Methorics of Coagulation Processes. XII.* The Influence of the Composition and the Properties of Solvent on the Coagulation of Negative Silver Halide Sols**

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Received May 5, 1955

The results of coagulation measurements on negative silver halide sols in statu nascendi in water-ethanol, water-acetone, water-dioxane, and water-glycine solutions are given. In the majority of cases a lowering of the dielectric constant of the coagulating medium causes a decrease of the coagulation values, but there are also cases in which the contrary behaviour has been observed. The results are interpreted on the basis of the present theories of the stability of lyophobic colloids. Neither Ostwald's theory nor the theory of Derjaguin-Verwey-Overbeek can be successfully applied. There is a close relationship betwen the coagulation values and the critical Bjerrum's distances for the formation of ion pairs, as was already proposed by Težak. The influence of the factors others than the dielectric constant is briefly discussed.

In a series of previous papers[1, 2, 3] the coagulation of silver chloride sols in water-ethanol, and of silver bromide sols in water-ethanol and water-dioxane mixtures was investigated. It was of interest to continue these studies by investigating the coagulation of negative silver halide sols in some other solvent mixtures. In this communication the results of coagulation measurements on silver chloride sols in water-acetone mixtures, on silver bromide in water-acetone and water-glycine solutions, and on silver iodide in water-ethanol, water-acetone and water-glycine solutions were given and compared with previously reported data. The results are interpreted on the basis of the present theories of the coagulation and the stability of lyophobic colloids.

EXPERIMENTAL

Sols in statu nascendi were used. The method of preparation of such sols and the method of observation of the coagulation process was described previously.[4] Solutions of all components contained the same amount of organic solvent, the only exception being that silver nitrate solutions did not contain glycine. In this way the composition of the solvent mixture used was not changed by mixing of the reaction components (with the exception of glycine solutions).

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* Contribution No. 47 from the Laboratory of Physical Chemistry.

** This paper is based on a part of a thesis submitted by J. Kratohvil to the Faculty of Science, University of Zagreb (April, 1954), in partial fulfillment of the requirements for the degree of Doctor of Chemical Sciences.

Since we were especially interested in the effect of the dielectric constant of the medium on coagulation, the isodielectric solvent mixtures were prepared. The composition of mixtures used and the corresponding dielectric constants were interpolated from the data of Akerlöf and Short[5], and are given in Table I. All the data are for 20° C.

Dielectric constants of aqueous glycine solutions used in our experiments amount, according to the data of Wyman and McMeekin[6], to 103 for 1.0 *M* glycine and to 126 for 2.0 *M* glycine.

TABLE I.

The compositions of solvent mixtures used in coagulation measurements and the corresponding dielectric constants at 20°C

Conc. of organic solvent; wt. %			Dielectric constant
Ethanol	Acetone	Dioxane	
0.0	0.0	0.0	80.4
10.0	10.0		74.7
20.0			68.7
29.6	30.0		62.7
39.4			56.8
49.0	47.5	33.0	51.0
58.5			45.5
68.0	65.0	45.0	40.0
77.5			35.0
86.8	80.0	56.0	30.5

Chemicals of analytical purity grade were used. Solvents were distilled several times over $AgNO_3$.

The analysis of the kinetics of coagulation was performed in the same way as described in a previous paper[4]. It showed that the change in the velocity and the character of coagulation for all solvent mixtures used was most distinct about ten minutes after mixing the reacting components. The 10-minutes tyndallograms[4] were, therefore, used for obtaining the coagulation values of the coagulating electrolytes.

The concentrations of all the components are given for the total volume (10.0 ml.) of the reaction mixture.

RESULTS

Typical precipitation curves of silver halides in mixed solvents. — In a previous paper[7] we tried to determine the concentration regions of the ionic precipitating components in which the separation of the solid phase (Ag halides) in mixed solvents is possible. For this reason, the complex solubility of silver halides in solvent mixtures was investigated and the general solubility curves were constructed. It seemed necessary to determine the stable and unstable (in colloid-chemical sense) regions of the typical precipitation curve.[3, 8] In Fig. 1 we have shown, as an example, the precipitation curves of AgCl in water and in 65% acetone. It is apparent that the

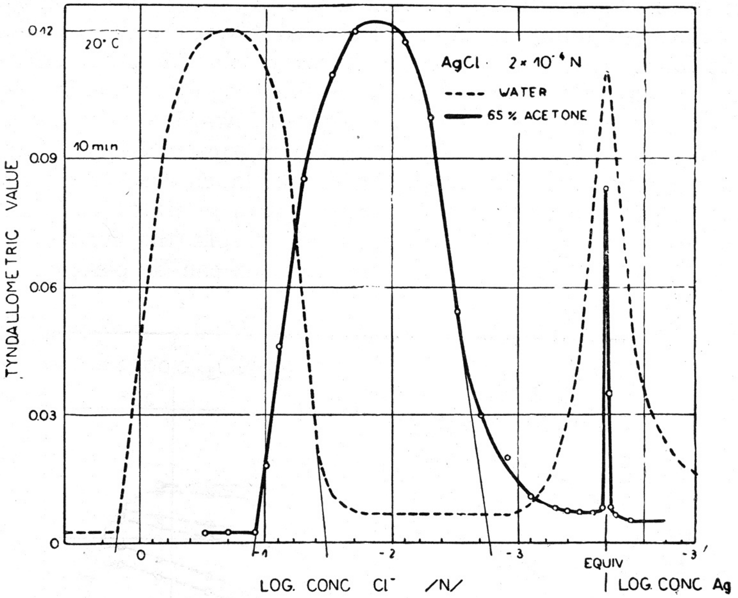

Fig. 1. The typical precipitation curves of AgCl in water and in 65% acetone 10 minutes after the mixing of the reacting components. Green light; 20° C.

