

Stability of Dispersions in Polar Organic Media

I. Electrostatic Stabilization

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Electrostatically stabilized sols of silver, silver iodide, α -goethite, and copper phthalocyanine in methanol, ethanol, isopropanol, and acetone have been prepared and characterized. Coagulation concentrations with electrolytes of various charge numbers have been determined in water, in organic solvents containing 0.5% water, and in mixtures of water and ethanol or acetone of various compositions. Coagulation by monovalent counterions is due to compression of the double layer. With bi- and multivalent counterions coagulation is primarily caused by charge neutralization (equivalent coagulation) in media with a high content of the organic solvent, but by compression of the double layer in water-rich media. Charge reversal by bi- and trivalent cations and restabilization of the positive sol have been found for the silver sol in ethanol.

1. INTRODUCTION

A great deal of information is available on the stability of colloidal suspensions in water and also in nonpolar organic solvents. Similar data on suspensions in polar organic media, such as the lower alcohols and ketones, are relatively scarce. A survey of the older literature can be found in Freundlich's "Kapillarchemie" (1). Special mention may be made of the work of Weiser and Mack (2), who have dispersed a variety of solids (HgS , Ag_2S , MnO_2 , and others) in methanol, propanol, and acetone and determined their stability against added electrolytes. More recently Težak and his school (3) and Lyklema and co-workers (4) investigated the stability of silver halides in mixtures of water and organic solvents.

In general it is more difficult to prepare stable organosols than the corresponding

sols in water. Coagulation concentrations are often very low, but it is not at all certain whether the suggested proportionality between the coagulation concentration and the cube of the dielectric constant (5) is of general application.

In order to have more data on which to base an interpretation of the stability of this type of sol, we have investigated a number of colloid materials when stabilized by electric charge in the lower alcohols, acetone, and in their mixtures with water.

2. PREPARATION AND CHARACTERIZATION OF SOLS

In order to draw as much as possible on the experience gained with the preparation and purification of hydrosols, we have prepared our organosols by diluting concentrated and purified hydrosols by up to 199 volumes of organic solvent.

This method was used for sols of silver, silver iodide, and α -goethite in methanol, ethanol, isopropanol, and acetone. Sols of

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copper phthalocyanine (CPC) were prepared by mechanical dispersion of the finely divided dry powder in pure ethanol, in which a dispersing agent had been dissolved.

The sols were characterized with the aid of electron microscopy, analytical centrifugation, chemical analysis, and microscopic electrophoresis. More details on preparation and characterization can be found in (6).

2a. The Silver Sols

The concentrated silver hydrosol was prepared by a variant of the Carey Lea method (7, 8). A mixture of 28 ml of a solution of Na_3 citrate $\cdot 2\text{H}_2\text{O}$ (400 g liter⁻¹) with 20 ml of a solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (300 g liter⁻¹) was prepared. This mixture was added to 20 ml of an AgNO_3 solution (100 g liter⁻¹) under vigorous stirring. The blue-black precipitate of coagulated silver was isolated by centrifugation, redispersed in 40 ml water, and reflocculated with 20 ml of the citrate solution. After four of these coagulation/redispersion cycles, the silver was precipitated with a water/ethanol (1/4 vol/vol) mixture, redispersed in a small volume of water, and reprecipitated with the water/ethanol mixture. After centrifugation the silver was again redispersed in 50 ml water, to yield a concentrated hydrosol containing 25.4 g of silver per liter (=235 mmole liter⁻¹). By dilution up to 99.5 vol% with the organic solvents, stable silver sols could be obtained in MeOH and EtOH. The stability was low, however, when *i*-PrOH or Me₂CO were used as the solvents.

The particle radius, as estimated from electron microscopy or sedimentation, varied from 35 to 60 Å for different preparations. In the hydrosol the particles were spherical and displayed a narrow size distribution. In the organosols some aggregation to doublets and triplets was noted. From chemical analysis of the hydrosol and the conductivity of the supernatant it was

found that the supernatant had a pH of 6.7 and contained 7 mmole l⁻¹ of Na⁺ and 7.89 mEq liter⁻¹ of citrate. 10.11 mEq liter⁻¹ of citrate was adsorbed on the silver, 2.61 mmole liter⁻¹ of Na⁺ formed the counterions, the remainder of the charge of 10.11 mEq liter⁻¹ citrate being compensated by H⁺ and Ag⁺ on the metal.

The net surface charge of the silver is negative and amounted to -252 C liter⁻¹, or for spherical particles of 60-Å radius to -20.8 μC cm⁻². Electrokinetic charge densities, as calculated from the ζ-potential of the dilute organosols, were very much lower, varying from -0.2 to -0.5 μC cm⁻².

