigma_{st} = \frac{\pm zF\Gamma_{max}}{1 + \dfrac{55.346 \text{ mol } l^{-1}}{c} \exp(\pm \dfrac{zF\phi_d}{RT} - |\dfrac{\phi_{ads}}{RT}|)} \tag{22}$$

In the $\pm$ signs the upper sign refers to positive counterions, the lower sign to negative counterions.

With Stern (19) we assume that the adsorption obeys a Langmuir type isotherm, in which Γ_{max} represents the amount of adsorption sites per unit area. The adsorbed ions are presumably closer to the surface (in the inner Helmholtz plane, see Grahame Ref. 23) than the last Gouy ions. The adsorption potential, ϕ_{ads}, contains therefore also a contribution $(zF(\phi_{i.H.p.} - \phi_d)$, in addition to a contribution from local effects, but since $\phi_{i.H.p.}$ is greatly model dependent, we shall not attempt to split ϕ_{ads}. We have also assumed that we may neglect the curvature of the surface in σ_{st}.

We have already argued that σ_{st} must be fairly large, even when c is as low as the $c.c.$ for multivalent ions. This can only be attained, if $|\phi_{ads}|$ increases so strongly with z that $c \exp(|\phi_{ads}/RT|)$ remains more or less constant at the $c.c.$ An adsorption potential increasing linearly with z suggests ion pair formation of the counterions with ions of the surface charge. This again would require Γ_{max} to be equal to or even somewhat smaller than the amount of surface charge, σ_0/F.

Relation between c.c. and z

In order to obtain the S.H. relation between c and z by elimination of ϕ_d from the coagulation equation (19) and the charge equations (20, 21 and 22) we have now to introduce numerical parameters. We have chosen water at 25°C with $\varepsilon = 78.304$ as the dispersion medium. We omitted corrections for particle size, i.e. we assumed $\kappa a \gg 1$ and $a \gg \Delta$. We have made calculations covering a range of values of A (from 0.3 - 30 x 10^{-20} J), with some emphasis on $A = 3 \times 10^{-20}$ J), of the $c.c.$ for monovalent ions (10-300 m mol l^{-1}) of $F\Gamma_{max}$ (from 0.7-50 μ C cm^{-2} and taken to be equal to $|\sigma_0|$). For the thickness of the Stern layer we took $\Delta = 4$ Å. For each combination of A, $c.c.$, and $F\Gamma_{max}$ we fitted adsorption potentials to the equation

$$|\phi_{ads}/RT| = p + qz \tag{23}$$

A fairly narrow range of constants p and q then leads to reasonable values for the $c.c.$'s for di- and trivalent ions. The same equations (19-22) allow, of course, the calculation of ϕ_{ads} from experimental $c.c.$'s.

case 1. No ions in Stern layer

As a starting point we consider the case that there are no ions adsorbed in the Stern layer ($\sigma_{st} = 0$). For low potentials we expect then that the coagulation concentrations are in the ratio $1 : 1/4 : 1/9$ for $z = 1$, 2 and 3. For high potentials these ratios should go to $1 : (1/2)^6 : (1/3)^6$. One should realize, however, that one must go to rather extreme cases to reach these ideal limits.

For $A = 10^{-20}$ J, $c.c.$ ($z=1$) = 30 m mol l^{-1} and $\Delta = 0$ the surface potential is only 17.4 mV but the ratios for $z = 2$ and $z = 3$ are found at $1/4.5$ and $1/12$ instead of at $1/4$ and $1/9$. Choosing $\Delta = 4$ Å changes ϕ_d to 13.8-14.0 mV but the ratios of coagulation concentrations are only slightly changed as should be expected since κ in $\kappa\Delta$ is itself proportional to $(cz^2)^{\frac{1}{2}}$.

TABLE 1. Coagulation at high surface charge density but with $\sigma_{st} = 0$.

A in 10^{-20} J	z	c in m mol l^{-1}	Δ in Å	σ_{st} in μ C cm^{-2}	σ_d	$-\phi_d$ in mV	S.H. relation
30	1	30*	0	0	23.6	161.8	c (1) =
	2	0.629	0	0	23.6	130.5	= 48 c (2) =
	3	0.05717	0	0	23.6	107.5	= 525 c (3)
30	1	100	4	0	18.30	118	c (1) =
	2	0.832	4	0	18.31	120	= 120 c (2) =
	3	0.0645	4	0	18.23	102	= 1550 c (3)

* At $A = 30$ and $\Delta = 0$, $c = 100$ did not lead to a curve of the stable type (see Fig. 1) even with $\sigma_d \to \infty$.