TABLE II.

Coagulation values of KNO_3, $Ba(NO_3)_2$ and $La(NO_3)_3$ for negative AgBr and AgI sols in aqueous glycine solutions. Sol concentration: 0.0002 *M*

C_{co} (*N*)	Conc. glycine (*M*)	AgBr C_{HBr} (*N*)			AgI $C_{KI(HNO_3)}$ (*N*)	
		0.00022	0.0004	0.002	0.002	0.002 + 0.002 *N* HNO_3
C_K	0.0	0.0245		0.0625	0.135	0.135
	1.0	0.075		0.105	0.22	0.22
	2.0			0.22		
C_{Ba}	0.0			0.00234	0.002	0.002
	1.0			0.0054	0.0044	0.0044
	2.0			0.011		
C_{La}	0.0		0.00011	0.000069	0.000048	0.000037
	1.0		0.00027	0.00019	0.00019	0.00015
	2.0			0.00063		

change of the medium greatly influences the precipitation curve: 1) the limit of the complex solubility of AgCl is shifted toward smaller concentrations of chloride ions[7], and thus the region in which the formation of solid phase is possible is diminished; 2) the limit of the coagulating action of H^+ ions (from HCl) on negative AgCl sol is also shifted toward smaller concentrations; 3) the width of the isoelectric (equivalence) maximum is considerably diminished, so that, for obtaining stable AgCl sols, much smaller excess of stabilizing ions (Cl^-) is necessary in 65% acetone than in water. All these changes cause also the decrease of the region of stable sols (the region between the maxima), in which the coagulation measurements can be performed.

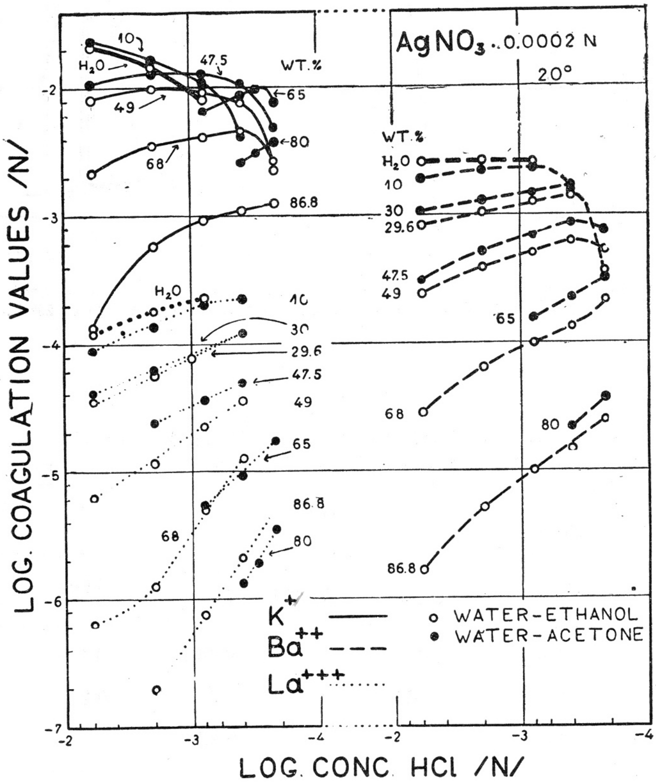

Fig. 2. Coagulation values of KNO_3, $Ba(NO_3)_2$ and $La(NO_3)_3$ for negative AgCl sols as a function of the concentration of stabilizing (Cl^-) ions in isodielectric mixtures of water-ethanol and water-acetone.

Coagulation measurements. — In the region of negative stable sols we used several systems containing always the same concentration of the sol, i. e. the same concentration of silver nitrate, and different concentrations of the stabilizing halide ions, ranging from small excess in comparison to the sol concentration to the coagulation limit. This range was greatly reduced in the water-acetone mixtures because of the enormous increase of complex solubility in these media[7]. The sol concentration amounted in all experiments to 0.0002 *M*. The coagulating action of potassium, barium, and lanthanum nitrate in various solvent mixtures was investigated with these systems.

The results of coagulation measurements are represented graphically as plots of the logarithms of the coagulation values of neutral electrolytes for various sols and various media against the logarithms of the total concentrations of the stabilizing halide ions (Figs. 2, 3, 4, and 5). For the sake of completness and comparison, the results of the previous investigations[1, 2, 3] are also included. The coagulation values in glycine solutions are tabulated in Table II.