2b. The Silver Iodide Sols

AgI sols were prepared as described by H. de Bruyn (9). Five hundred milliliter of 0.1 M AgNO_3 was added slowly to an equal volume of 0.11 M KI under vigorous agitation. The salt concentration was reduced to about 0.1 mM by dialysis against double-distilled water in Visking dialysis tubing Type 36/32. Subsequently the sol was electro-dialyzed in a five-chamber electro-dialyzer between Sartorius cellulose-acetate membranes, Type SM 11736, pore size < 50 Å at a current density of about 0.1 mA cm⁻² membrane surface. When the conductivity became constant the sol was electrode-canted to a volume of 200 ml. Five such batches were combined, and electro-dialysis and electrode-cantation were repeated until pI = 6 and the AgI concentration was 500 mmole liter⁻¹. This stock sol was aged for 3 days at 80°C. During this aging process the sol coarsened, iodide was desorbed, and the pI decreased to about pI ≈ 4.

Stable organosols could be prepared by dilution to 99.5% by volume with MeOH, EtOH, *i*-PrOH, and Me₂CO. From a conductometric titration with NaOH and pH and pI measurements of the supernatant of the stock hydrosol we were able to calculate a total of 1.16 mEq liter⁻¹ of titratable

H⁺ ions. Of this total 0.16 mEq liter⁻¹ was present as HI in the intermicellar liquid and 1.00 mEq liter⁻¹ compensated the surface charge which was thus due to an excess of 2 μ Eq I⁻ mmole⁻¹ AgI.

The determination of the particle size and the specific surface area in AgI sols is subject to difficulties, as recently reviewed by Koopal (10). We found an average particle radius of 960 Å from sedimentation experiments, corresponding to a specific surface area of about 5.5 m² g⁻¹ AgI. With this surface area a specific surface charge density of $\sigma = -14.9 \mu\text{C cm}^{-2}$ is calculated. This value is about 4 or 5 times higher than literature values for similar AgI suspensions that were based on the electric capacity of the double layer.

We conclude that the actual specific surface area of our AgI must have been about 20–25 m² g⁻¹ and that the average radius of the particles is about 250 Å.

2c. The Goethite (α -FeOOH) Sols

The concentrated hydrosol was prepared by following the method of Dousma and de Bruyn (11). A 0.625 M solution of Fe(NO₃)₃·9H₂O was titrated very slowly under agitation with 2.08 M NaOH, injected through a capillary until the pH reached a value of about 2. The sol was dialyzed against double-distilled water for 10 days and concentrated by vacuum distillation at 28°C. During the dialysis the pH rose from 2 to 5.2.

After dialysis and concentration the composition of the sol was: [α -FeOOH] = 520 mM, [NO₃⁻] = 29.9 mM, [Na⁺] = 0.033 mM, pH = 5.2. The nitrate ions obviously serve as the counterions for the positive charge of the goethite particles. This implies a surface charge of 0.65 mEq g⁻¹ FeOOH = 63 C g⁻¹ FeOOH.

Since at pH 5.2 the hydrosol already showed signs of gelation and dilution with organic solvents led to immediate coagulation, the surface charge was increased by

adding HNO₃ to reach pH = 3.8. Now upon dilution with 199 volumes of the four organic solvents, stable sols were formed, although the stability in i-PrOH and Me₂CO was low. The stock sol of α -FeOOH had the following composition: [α -FeOOH] = 520 mM, [NO₃⁻] = 46 mM, [Na⁺] = 0.033 mM, pH = 3.8, conductivity κ (25°C) = 1.04·10⁻³ Ω^{-1} cm⁻¹.

Electron micrographs of a sol that was aged for 2 months at room temperature showed two types of particles, very small spherical particles with an estimated radius of 25 Å and groups ("rafts") of long rods with a length of about 400 Å and a diameter of about 50 Å. Ultracentrifugation showed only the small particles with a radius of 35 Å. The specific surface area is rather uncertain given the presence of two groups of particles, but must be in the order of 200 m² g⁻¹ FeOOH. This leads to a surface charge density of the stock sol of about 50 $\mu\text{C cm}^{-2}$ FeOOH.

2d. Copper Phthalocyanine (CPC) Dispersions

CPC was supplied to us by Dr. A. Topham (ICI, Organics Division) as a finely divided powder in the β -form. The BET surface area was 29.9 m² g⁻¹. CPC stock dispersions were prepared in capped glass vials by mixing 1.0 g CPC, 0.23 mEq of a stabilizing agent, and 8.7 g EtOH with 17.5 g of 3-mm-diameter Ballotini glass beads and shaking the mixture overnight. For coagulation experiments the stable dispersion thus obtained was diluted 200-fold with EtOH to a final concentration of 0.5 g CPC liter⁻¹.

Sedimentation analysis led to an average particle radius of 1160 Å and a specific surface area of 16.2 m² g⁻¹ CPC. The shape of the particles is roughly spherical. The stabilizing agents used by us were CPC SO₃H-DEEPO and CPC SO₃H-TEAH. CPCSO₃H is a sulphonated CPC with 1.3 mole SO₃H mole⁻¹ CPC. DEEPO is diethyl-

TABLE I
Dissociation Percentages for LiNO₃
in Pure Organic Solvents^a

c	MeOH	EtOH	i-PrOH	Me ₂ CO
10 ⁻⁶	100	100	100	98
10 ⁻⁵	100	100	98	87
10 ⁻⁴	99	100	88	53
10 ⁻³	99	99	59	23
10 ⁻²	92	94	31	9
10 ⁻¹	66	87	17	3.5

^a The concentrations, *c*, are given in equiv liter⁻¹. Temperature 25.0°C.

aminoethanol polypropyleneoxide, MW 806, and TEAH is tetraethylammonium hydroxide.