At the other end of the scale even for a surface potential as high as 162 mV (for $z = 1$) the ideal concentration ratio is not yet reached as is shown in Table 1. There it can also be seen that now the introduction of a finite thickness ($\Delta = 4$ Å) of the still empty Stern layer leads to an overshooting of the ideal z^{-6} ratios. This is due to the fact that the $e^{4\kappa\Delta}$ factor in eq. (19), which increases c, has a much greater influence at the high concentration of the monovalent case than at the low concentrations of the multivalent coagulations.

case 2. Stern adsorption potential, ϕ_{ads}, independent of charge number

As mentioned before charge in the Stern layer is needed to explain that the total charge is high at low surface potential, ϕ_d. The simplest case to consider then is a constant adsorption potential, ϕ_{ads}. But, as shown in Table 2, this does not lead to a much greater spreading of the $c.c.$'s. The constant adsorption potential pushes ions to the Stern layer through the $\exp(-|\phi_{ads}/RT|)$ term in eq. (22), but since c decreases faster than z^{-1} according to eq. (19) the net effect is a decrease of the Stern charge with increasing z. This is overcompensated by the influence of the $\exp(\pm zF\phi_d/RT)$ term but the total effect on the $c.c.$'s remains small. Table 2 gives two examples for $A = 3 \times 10^{-20}$ J and $A = 10 \times 10^{-20}$ J. For other values of the parameters the effect of constant ϕ_{ads} is similar.

TABLE 2. Coagulation changes due to an adsorption potential, ϕ_{ads}, independent of z. $F\Gamma_{max} = -\sigma_o$. $\Delta = 4$ Å.

A in 10^{-20} J	z	c in m mol 1^{-1}	$-\dfrac{\phi_{ads}}{RT}$	$-\sigma_o$ in μ C	σ_{st} cm^{-2}	σ_d	$-\phi_d$ in mV	S.H. relation
3	1	100	0	2.0657	0.011	2.055	27.2	c (1) =
	2	16.74	0	2.0657	0.011	2.054	28.5	= 6 c (2) =
	3	3.85	0	2.0657	0.015	2.051	30.1	= 26 c (3)
3	1	100	5.618	5	2.945	2.055	27.2	c (1) =
	2	11.95	5.618	5	3.353	1.647	27.5	= 8 c (2) =
	3	2.533	5.618	5	3.586	1.414	27.5	= 40 c (3)
10	1	100	0	4.568	0.063	4.505	52.7	c (1) =
	2	6.002	0	4.568	0.097	4.471	59.0	= 17 c (2) =
	3	0.593	0	4.568	0.140	4.428	58.8	= 168 c (3)
10	1	100	4.464	10	5.495	4.505	52.7	c (1) =
	2	4.649	4.464	10	6.723	3.282	54.5	= 22 c (2) =
	3	0.5015	4.464	10	7.344	2.658	51.6	= 199 c (3)

case 3. Stern adsorption potential, ϕ_{ads}, increasing with the charge number.
$|\phi_{ads}/RT| = p + qz$

When we allow ϕ_{ads} to increase with z, the calculated spread of the $c.c.$'s becomes larger. If reasonable S.H. concentrations are to be obtained ($c(1)/20 - c(1)/100$ for $c(z=2)$; and $c(1)/400 - c(1)/4000$ for $c(z=3)$) the choice of ϕ_{ads} is limited to a fairly narrow range. It appears to be easy to adapt ϕ_{ads} to all combinations of A, σ_o so as to obtain reasonable values of the $c.c.$. In Table 3 we show two cases to be compared with the examples of Table 2 and a series of five cases where the same values of $|\phi_{ads}/RT| = 2 + 3z$ have been used for the whole range of values of A. The first two examples show how by simply increasing the values of ϕ_{ads} for $z=2$ and $z=3$ $c.c.$'s are obtained that follow the S.H. rule. The other five examples shows that the same set of ϕ_{ads} leads to a somewhat larger spread of $c.c.$'s at high A than at low A, as might be expected from the fact that the Stern potential ϕ_d increases markedly with A. Table 4 gives examples where ϕ_{ads} is chosen strictly proportional with z; thus $\phi_{ads} = qz$. Here also acceptable S.H. concentrations are obtained although the ratio $c(1)/c(2)$ is on the low side for the lower values of A.
The linear relation between ϕ_{ads} and z has been chosen, since the constant term may represent a non specific interaction between the adsorbed ion and the interface, e.g. due to a local disturbance of the water structure. The term proportional to z represents electrostatic interaction with the potential at the inner Helmholtz plane ($\phi_{i.H.p.}$) and also the electrostatic energy in ion pair formation with the ions carrying the surface charge σ_o.