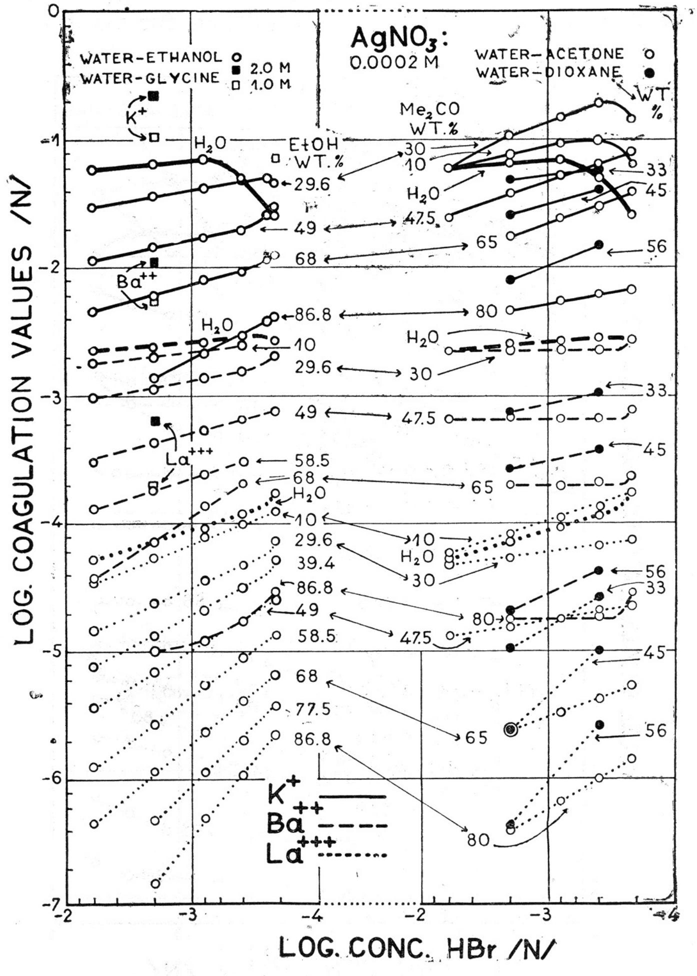

Fig. 3. Coagulation values of KNO_3, $Ba(NO_3)_2$ and $La(NO_3)_3$ for negative AgBr sols as a function of the concentration of stabilizing (Br^-) ions in isodielectric mixtures of water-ethanol, water-acetone and water-dioxane. The results for 1.0 and 2.0 *M* glycine solutions are also included.

The results obtained may be summarized as follows:

1) In the majority of cases an increase of concentration of the organic solvent (ethanol, acetone and dioxane), i. e. a decrease of the dielectric constant of the coagulating medium, caused a decrease of coagulation values; in the presence of glycine coagulation values were greater than in pure aqueous solutions.

2) There are cases in which departures from this general trend were observed, especially at smaller concentrations of the stabilizing ions and with smaller amounts of the organic solvent. In such cases coagulation values first increased and then decreased relative to the values for water.

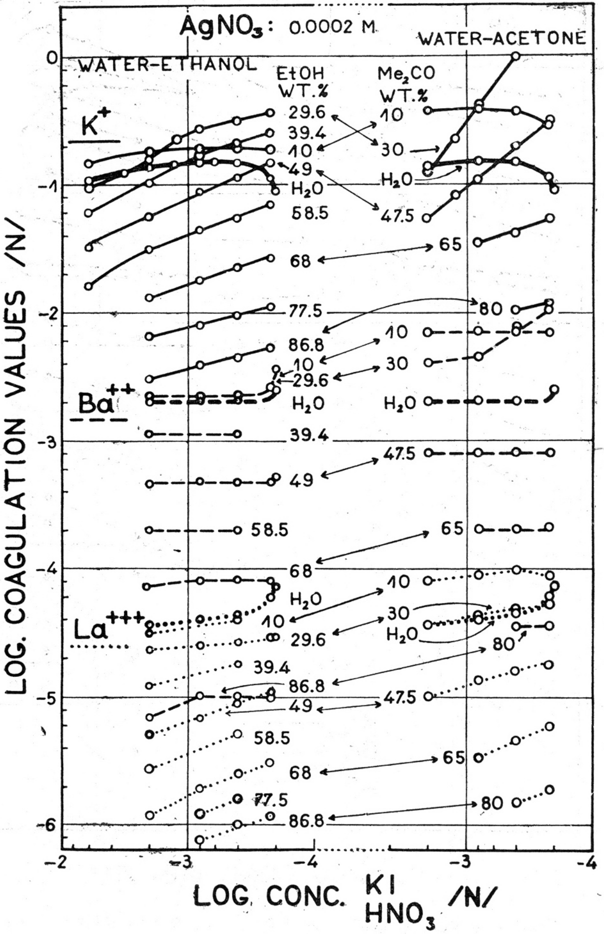

Fig. 4. Coagulation values of KNO_3, $Ba(NO_2)_3$ and $La(NO_3)_3$ for negative AgI sols as a function of the concentration of stabilizing (I^-) ions in isodielectric mixtures of water-ethanol and water-acetone.

3) The coagulation values were not the same for mixtures of equal dielectric constant, except in few cases (AgCl coagulated with Ba- and La-ions).

4) In the majority of cases the coagulation values decreased with increasing concentration of the stabilizing ions. A very interesting departure from such a trend was observed in the case of AgI in water-ethanol and water-acetone, and of AgBr in water-acetone media coagulated with barium nitrate, where the coagulation values remained constant at all concentrations of the stabilizing ions.

It may be also noted that the coagulation values of potassium and barium nitrates for all three sols were not sensitive at all to the acidity of solutions. However in the case of coagulation by lanthanum nitrate the acidity of the medium had a definite influence as can be seen from Fig. 5.

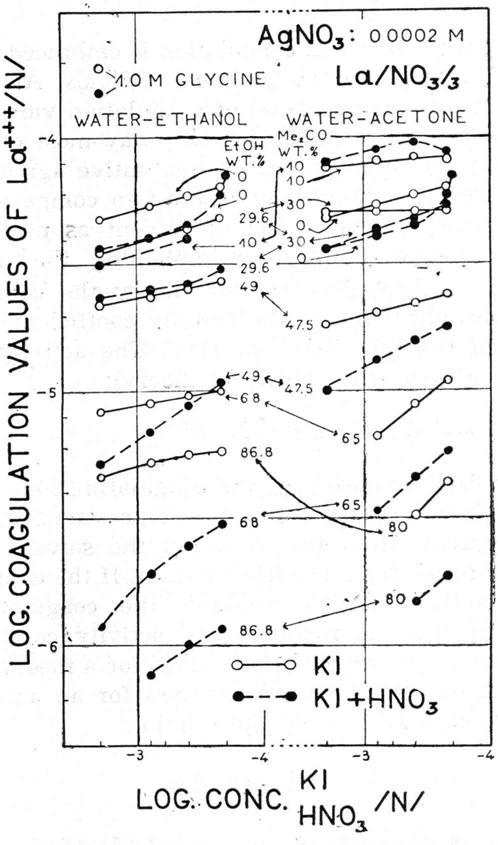

Fig. 5. The comparison of the coagulation values of $La(NO_3)_3$ for negative silver iodide sols in neutral and acidic solutions (HNO_3). The concentrations of nitric acid were the same as the concentrations of KI.