3. DISSOCIATION OF ELECTROLYTES

Electrolytes are less completely dissociated in organic solvents than in water due to the lower dielectric constants of these solvents. We have estimated the degree of dissociation from conductivity measurements. The interpretation of these conductivity data is difficult, since even for 1/1 electrolytes the influence of the

ionic atmospheres on activity and mobility and the incomplete dissociation have to be taken into account. We have used Shedlovsky's method (12) for describing the concentration dependence of the mobilities and the law of mass action with calculated Debye-Hückel activity coefficients for the dissociation. From the thermodynamic dissociation constant thus found we calculated degrees of dissociation as shown in Table I.

The analysis of the conductivity of non-symmetric electrolyte solutions is complicated by the large Debye-Hückel effects and especially because the mobility of intermediate ions such as MgNO₃[±] must also be estimated from the measurements.

The calculated degrees of dissociation are therefore less accurate for nonsymmetric electrolytes than for 1/1 electrolytes. Table II summarizes the degrees of dissociation in the relevant concentration range. We estimate the accuracy of these figures at 10–20%.

We also determined some conductivities in organic solvents with 0.5 vol% water added. For MeOH and EtOH this had only

TABLE II

Degrees of Dissociation for the First (α_1), Second (α_2), and Third (α_3) Stages of Dissociation in Percentages for Mg(NO₃)₂, Ca(NO₃)₂, and La(NO₃)₃ in Pure Organic Solvents^a

c	MeOH			EtOH			i-PrOH			Me ₂ CO		
	α_1	α_2	α_3	α_1	α_2	α_3	α_1	α_2	α_3	α_1	α_2	α_3
Mg(NO₃)₂												
10 ⁻⁵	100	100	—	100	70	—	70	0	—	100	10	—
10 ⁻⁴	100	99	—	90	30	—	50	0	—	35	0	—
10 ⁻³	100	90	—	60	10	—	25	0	—	10	0	—
Ca(NO₃)₂												
10 ⁻⁵	not determined			90	0	—	25	0	—	not determined		
10 ⁻⁴	not determined			70	0	—	15	0	—	not determined		
10 ⁻³	not determined			40	0	—	5	0	—	not determined		
La(NO₃)₃												
10 ⁻⁵	100	80	0	90	10	0	30	5	0	40	5	0
10 ⁻⁴	100	50	0	60	3	0	8	0	0	8	0	0
10 ⁻³	90	30	0	25	0	0	3	0	0	4	0	0

^a *c* in equiv liter⁻¹. Temperature 25.0°C.

a minor effect on the dissociation. The degree of dissociation in Me_2CO at 10^{-4} equiv liter $^{-1}$ increased by about 10%. With i-PrOH the dissociation of $\text{Mg}(\text{NO}_3)_2$ increased considerably at 10^{-4} equiv liter $^{-1}$, with α_1 becoming 70–80% and $\alpha_2 = 5$ –10%. The dissociation of $\text{La}(\text{NO}_3)_3$ in i-PrOH also improved, with α_1 going to about 25% but α_2 remaining negligible.

An important conclusion of these conductivity measurements is that in isopropanol and acetone practically no ions with a charge number higher than unity are to be found, whereas in methanol and ethanol bivalent ions are present in sufficient concentrations to affect double-layer structure.

Although free multivalent cations are not present in the bulk-solution phase, they may be adsorbed strongly in the Stern layer as illustrated in Fig. 1.

4. COAGULATION THEORY

In this paper we consider only dispersions stabilized by electric charge. This means that the total Gibbs energy, G_T , of interaction between two particles is given by

$$G_T = G_A + G_R, \quad [1]$$

where for spherical particles of radius a at a distance H between the surfaces, the Gibbs energy of attraction is due to van der Waals forces and is given by

$$G_A = - \frac{Aa}{12H}. \quad [2]$$

The repulsion is due to the overlap of the two electrical double layers and can be expressed as

$$G_R = +2\pi\epsilon\epsilon_0 a \left(\frac{4RT\gamma}{zF} \right)^2 e^{-\kappa H}. \quad [3]$$

In these equations A is the Hamaker constant, ϵ is the dielectric constant of the medium, ϵ_0 is the permittivity of the vacuum, κ is the reciprocal Debye–Hückel length,

$$\kappa = \left(\frac{2F^2 z^2 c}{\epsilon\epsilon_0 RT} \right)^{1/2}, \quad [4]$$

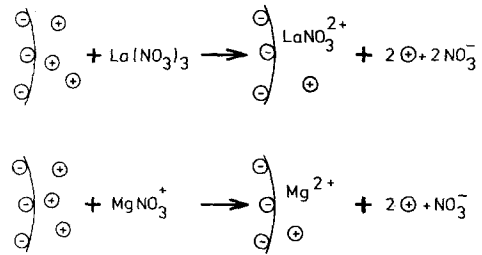


FIG. 1. Reactions between incompletely dissociated salts and the surface charge.

z is the charge number of both counterions and co-ions, and

$$\gamma = \tanh(zF\phi_d/4RT), \quad [5]$$

with ϕ_d being the potential at the outer Helmholtz plane (boundary between Gouy and Stern layers). The limitation to symmetrical electrolytes is not a serious drawback, since the charge number of the co-ion is usually of negligible influence.