TABLE 3. Coagulation concentrations under the influence of an adsorption potential increasing with z. $|\phi_{ads}/RT| = p + qz$. $FT_{max} = -\sigma_o$. $\Delta = 4 \text{ Å}$.

A in 10^{-20} J	z	c in m mol l^{-1}	$-\dfrac{\phi_{ads}}{RT}$	$-\sigma_o$	σ_{st}	σ_d	$-\phi_d$ in mV	S.H. relation
				in μ C cm^{-2}				
3	1	100	5.618	5	2.945	2.055	27.2	c (1) =
	2	2.101	8.418	5	4.532	0.468	20.2	= 48 c (2) =
	3	0.0885	11.218	5	4.917	0.0844	12.1	= 1130 c (3)
10	1	100	4.464	10	5.495	4.505	52.7	c (1) =
	2	1.375	7.464	10	9.098	0.905	38.0	= 73 c (2) =
	3	0.0599	10.464	10	9.853	0.150	21.9	= 1669 c (3)
0.3	1	123.9	5	1.0	0.316	0.684	8.48	c (1) =
	2	6.093	8	1.0	0.735	0.265	7.34	= 20 c (2) =
	3	0.2484	11	1.0	0.949	0.051	4.66	= 499 c (3)
1.0	1	154.8	5	2.5	1.080	1.420	15.6	c (1) =
	2	4.741	8	2.5	2.071	0.429	13.1	= 33 c (2) =
	3	0.1745	11	2.5	2.426	0.075	8.0	= 887 c (3)
3.0	1	136.5	5	5	2.578	2.422	27.4	c (1) =
	2	2.781	8	5	4.424	0.577	21.4	= 49 c (2) =
	3	0.1036	11	5	4.905	0.096	12.6	= 1318 c (3)
10.0	1	62.38	5	7.5	4.106	3.394	50.8	c (1) =
	2	1.0195	8	7.5	6.819	0.681	34.9	= 61 c (2) =
	3	0.0439	11	7.5	7.389	0.113	20.0	= 1420 c (3)
30.0	1	31.13	5	30	23.411	6.590	96.4	c (1) =
	2	0.2844	8	30	29.239	0.766	53.0	= 109 c (2) =
	3	0.0146	11	30	29.880	0.122	29.5	= 2134 c (3)

In many cases most of the countercharge is in the Stern layer and consequently $\phi_{i.H.p.}$ is not much above ϕ_d. Therefore the ion pair formation is assumed to be the most important portion of the qz term in ϕ_{ads}. The interaction energy E, per mole between counterions and surface ions (assumed to be univalent) is

$$E = -\frac{zeF}{4\pi\varepsilon_o r} \tag{24}$$

where r is the distance between the centers of the two ions and ε an average dielectric constant in the surface region. For $\varepsilon = 40$ and $r = 5$ Å we find:

$$q = \frac{eF}{4\pi\varepsilon\varepsilon_o rRT} = 2.80 \tag{25}$$

a value fitting quite well in the range of values shown in Tables 3 and 4.

TABLE 4. Coagulation concentrations with an adsorption potential of the type $|\phi_{ads}/RT| = qz$. $F\Gamma_{max} = -\sigma_o$. $\Delta = 4$ Å.

A in 10^{-20} J	z	c in m mol l^{-1}	$-\dfrac{\phi_{ads}}{RT}$	$-\sigma_o$ in μ	σ_{st} C	σ_d cm^{-2}	$-\phi_d$ in mV	S.H. relation
0.3	1	106.5	3.7	0.7	0.068	0.632	8.44	c (1) =
	2	7.46	7.4	0.7	0.398	0.302	7.56	= 14.3 c (2) =
	3	0.222	11.1	0.7	0.653	0.047	4.54	= 480 c (3)
1.0	1	126.5	3.7	1.5	0.217	1.283	15.6	c (1) =
	2	5.91	7.4	1.5	1.002	0.498	13.6	= 21.4 c (2) =
	3	0.1575	11.1	1.5	1.432	0.069	7.8	= 803 c (3)
3.0	1	129.2	3.7	3.0	0.646	2.355	27.4	c (1) =
	2	3.62	7.4	3.0	2.298	0.703	22.6	= 36 c (2) =
	3	0.0951	11.1	3.0	2.911	0.089	12.3	= 1358 c (3)
10	1	106.4	3.7	7.5	2.836	4.664	52.8	c (1) =
	2	1.377	7.4	7.5	6.594	0.906	38.0	= 77 c (2) =
	3	0.0414	11.1	7.5	7.394	0.107	19.6	= 2568 c (3)
30	1	47.2	3.7	30	20.27	9.73	105.4	c (1) =
	2	0.347	7.4	30	28.98	1.03	58.0	= 136 c (2) =
	3	0.0140	11.1	30	29.88	0.116	29.1	= 3376 c (3)