DISCUSSION

There are many papers dealing with the influence of the solvent on the precipitation and coagulation phenomena (for a rather incomplete review see Ostwald[9]), but only few deal with silver halide sols. Jirgensons[10] noted that the addition of glycine, urea and formamide caused a stabilization of AgCl sols which we also found for glycine solutions (Table II). Basinski[11] investigated the coagulation of AgI sols in water-methanol and water-ethanol mixtures (up to 40% of organic solvent), while Mackor[12] used the same sol for studying the influence of acetone on stability. The results of Basinski and Mackor are also similar to ours.

The data in the literature seem to indicate a sensitization of most lyophobic sols on addition of organic solvents. However, much controversy exists between various authors. Such a situation was caused by many factors: the systematic investigations have been very scarce; the sols used were not well defined and their preparation was not reproducible; the experimental techniques used for observation of the coagulation process were very different; most of the investigators used only small (up to 30%) additions of other solvents, etc.

The influence of the solvent on coagulation is embraced in several theories of the stability and coagulation of lyophobic colloids. All these theories, as we shall see below, predict a reduction of coagulation values with decreasing dielectric constant of the medium, and in this way most of our data and the results of many other investigators are in qualitative agreement with theoretical prediction. However, it seemed of interest to compare the experimental findings with the quantitative effect of solvent as postulated by various theories and to see the possibilities for explaining the anomalous results.

Ostwald theory. — According to this theory the coagulation occurs at an approximately constant value of the activity coefficient of the coagulating ion, independently of the type of electrolyte[9]. The activity coefficient of an ion is given by the relation (Debye-Hückel theory):

$$-\log f_i = 363.2\, z_i^2\, I^{1/2}/D^{3/2} \tag{1}$$

(for 20° C), where z_i is the valency of the coagulating ion, D is the dielectric constant of the medium, and I denotes the ionic strength of the electrolyte solution. It is apparent from this equation the solvent will influnce the activity coefficient through the dielectric constant. If the change of the medium causes a decrease in the dielectric constant, the coagulating concentration will also decrease in order to maintain the activity coefficient constant. It is also possible to predict the coagulation values for a medium of the dielectric constant D_x, if we know the coagulation values for an another medium, e. g. water (dielectric constant D_W), using the relation:

$$C_D = \tau_D\, C_W \tag{2}$$

where

$$\tau_D = \varphi_W^2/\varphi_D^2 \quad \text{and} \quad \varphi_D = 0.504\, D_W^{3/2}/D_X^{3/2} \tag{3}$$

($\varphi_W = 0.504$ for 20° C). Equation (2) should be valid, according to Ostwald, for all lyophobic sols and for ions of all valencies.

We have used the results of coagulation of AgBr sols in water-ethanol mixtures (Fig. 3) to verify Ostwald's theory. These results are qualitatively in good agreement with the theory. In Tables III, IV and V we have given the results of this verification. However, the quantitative agreement is rather poor: the activity coefficients at coagulating concentrations are far from

TABLE III.

The results of the interpretation of coagulation measurements on silver bromide sols in water-ethanol mixtures according to the theory of Ostwald. Coagulation electrolyte: KNO_3

Ethanol wt %	$C_{HBr} \times 10^4$ (M)	$C_{exp} \times 10^2$ (M)	$C_{calc} \times 10^2$ (M)	f
0	2.2	2.45		0.834
	4.0	4.9		0.775
	8.0	6.75		0.740
	20.0	6.25		0.748
	60.0	5.6		0.761
29.6	2.2	4.5	1.16	0.700
	4.0	4.75	2.32	0.694
	8.0	4.0	3.2	0.715
	20.0	3.6	2.96	0.726
	60.0	2.9	2.66	0.751
49	2.2	2.88	0.622	0.676
	4.0	1.86	1.24	0.736
	8.0	1.66	1.71	0.744
	20.0	1.41	1.59	0.760
	60.0	1.1	1.42	0.786
68	2.2	1.2	0.304	0.695
	4.0	0.9	0.606	0.731
	8.0	0.76	0.836	0.750
	20.0	0.575	0.775	0.779
	60.0	0.46	0.684	0.800
86.8	2.2	0.4	0.133	0.730
	4.0	0.28	0.266	0.768
	8.0	0.215	0.367	0.795
	20.0	0.135	0.34	0.833

constant and there is no agreement between the calculated (from eq. 2) and experimentally determined coagulation values. The calculated values are always greater.

TABLE IV.

The results of the interpretation of coagulation measurements on silver bromide sols in water-ethanol mixtures according to the theory of Ostwald. Coagulation electrolyte: $Ba(NO_3)_2$

Ethanol wt. %	$C_{HBr} \times 10^4$ *(M)*	$C_{exp} \times 10^4$ *(M)*	$C_{calc} \times 10^4$ *(M)*	f
0	2.2	13.2		0.746
	4.0	13.8		0.741
	8.0	13		0.748
	20.0	11.7		0.759
	60.0	10.9		0.774
29.6	2.2	10	12.5	0.678
	4.0	7.5	13.1	0.726
	8.0	6.65	12.3	0.740
	20.0	5.5	11.1	0.761
	60.0	4.73	10.3	0.776
49	2.2	3.58	6.7	0.740
	4.0	3.15	7	0.754
	8.0	2.69	6.6	0.770
	20.0	2.16	5.95	0.791
	60.0	1.98	5.55	0.800
68	2.2		3.27	
	4.0	1	3.42	0.796
	8.0	0.66	3.22	0.830
	20.0	0.396	2.9	0.866
	60.0	0.182	2.7	0.907
86.8	2.2	0.133	1.44	0.882
	4.0	0.09	1.5	0.901
	8.0	0.0575	1.41	0.921
	20.0	0.047	1.27	0.928

It is well known that many phenomena can be described by the theory of Ostwald, but under condition that there are no specific interactions.[13] The above results indicate that there exists probably a specific adsorbability and a special structure of the ions in the methoric layer and in the solution.