Equations [2] and [3] require that $H \ll a$. Moreover Eq. [3] is only a good approximation for large κH and still acceptable down to $\kappa H \sim 1$. These equations can be refined so as to extend the range of their validity as mentioned in Ref. (13). The main refinements are the use of a better approximation than Eq. [2] for the attraction and taking the thickness, d , of the Stern layer into account by multiplying the right-hand side of Eq. [3] by $\exp(-2\kappa d)$. Such refinements do not alter the essential conclusions as derived from Eq. [6] below.

Applying the usual condition for the limit of rapid coagulation, $G_T = 0$ and simultaneously $dG_T/dH = 0$, the coagulation concentration, c_c , is found to be

$$c_c = \frac{1152e^{-2}(4\pi\epsilon\epsilon_0)^3(RT)^5}{\pi F^6} \frac{\gamma^4}{A^2 z^6}. \quad [6]$$

For high values of ϕ_d ($\gamma \rightarrow 1$) or if ϕ_d is independent of z and c under coagulation conditions, Eq. [6] reduces to

$$c_c = C' \frac{\epsilon^3}{A^2 z^6}. \quad [7]$$

TABLE III

Dielectric Constant, ϵ , and Value of $[\epsilon(\text{H}_2\text{O})/\epsilon(\text{organic solvent})]^3$ at 25°C

Solvent	H ₂ O	MeOH	EtOH	i-PrOH	Me ₂ CO
$\epsilon(14)$	78.54	32.70	24.55	19.22	20.70
$[\epsilon(\text{H}_2\text{O})/\epsilon(\text{solvent})]^3$	1	13.86	32.74	68.24	54.62

When ϕ_d is small ($\tanh x \rightarrow x$) we have

$$c_c = C'' \frac{\epsilon^3 \phi_d^4}{A^2 z^2} \quad [8]$$

Both equations predict that c_c is proportional to ϵ^3 . The first one explains the large difference between the coagulation concentrations for different charge numbers (Schulze-Hardy rule) by the factor z^{-6} . If the second equation applies, a strong decrease of c_c with increasing z can only be explained if ϕ_d decreases strongly with increasing z .

The large effect of the factor ϵ^3 is illustrated in Table III, where $[\epsilon(\text{water})/\epsilon(\text{organic})]^3$ is tabulated for the organic solvents that we have used. We note that 0.5% water in the organic solvent increases ϵ by about 1% and thus ϵ^3 by about 3%. This change is negligible compared to the values of $[\epsilon(\text{H}_2\text{O})/\epsilon(\text{solvent})]^3$.

Theoretical arguments may be advanced that the Hamaker constant A does not change very much in the transition from water as continuous medium to our four organic solvents (6, 15).

One aspect, not immediately apparent from Eq. [8], is that, especially with low values of ϵ and $z > 1$, adsorption of counterions in the Stern layer may neutralize the surface charge already at very low concentrations. In this case ϕ_d is abnormally low, thus the net coagulation concentration is very low, but the gross concentration is nearly equivalent to the charge of all the particles in a unit volume and thus nearly proportional to the sol concentration.

With this supposition we find

$$c_c(\text{gross}) = c_c(\text{net}) + \alpha c_{\text{sol}} \quad [9]$$

This phenomenon is sometimes referred to as equivalent flocculation.

The essential difference between coagulation by compression of the double layer and coagulation by charge neutralization is a quantitative one. On the addition of coagulating electrolyte, adsorption of added counterions in the Stern layer may occur. Usually the decrease of the repulsion between particles is mainly due to compression of the diffuse double layer with the change in charge being only of secondary importance. With coagulation by charge neutralization the loss of charge by adsorption in the Stern layer is the main cause of the decrease of the repulsion, which may occur already at a very low net concentration with no or hardly any increase in κ .

5. ELECTROPHORESIS

In order to show that the particles indeed carry an electric charge, but mostly to obtain an estimate of ϕ_d , we carried out some electrophoresis experiments, assuming that the electrokinetic potential, ζ , does not differ much in magnitude from ϕ_d . We used a Rank Brothers apparatus, Mark II, with a thin-walled cylindrical ($d \sim 2$ mm) Pyrex cell. For illumination we used a slightly defocused 3-mW He-Ne laser, Spectra Physics Model 133. Ag, AgI, and CPC particles could be seen in dark-field illumination, but the α -FeOOH particles did not scatter enough light to be visible. The organosols were diluted 100 to 500 \times with intermicellar liquid and electrolyte solution, until the concentration of particles was suitable for the measurement. Details of these measurements are described in (6).