NON AQUEOUS MEDIA

In polar organic media (such as the lower alcohols and ketones) and their mixtures with water (24) the coagulation concentrations for monovalent ions are usually much lower than those for the same particles in water. This is in part explained by the lower value of ε in the coagulation equation (19), often combined with a pronounced adsorption of the counterions in the Stern layer. With bi- and multivalent ions this adsorption is so strong that the coagulation can be described as due to charge neutralization based upon ion pair formation. The analytical concentration of the coagulating electrolyte is just equivalent to the surface charge of the particles. The free concentration is extremely low.
In our terminology, in these solvents ϕ_{ads} has very high negative values especially for counterions with $z > 1$. As an illustration we give in Table 5 an example (still for water at 25°C) in which ϕ_{ads} has been taken equal to -11.2 RT and -16.8 RT for $z = 2$ and 3 respectively, leading to very low $c.c.$'s.

TABLE 5. Very high adsorption potentials ($|\phi_{ads}/RT| = 5.618\ z$) lead to very low $c.c.$'s. Water at 25°C. $F\Gamma_{max} = -\sigma_o$. $\Delta = 4$ Å.

A in 10^{-20} J	z	c in m mol l^{-1}	$-\dfrac{\phi_{ads}}{RT}$	$-\sigma_o$ in μ	σ_{st} C	σ_d cm^{-2}	$-\phi_d$ in mV	S.H. relation
3	1	100	5.618	5	2.945	2.055	27.19	c (1) =
	2	0.2631	11.236	5	4.903	0.097	12.61	= 380 c (2) =
	3	0.000853	16.854	5	4.999	0.002	3.77	= 1.17 x 10^5c(3)

CONCLUSION

The Schulze Hardy rule as it is found experimentally with $c.c.$'s decreasing strongly with increase of the counterion charge and at a rather low, but finite ζ-potential (and Stern potential, ϕ_d) requires two elements for its explanation.

1. The interplay between van der Waals attraction and electrostatic repulsion explains that coagulation occurs when $\phi_d{}^4/z^2c$ (more precisely γ^4/z^6c) reaches a certain value and this justifies the Eilers and Korff relation, ζ^2/κ = constant at the $c.c.$
2. Adsorption of counterions in the molecular condenser due to an adsorption potential that increases regularly with the charge number is required to explain the concentrations at which the above critical value of $\phi_d{}^4/z^2c$ is reached. Such an adsorption may be due to the formation of ion pairs with the surface charge groups, but other mechanisms are not excluded.

This interpretation of the S.H. rule contains elements of several previous theories and shows why the coagulation theories of Freundlich (adsorption), Ostwald (z^6c = const.), Težak (ion pair formation) and Eilers and Korff (ζ^2/κ = const.) could fit the facts so well. In particular the Hardy and Težak relation, $\log c.c. = a - bz$, follows from our eqs. (22) and (23) if as a very rough approximation the denominator of eq. (22) is assumed to be constant. It is gratifying that this approach which stresses charge numbers, but neglects specific effects comes to the same conclusion with respect to counterion adsorption as Lyklema's (25) earlier approach which was mainly based on specific (lyotropic) effects.
Two shortcomings of the present development should be noted.
1. For low A, ϕ_d at the $c.c.$ is always low and this agrees with the interpretation of σ_0 as a function of ϕ_0 and c. However, in some cases ζ for monovalent ions is not low at the $c.c.$ (Example: AgI). Could ζ be larger than ϕ_d?
2. When counterions are strongly adsorbed reversal of charge becomes possible above the $c.c.$ With our choice, $FT_{max} = -\sigma_0$, charge reversal is not possible for $z = 1$ but remains possible for $z > 1$. Experimentally charge reversal is not found so regularly, although with $z > 2$ and with solvents with a lower dielectric constant, even for $z = 2$ (Ref. 24), it is rather the rule than the exception. It may be necessary to introduce a value of FT_{max} which is smaller than $-\sigma_0$, or to understand why ion pair formation virtually stops in water when the surface charge is neutralized.
It appears now to be worthwhile to have a fresh look at old data or collect new data on the relation between analytical charge (σ_0), surface potential ϕ_0 (if available), ζ potential (as a substitute for ϕ_d) and coagulation concentration. This might lead to a refinement or replacement of the Stern model used here.
Defects of the theory in quantitative respect might help in obtaining information on structural forces. Comparison of coagulation by monovalent ions, which occurs at small distances of interaction, where structural forces might predominate, with coagulation by multivalent ions where $1/\kappa$ and H at coagulation are large should be particularly helpful for this purpose.

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