TABLE V.

The results of the interpretation of coagulation measurements on silver bromide sols in water-ethanol mixtures according to the theory of Ostwald. Coagulation electrolyte: $La(NO_3)_3$

Ethanol wt. %	$C_{HBr} \times 10^4$ *(M)*	$C_{exp} \times 10^6$ *(M)*	$C_{calc} \times 10^6$ *(M)*	f
0	2.2	55.4		0.827
	4.0	36.7		0.857
	8.0	29.7		0.870
	20.0	23.1		0.885
	60.0	16.7		0.900
29.6	2.2	24.2	78.6	0.835
	4.0	15.2	52.1	0.866
	8.0	11.3	42.2	0.882
	20.0	7.46	32.8	0.900
	60.0	4.6	23.7	0.924
49	2.2	8.2	42.1	0.865
	4.0	5.53	28	0.888
	8.0	3.86	22.6	0.905
	20.0	2.2	17.6	0.927
	60.0	1.16	12.7	0.947
68	2.2	2.1	20.6	0.900
	4.0	1.27	13.6	0.922
	8.0	0.746	11	0.940
	20.0	0.374	8.58	0.956
	60.0	0.142	6.2	0.974
86.8	2.2	0.713	9.03	0.912
	4.0	0.35	6	0.938
	8.0	0.16	4.85	0.958
	20.0	0.0483	3.76	0.976

Derjaguin-Verwey-Overbeek theory. — According to the theory of Derjaguin[14] and of Verwey and Overbeek,[15,16] coagulation values of neutral electrolytes are proportional to the third power of the dielectric constant of the medium:

$$C_{co} = 1.575 \cdot 10^{-30}\, D^3 \gamma^4 / A^2 v^6 \quad \text{(mols/l.)} \tag{4}$$

(for 20° C). A is the van der Waals-London constant, v is the valency of the coagulating ions and γ is defined by the relations:

$$\gamma = (e^{z/2} - 1)/(e^{z/2} + 1), \qquad z = v\, \varepsilon\, \psi_\delta / kT \tag{5}$$

where ε is the elementary electrical charge, k is the Boltzmann constant, T the absolute temperature, and ψ_δ denotes the Stern potential of the double layer.

If the constant A of the van der Waals-London forces does not vary with the change of dielectric constant, then Φ as defined by

$$\Phi = D^3 \gamma^4 / C_{co}\, v^6 \tag{6}$$

should be constant for all the values of C_{co} measured.

Φ can be calculated provided γ given by (5) is known. The calculation of γ requires the knowledge of ψ_δ, which is a quantity not unambiguously defined and not measurable by a direct experimental method.[17] For this reason it is impossible at present to check the Derjaguin-Verwey-Overbeek theory using our experimental data.*

Mackor,[12, 18] who investigated the coagulation and the properties of the electrical double layer of AgI in water-acetone mixtures, also tried to interpret the results obtained by the use of Verwey-Overbeek theory. On the assumption that the capacities of the double layer on AgI can be compared with those on mercury, he was able to compute the values of the Stern potential ψ_δ for various water-acetone mixtures, and to calculate the Φ values using eq. (6). The results showed that Φ varies over more than two powers of ten. In order to bring the Φ values more in line, Mackor made the arbitrary assumption that the attractive van der Waals-London forces are inversely proportional to $d^{1.6}$ (d = half the distance of separation of two molecular condensers) instead of to the square of the distance, as is assumed in the original version of the theory, and also introduced into the calculations the finite thickness of the molecular condenser. Although the new Φ values were much nearer to a constant, some differences still persisted. To explain this and the change of the coagulation values at smaller concentrations of acetone, which are quite similar to ours (Fig. 4), Mackor calculated the values of A corresponding to each Φ value. A parabolic line was obtained with a minimum value at 40 vol. % acetone, the difference between the minimum and maximum values being 2×10^{-13} ergs. Mackor concluded that »the lowering of A by small amounts of acetone would therefore explain the stabilization of the

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* In the original version of the Verwey-Overbeek theory, the use was made of the surface potential ψ_0 (the ionic part of the Galvani potential difference). Since the values of this potential (for AgI, at least) are large even for small contents of the potential-determining ions (Kruyt,[16] p. 310), it can be taken with very good approximation that $\gamma^4 \cong 1$. So it becomes possible to calculate the Φ values from eq. (6). We performed such calculations using our experimental data. Φ values varied over more than two powers of ten indicating always greater coagulation values than we obtained experimentally.

AgI sol.« In view of the fact the A constant, measured or calculated, shows a »spectrum« od values ranging from 10^{-10}—10^{-12} ergs (Overbeek and Sparnaay[19]) to $\leqslant 5 \times 10^{-14}$ ergs (Derjaguin and Abricossova[20]), it seems to us that the conclusions of Mackor are, at least, premature.

We tried also to explain the experimental results on the basis of a theory of coagulation developed by one of us (B. T.). It was possible to deduce the following relationship between the factors influencing the stability of a sol:[21]

$$_{c}d + r_i = {}_{s}d(\log C_{fix} - \log C_{co}) \tag{7}$$

where r_i denotes the radius of the coagulatiing ion, and C_{co} its coagulation values (expressed in normalities). $_{s}d$ is a distance determined mainly by the density of the stabilizing ions on the surface. C_{fix} denotes the concentration of an uncharged species of particles which exert the same interaction as the charged ions by potentials others than coulombic. The last two quantities can be taken, in ideal case at least, as specific and constant for a particular sol.