Zeta-potentials have been calculated with the use of the theory of Wiersema *et al.* (16). From the ζ -potential the electrokinetic surface charge density, σ_e , could be calculated. It was always lower and usually much lower than the analytical charge density, σ_a .

TABLE IV
Electrokinetic Potentials and Surface Charge Densities in Sols of Ag, AgI, and CPC
in EtOH at 25°C upon Addition of LiNO₃

Dispersed phase	Coagulation concn ^a c_c (mM)	Ionic concn ^a (mM)	Electrokinetic mobility (10^{-4} cm ² V ⁻¹ sec ⁻¹)	$-\zeta$ (mV)	$-\sigma_e$ ($\mu\text{C cm}^{-2}$)	$-\sigma_a$ ($\mu\text{C cm}^{-2}$)
Ag	1.35	0.014	0.95	71	0.43	21
		0.5	0.76	62	0.44	21
		1.0	0.69	55	0.46	21
		1.5	0.60	47	0.43	21
AgI	4.4	0.0045	1.06	94	0.061	$\sim 3^b$
		0.1	0.85	63	0.118	
		1.0	0.80	47	0.227	
		4.0	0.79	44	0.40	
		10.0	0.76	41	0.54	
CPC + CPC SO ₃ H + DEEPO	2.5	no salt	0.99	92	0.1	$\leq 75^c$
		0.1	0.84	62	0.12	
		1.0	0.73	42	0.2	
CPC + CPC SO ₃ H + TEAH	6	no salt	0.98	91	0.1	

^a Not corrected for incomplete dissociation.

^b See Section 2b.

^c Maximum value assuming that all CPC SO₃H is adsorbed on the BET area.

As an illustration we give a few results obtained in EtOH in Table IV. In the other media the same trends were observed, and ζ -potentials and surface charge densities were of the same order of magnitude as in EtOH. The ζ -potentials are negative and are high enough to generate a strong potential barrier against coagulation, but low in the context of Eqs. [6]–[8]. The absolute value of ζ always decreases with increasing electrolyte concentration, and σ_e remains constant (Ag) or increases (AgI) with electrolyte concentration. Presumably the adsorption of citrate on the silver particles is maximal already at low salt content and does not increase on compression of the double layer, whereas sufficient I⁻ is present in the intermicellar liquid of the dilute AgI sol to increase the surface charge by further adsorption when the double layer is compressed.

6. COAGULATION EXPERIMENTS

Coagulation concentrations were determined in a so-called coagulation series. In a

series of carefully cleaned test tubes 5 ml of an organosol, containing 1% by volume of water, is mixed with 5 ml of electrolyte in pure organic solvent with constant increments of electrolyte concentration between successive tubes.

After a certain program of stirring and waiting the coagulation was observed visually. For studies in pure water or in mixtures of water and organic solvent the same method was used for evaluating the coagulation with suitably adapted solutions.

The coagulation series furnishes a quick method to obtain a large number of coagulation concentrations. These concentrations do not correspond exactly to the conditions of Eqs. [6]–[8], but to a coagulation with a small remaining energy barrier. Coagulation concentrations found in this way are thus slightly smaller (e.g., by 5 or 10%) than c_c defined by the conditions $G_T = dG_T/dH = 0$. The difference is immaterial for our further interpretation.

The coagulation concentration is defined operationally as follows: For the Ag sol

TABLE V

Coagulation Concentrations (mM) for Ag, AgI, and α -FeOOH in 99.5% EtOH and for CPC in Pure EtOH

Electrolyte	Dispersed phase (concn of counterion, ^a meq liter ⁻¹)						
	Ag ^a ([Na ⁺] = 0.048)			AgI ([I ⁻] = 0.006)	α -FeOOH ([NO ₂ ⁻] = 0.23)	CPC + salt I ^b ([DEEPO] = 0.115)	CPC + salt II ^b ([TEAH] = 0.115)
	$c_c(1)$	c_{rest}	$c_c(2)$				
LiNO ₃	1.35			4.4	3.0	2.5	6.0
NaNO ₃	0.39			—	—	—	—
AgNO ₃	0.070			0.0075	—	—	—
HNO ₃	0.048			3.9	—	—	—
HClO ₄	0.050			<3.6	—	—	—
LiClO ₄	0.9 < c_c < 1.2			—	—	—	—
Li acetate	—			7.0	9.0	—	—
Na acetate	0.38			—	0.30	—	—
K acetate	0.25			—	0.34	—	—
Mg(NO ₃) ₂	0.018	0.032	7.0	0.004	—	0.030	0.050
Ca(NO ₃) ₂	0.018	0.035	0.33	0.008	—	—	—
Co(NO ₃) ₂	0.026	0.032	1.10	0.005 < c_c < 0.010	—	—	—
Cd(NO ₃) ₂	0.020	0.032	0.80	0.010	—	—	—
Al(NO ₃) ₃	0.016	0.035	2.8	—	—	—	—
La(NO ₃) ₃	0.016	0.023	0.22	0.0022 ^d	—	0.030	0.045

^a Bi- and trivalent cations produced charge reversal and restabilization. $c_c(1)$ is the first coagulation concentration, c_{rest} is the concentration where the positive sol became stable, and $c_c(2)$ is the coagulation concentration of the positive sol.