$_{c}d$ represents Bjerrum's critical distance for the formation of ion pairs:

$$_{c}d = z_1 z_2 e^2/2 D k T \tag{8}$$

where z_1 and z_2 denote the valencies of the coagulating and the stabilizing ions, respectively, e is the elementary electrical charge, D is the dielectric constant of the medium, k Boltzmann constant, and T the absolute temperature.

From eq. (7) and (8) we see that the coagulation values should be lowered by decreasing the dielectric constant. If we assume that the radius of the coagulating ion does not vary with the change in the composition of the solvent, the relation between the logarithms of the coagulation values for various media and the corresponding Bjerrum's distances should be linear.*

In several previous papers[1,2,3,23,24] we have already interpreted some of our results along the lines indicated above. Very good linear relationships were obtained. In Figs. 6, 7, 8, 9, and 10 we have shown the results of such interpretation primarily for cases where the linear relationship was not so distinct. Nevertheless, the linearity is again evident except at smaller additions of organic solvents.

In Fig. 11 we have plotted the logarithms of the coagulation values against Bjerrum's distances for some dialyzed sols of As_2S_3 (Ostwald[9]), HgS (Weiser and Mack[25]) and AgI (Mackor[12]) in various solvent mixtures (we assumed that the charge z_2 of the stabilizing ions in these sols, as in ours, is one). The fact that the coagulation of dialyzed sols can be successfully interpreted in the same

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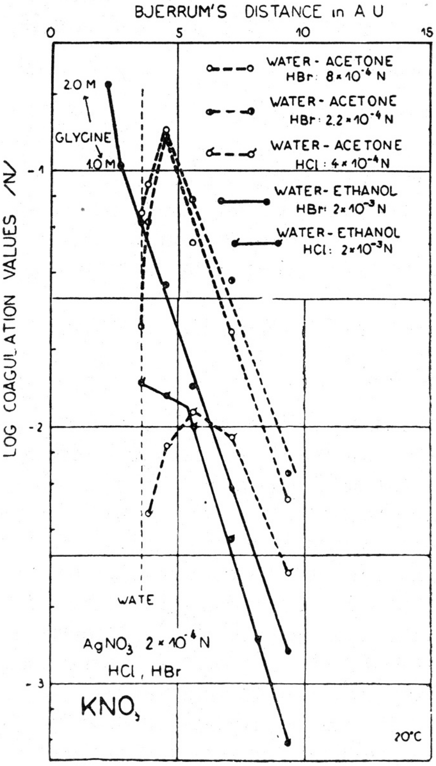
* The suggestion of Jonker,[22] that »if Težak would plot his log C values against log D and against log z^+ he would find that his experiments are roughly in accordance with the theoretical formula given by Derjaguin and by Verwey and Overbeek«, is not promising. From eq. (4) it follows that $\log C_{co}$ is proportional to $3 \log D$. This means that plots of $\log C_{co}$ against $\log D$ should give straight lines with slopes 3. In fact, we found that plots of $\log C_{co}$ against $1/D$ (from Bjerrum's formula) gave straight lines, and so the suggestion of Jonker becomes meaningless. Nevertheless, we have tried to interpret our results as indicated by Jonker, but we always obtained curved lines. When the »best« straight lines were drawn through the points on these curves, slopes greater than 3 (up to 8) were obtained, which is in accordance with the findings given in footnote on the page 84.

way as the coagulation of silver halide sols *in statu nascendi,* corroborates the conclusion of Schulz and Težak[26] that the results obtained on freshly prepared sols do not represent anything peculiar and specific for such systems, and that the results for sols obtained by both methods of preparation can be compared.



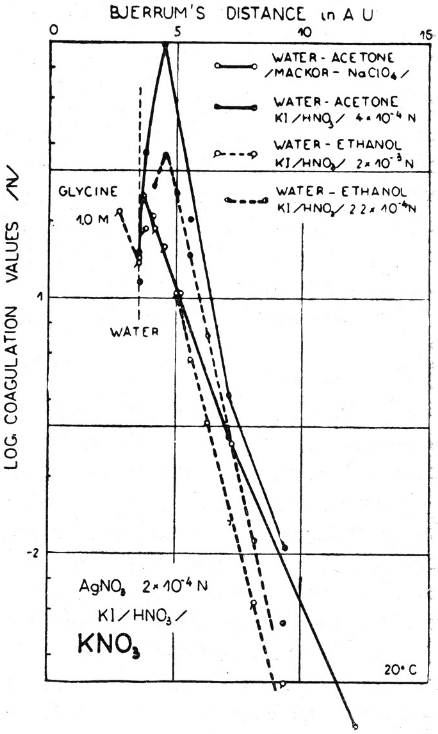


Fig. 6. Plot of Bjerrum's distances in Å. *vs.* log of coagulation values og KNO_3 for negative AgCl and AgBr sols in water-ethanol, water-acetone and water-glycine solutions.

Fig. 7. Plot of Bjerrum's distances in Å. *vs.* log of coagulation values of KNO_3 for negative AgI sols in water-ethanol, water-acetone and water-glycine solutions.

The success of applying Bjerrum theory of ionic association to coagulation phenomena becomes more interesting in view of the renewed and increasing use of this theory on various physico-chemical processes, especially in mixed or non-aqueous solvents. In an excellent summary of the present status of the theory of electrolytes,[27] Kraus concluded that while Bjerrum's theory reproduces the experimental results as a function of dielectric constant rather successfully for a given type of solvent mixture, it yields only approximate values as we go from solvent to solvent. Obviously, some constitutional factors of the ions as well as of the solvent molecules must be considered. The same conclusions were reached by Sadek and Fuoss.[28] In a series of papers Grunwald[29] applied Bjerrum's theory to the description of the deviations of activity coefficients of ionic species from unity in media of

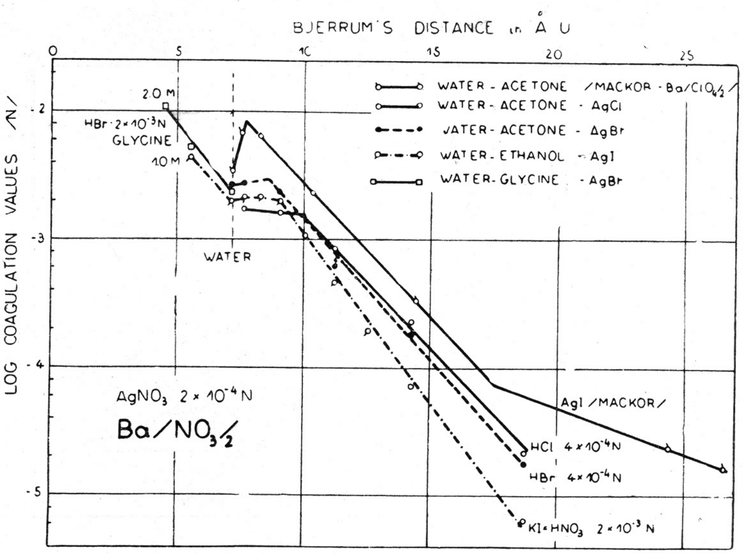


Fig. 8. Plot of Bjerrum's distances in Å. *vs.* log of coagulation values of $Ba(NO_3)_2$ for negative AgCl, AgBr and AgI sols in water-ethanol, water-acetone and water-glycine solutions.

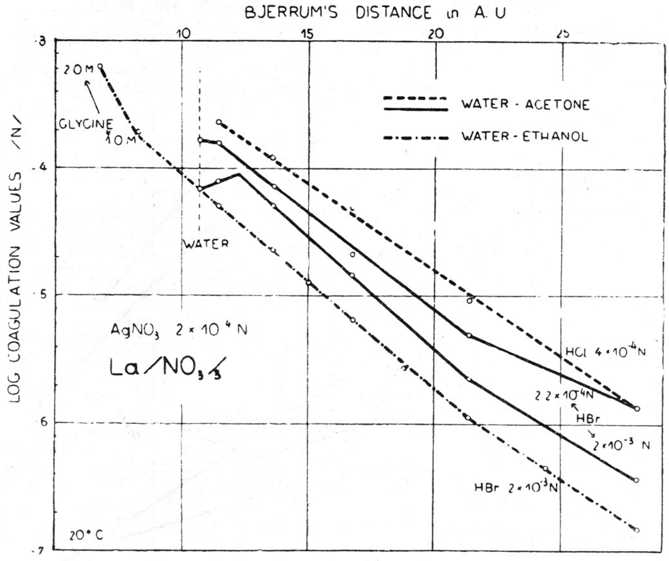


Fig. 9. Plot of Bjerrum's distances in Å. *vs.* log of coagulation values of $La(NO_3)_3$ for negative AgCl and AgBr sols in water-ethanol, water-acetone and water-glycine solutions.

lower dielectric constant. Among many other relevant papers we may note two, both of which are of particular importance to us. Schellman[30] succeded in applying Bjerrum's ion association theory to the binding of anions by proteins. For the binding of chloride by serum albumin he obtained results essentially in accordance with the thermodynamics of this reaction. Gregor[31]

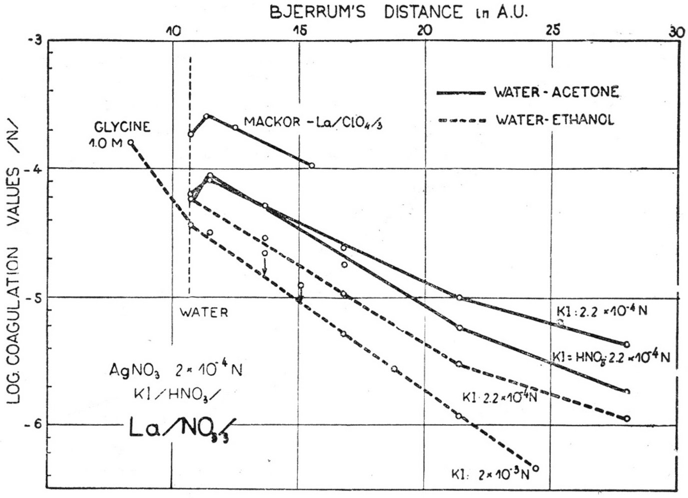


Fig. 10. Plot of Bjerrum's distances in Å. *vs.* log of coagulation values of $La(No_3)_3$ for negative AgJ sols in water-ethanol, water-acetone and water-glycine solutions.