^b Salt I = CPC SO₃H + DEEPO; salt II = CPC SO₃H + TEAH.

^c Analytical concentrations of counterions, including free ions, ions in the double layer, and ions in incompletely dissociated molecules.

^d In 97.5% EtOH, since La(NO₃)₃ is not sufficiently soluble in 99.5% EtOH.

(final concn 127 mg liter⁻¹ = 1.176 mM Ag), the coagulation concentration was that electrolyte concentration that left the supernatant above the sediment after standing 24 hr just transparent enough to allow a black line on a white background to be seen through the solution.

In the case of the AgI sol (final concn 587 mg liter⁻¹ = 2.5 mM AgI), it was the concentration that left the supernatant completely clear (1/1 electrolytes), or that showed the greatest change in optical density between two successive concentrations (multivalent electrolytes) after standing 24 hr.

For the FeOOH sol (final concn 231 mg liter⁻¹ = 2.6 mM α -FeOOH), it was the lowest concentration at which visible flocs

were formed, after the dispersion had been left for 1 hr, stirred briefly, and again left for 1 hr to allow coagulation to take place.

The CPC sol (final concn 500 mg liter⁻¹ = 0.868 mM CPC) coagulated upon the addition of electrolytes, but the supernatant kept a bluish-green tinge (due to dissolved CPC SO₃H) even at 100 mM LiNO₃. Therefore c_c for CPC was defined as the lowest concentration at which a sediment formed after 24 hr.

6a. Hydrosols and Organosols with 0–0.5% Water

Since we have more extensive coagulation data for EtOH than for any other solvent, we collect all our EtOH results in Table V and the coagulation data for water,

TABLE VI

Coagulation Concentrations (mM) for Ag, AgI, and α -FeOOH in Water and in 99.5% Organic Solvents

Dispersed phase	Electrolyte	H ₂ O	MeOH	EtOH	i-PrOH	Me ₂ CO
Ag	LiNO ₃	100	6.0	1.35	0.045	0.002
	Mg(NO ₃) ₂	0.28	—	0.018	—	—
	Ca(NO ₃) ₂	—	—	0.018	—	—
	La(NO ₃) ₃	0.034	—	0.016	—	—
AgI	LiNO ₃	150	9.6	4.4	1.3 (0.72) ^b	13 (1.03) ^b
	Mg(NO ₃) ₂	2.3	0.010	0.004	0.0025	0.05 < c _c < 0.1
	Ca(NO ₃) ₂	2.2	0.013	0.008	0.008	4.5
	La(NO ₃) ₃	0.050	—	0.0022 ^a	—	—
	AgNO ₃	0.009	0.0085	0.0075	—	—
α -FeOOH	LiNO ₃	60	18 (15.9) ^b	3.0	0.1	0.001
	MgSO ₄ ^c	0.15	—	—	—	—
	K ₃ Fe(CN) ₆ ^c	0.066	—	—	—	—

^a In 97.5% EtOH.^b Figures in parentheses are corrected for incomplete dissociation.^c The solubilities of these salts in the organic solvents were too low to allow them to be used as coagulants in the organic solvents.

the other three solvents, and a few EtOH data in Table VI.

The most striking feature of the results displayed in Table V is the charge reversal of Ag sols with bivalent and trivalent cations. This observation was confirmed by electrophoresis measurements. The first coagulation concentrations, $c_c(1)$, are close to being equivalent to the counterion concentration. This result suggests that most of $c_c(1)$ is used for charge neutralization, the actual concentration of coagulating ions being only a small fraction of this value. We therefore determined coagulation concentrations for a series of Ag concentrations from the standard concentration (127 mg liter⁻¹) down to one-fourth of this value. The observed linear relationship shown in Fig. 2 confirms Eq. [9] nicely and shows that the net coagulation concentration for Mg(NO₃)₂ is less than 0.5 μ mole liter⁻¹.

The H⁺ ion and the Ag⁺ ion also show equivalent coagulation of the silver sol in EtOH, but these univalent ions do not promote charge reversal.

Also, in the case of the AgI sol and the

CPC sol equivalent coagulation is found for the bi- and trivalent cations, but without reversal of charge.

Furthermore we note fairly pronounced differences between the c_c values for different 1/1 electrolytes that evidently reflect different adsorbabilities of cations and anions and different degrees of electrolyte dissociation.

Table VI confirms the general picture for other organic solvents. Equivalent or nearly equivalent coagulation is observed for bivalent and trivalent coagulating ions and in some cases (Ag and α -FeOOH in i-PrOH) even for monovalent ions.