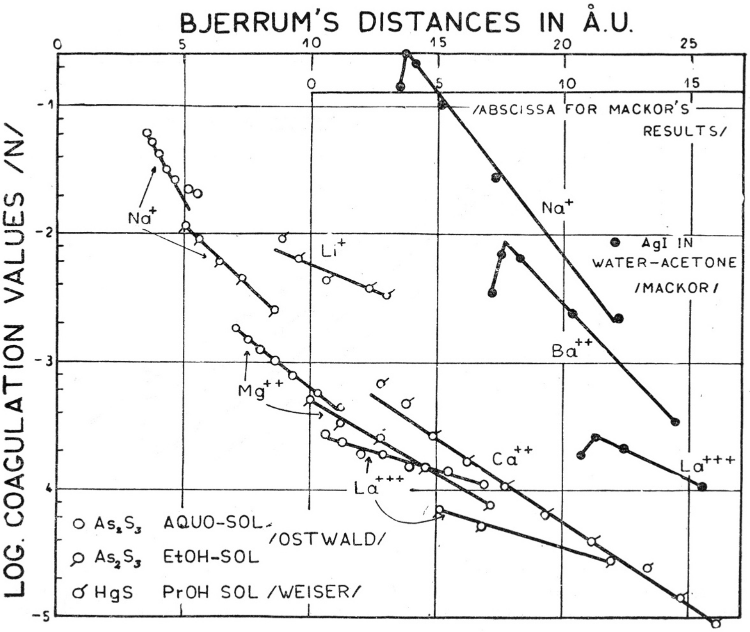


Fig. 11. Plot of Bjerrum's distances in Å. *vs.* log of coagulation values of various electrolytes for negative As_2S_3 (Ostwald[9]), HgS (Weiser[25]), and AgI (Mackor[12]) sols in mixed solvents.

studied the swelling of some polystyrene ion exchange resins in variety of mixed solvents. He arrived at the conclusion that ion pair formation in Bjerrum's sence may be considered as the primary effect in ion exchange.

It remains to find a reasonable explanation for the fact that in some cases we observed first an increase of coagulation values on addition of organic solvents instead of a decrease, and that the coagulation values were generally not the same for mixtures of equal dielectric constant. Unfortunately, we are not able at present to offer any definite explanation of these observations. But, it is very probable that some constitutional and structural factors are connected with the experimental facts. We will discuss them briefly with the intention to make the observed departures more understandable.

It is well known that ionic solubility of slightly soluble precipitates decreases with decreasing dielectric constant of the medium. Such a lowering of the solubility of solid phase causes a change in nucleation and formation of primary particles. This may results in a change in surface density and distribution of the stabilizing ions. As an example of the change in charge density we san mention the narrowing of the isoelectric maximum of silver chloride in acetonic solutions (Fig. 1).

On the other hand, the solvent greatly influences the complex solubility of silver halides in solutions with excess of halide ions.[7,32] In an extreme case, 0.0004 M KI in 82% acetone will dissolve about 0.00002 M of AgI, i. e., 10% of the total amount of the solid phase (0.0002 M). Thus, we shall have in the coagulating medium not only micelles and simple ions, but also the complex silver halide ions, monovalent and polyvalent. These ionic species may strongly influence the whole association-dissociation equilibrium of ions. We found that the coagulation values are not equal for various solvent compositions of the same dielectric constant, and similarly the complex solubilities of silver halides in isodielectric water-ethanol, water-acetone, and water-dioxane mixtures differed considerably for each solvent.[7,32]

Another factor which must be considered here is the possibility of selective aggregation and orientation of the solvent molecules in the vicinity of ions and charged surfaces. There exist some indications that ions are preferentially solvated by one kind of solvent molecules in a solvent mixture.[33,34,35,36] On the other hand the change in solvent composition may result in a great variation of the dipole part of the Galvani potential difference (χ potential), due to oriented adsorption of the solvent molecules at the boundary solid-solution. The change of the χ potential on silver iodide in water-acetone mixtures was observed by Mackor,[18] and some investigations which are now in progress in our laboratory indicate the same. In a previous paper[37] the possibility of introducing the χ potential as an important factor for the stability of lyophobic sols was shown. Comparison of our results obtained on silver bromide in acetonic solutions with those for silver iodide strongly support the view that the situation on the paricle surface was essentially and sometimes abruptly changed.

Taking into account all these complicating factors we may conclude that the change in the dielectric constant of the coagulating medium is the preponderant factor influencing the trend of the coagulation values in various solvents, and that the observed facts can be successfully described by applying Bjerrum's concept of ion-pair formation to the interaction between stabilizing and coagulating ions.

Note added in proof (July 19, 1955): In connection with our application of Bjerrum's concept of ionic association to coagulation processes, we can only regret the misinterpretation of Jonker [*Discussions Faraday Soc.* **18** (1955) 201], which was repeated by Derjaguin [*Kolloid. Zhur.* **17** (1955) 149]. Jonker said that »an objection against the use of the critical distance of Bjerrum used by Prof. Težak is that in c_d the valencies of the positive and the negative ions have the same importance, whereas it is known experimentally that the flocculation value depends in the first place upon the valency of the oppositely charged ions.« In many papers from our laboratory it was emphasized that z_1 and z_2 in Bjerrum's formula corresponds to the valencies of the coagulating counter ions and the stabilizing ions, respectively, and not to the valencies of positive and negative ions of the coagulating electrolyte, as was misunderstood by Jonker and Derjaguin.

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IZVOD

Metorika koagulacionih procesa. XII. Utjecaj sastava i svojstava otapala na koagulaciju solova argentum halogenida

J. Kratohvil i B. Težak

Prikazani su rezultati koagulacionih mjerenja na negativnim solovima argentum halogenida in statu nascendi u smjesama voda-etanol, voda-aceton i voda-dioksan, te u vodenim otopinama glicina. Usporedno sa smanjenjem dielektričke konstante medija smanjuju se u većini slučajeva i koagulacione vrijednosti. U nekim je slučajevima primijećeno, međutim, i protivno vladanje. Dobiveni rezultati interpretirani su u okvirima sadašnjih teorija stabiliteta liofobnih koloida. Konstatirano je, da nije moguće uspješno primijeniti ni Ostwaldovu teoriju niti teoriju Derjagina, Verweya i Overbeeka. Utvrđena je uska veza između koagulacionih vrijednosti i kritičkih Bjerrumovih udaljenosti za stvaranje ionskih parova. Ukratko je prodiskutiran utjecaj nekih drugih faktora osim dielektričke konstante.

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Primljeno 5. maja 1955.