The extremely low c_c values for Ag and α -FeOOH in Me₂CO probably indicate a nearly complete adsorption of the original counterions in the Stern layer (Na⁺ on citrate for Ag, NO₃⁻ on Fe³⁺ or H⁺ for α -FeOOH).

A typical Schulze-Hardy dependence of c_c on the counterion valence is only displayed in water as the continuous medium. In the organic solvents either equivalent coagulation occurs or (AgI in

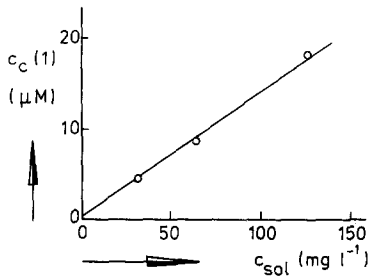


FIG. 2. Coagulation concentrations $c_c(1)$ for $\text{Mg}(\text{NO}_3)_2$ as a function of the silver sol concentration in 99.5% EtOH.

Me_2CO) the second dissociation of 2/1 electrolytes is so low that they behave as 1/1 electrolytes (typical example $\text{Ca}(\text{NO}_3)_2$), with some charge neutralization thrown in (as with $\text{Mg}(\text{NO}_3)_2$).

6b. Mixtures of Water and Organic Solvents

With this rather pronounced difference in behavior between hydrosols and organosols, it becomes interesting to investigate coagulation over a wide range of water/organic solvent mixing ratios. We therefore determined c_c 's in EtOH/ H_2O mixtures for the negative AgI sol and the positive $\alpha\text{-FeOOH}$ sol with electrolytes of various valences, and also studied the coagulation of $\alpha\text{-FeOOH}$ by LiNO_3 in $\text{Me}_2\text{CO}/\text{H}_2\text{O}$ mixtures. The results are given in Table VII.

In EtOH c_c 's for 1/1 electrolytes are seen to decrease regularly over the whole range with decreasing water content.

The 1/1 electrolyte in Me_2CO behaves similarly up to 50%, but then the c_c decreases much more rapidly. Equivalent coagulation is observed around 70% and a very low c_c is measured at 99.5% organic solvent.

Bi- and trivalent counterions show Schulze-Hardy behavior with AgI in EtOH at low EtOH content and equivalent coagulation at the other end of the range, the transition occurring gradually between 50% and about 95% for $\text{Mg}(\text{NO}_3)_2$ and more sharply around 70% for $\text{La}(\text{NO}_3)_3$.

The relative lack of the influence of the organic solvent/water mixing ratio on the c_c for MgSO_4 and $\text{K}_3\text{Fe}(\text{CN})_6$ with $\alpha\text{-FeOOH}$ in EtOH is due to the fact that for these salts nearly equivalent coagulation already occurs in water. This is confirmed by the influence of the sol concentration on the coagulation concentration as shown in Fig. 3.

7. DISCUSSION

We now return to the coagulation theory dealt with in Section 4. We have already noted that with bi- and trivalent counterions and high concentrations of organic solvent,

TABLE VII

Coagulation Concentrations (mM) for AgI and $\alpha\text{-FeOOH}$ in Mixtures of Water with EtOH or Me_2CO

Volume % organic solvent	AgI in $\text{H}_2\text{O}/\text{EtOH}$			$\alpha\text{-FeOOH}$			
				in $\text{H}_2\text{O}/\text{EtOH}$			in $\text{H}_2\text{O}/\text{Me}_2\text{CO}$
	LiNO_3	$\text{Mg}(\text{NO}_3)_2$	$\text{La}(\text{NO}_3)_3$	LiNO_3	MgSO_4	$\text{K}_3\text{Fe}(\text{CN})_6$	LiNO_3
0	150	2.3	0.050	60	0.150	0.066	60
10	140	2.2	0.055	48	0.130	0.066	55
30	130	1.6	0.040	36	0.110	0.066	40
50	100	0.55	0.014	22	0.110	0.060	22
70	70	0.15	0.0044	6	0.100	0.036	3.6
90	17	0.017	0.0026	1.4	0.090	0.026	0.160
95	—	—	0.0024	—	—	—	—
97.5	—	—	0.0022	—	—	—	—
99.5	4.4	0.004	—	3.0	—	—	0.001

equivalent coagulation (Eq. [9]) prevails. Are the other coagulation concentrations adequately described by double-layer compression, i.e., by Eqs. [6]–[8]?

As mentioned earlier the Hamaker constant, A , is not expected to show any drastic variations. Our data on electrophoresis (Table IV and additional data in Ref. (6)) indicate that ζ is never very high and that at the coagulation concentrations for LiNO_3 it remains between 40 and 60 mV with very few exceptions. Since the exact equality of ζ and ϕ_d is doubtful anyway and since the dielectric constant changes by a factor of 4 between water and our organic solvents, we first looked at how far the trend in the c_c 's is due to the factor ϵ^3 occurring in Eqs. [6]–[8]. In Table VIII values are collected for the parameter Q , where

$$Q = \frac{c_c(\text{organic solvent})}{c_c(\text{water})} \times \left(\frac{\epsilon(\text{water})}{\epsilon(\text{organic solvent})} \right)^3. \quad [10]$$

The dielectric constants of the mixtures have been taken from the tables of Akerlöf (17). Ideally, if differences in A and in ϕ_d are negligible, Q should equal 1. Those cases where we know that equivalent coagulation occurs are indicated by *italics*. The bold-face values refer to the transition range between double-layer compression and equivalent coagulation. The remaining Q values vary roughly within a factor of 3 above and below 1. We believe these data provide adequate confirmation that double-layer compression is the main driving force for coagulation. Values of Q that are lower but not much lower than 1 may be explained by the fact that the factor $\exp(-2\kappa d)$ that should have been included in Eq. [3] has a larger effect for water than for the organic solvents. The fact that ζ (to be representative for ϕ_d) is somewhat larger for water than for the solvents works in the same direction.

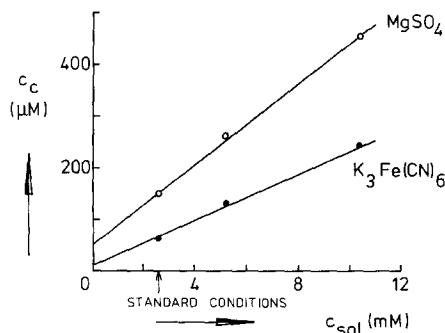


FIG. 3. Coagulation concentration c_c for the α -FeOOH hydrosol, showing equivalent coagulation in accordance with Eq. [9].

The high values of Q for the water-rich solvent mixtures may perhaps be due to a thicker Stern layer in the solvent than in pure water, but a relatively high ϕ_d in these mixtures may be another reason.

As a matter of fact our data on the double-layer composition are not extensive enough for the interpretation of these small variations in Q .

8. CONCLUSIONS

In polar organic solvents and in their mixtures with water, true colloid stabilization by electric charge is possible for a wide range of colloid materials. Addition of small concentrations of electrolytes leads to coagulation.

Down to about $\epsilon = 50$ (~50% organic solvent) c_c 's are reasonably proportional to ϵ^3 , which indicates that double-layer compression with some extra adsorption in the Stern layer is the main cause of coagulation. For lower dielectric constants, down to and including the pure organic solvents, the proportionality to ϵ^3 is maintained for monovalent electrolytes in MeOH and EtOH but not in *i*-PrOH and Me_2CO , although their dielectric constants are not drastically lower than those of the former. But the dissociation of electrolytes and presumably also the dissociation between the counterions and the surface charge are

TABLE VIII

Values of $Q = [c_c(\text{solvent})/c_c(\text{water})] \times [\epsilon(\text{water})/\epsilon(\text{solvent})]^3$ for Ag, AgI, and α -FeOOH in Various Solvents and with Various Electrolytes. Percentages of Organic Solvent are Percentages by Volume

Dispersed phase	Solvent	Q for various electrolytes				
		LiNO ₃	Mg(NO ₃) ₂	La(NO ₃) ₃		
Ag	MeOH	0.78	—	—		
	EtOH	0.44	2.09	15.3		
	i-PrOH	0.029	—	—		
	Me ₂ CO	0.001	—	—		
	MeOH	0.81	0.06	—		
AgI	EtOH					
	10%	1.12	1.15	1.32		
	30%	1.61	1.29	1.48		
	50%	2.20	0.79	0.92		
	70%	3.27	0.46	0.62		
	90%	2.18	0.14	1.00		
	99.5%	0.92	0.05	1.27 ^a		
	i-PrOH	0.32	0.07	—		
	Me ₂ CO	0.37	1.78	—		
		LiNO ₃	MgSO ₄	K ₃ Fe(CN) ₆	Solvent	LiNO ₃
α -FeOOH	MeOH	3.65	—	—	i-PrOH	0.10
	EtOH				Me ₂ CO	
	10%	0.96	1.04	1.20	10%	1.10
	30%	1.11	1.36	1.85	30%	1.25
	50%	1.21	2.42	3.00	50%	1.21
	70%	0.70	4.67	3.82	70%	0.49
	90%	0.45	11.54	7.58	90%	0.079
	99.5%	1.57			99.5%	0.0009

^a In 97.5% EtOH.

lower in i-PrOH and Me₂CO (Tables I and II).

AgI sols are exceptional in that here double-layer compression remains the main effect, even in i-PrOH and Me₂CO.

It is very typical that for these organo-sols and mixed hydroorganosols the discharge mechanism (leading to equivalent coagulation) becomes prevalent for $\epsilon < 50$ and for *bi- and trivalent counterions*.

We found two cases of extremely low c_c 's (Ag and α -FeOOH in Me₂CO, Q (Eq. [10] ≈ 0.001) that we explain as loss of dissociation of the surface groups (one might say: equivalent coagulation due to its own counterions) in this medium.

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