METHORICS OF THE COAGULATION PROCESSES. I. MECHANISM OF COAGULATION OF HYDROPHOBIC SOLS

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In order to emphasize the necessity that theory should embrace the whole experimental evidence about coagulation, a short review of the findings and empirical rules concerning the coagulation phenomena are given. Among them has been pointed out Schulze-Hardy's rule, the relationship between the ionic size and the coagulation value, Burton-Bishop's rule, the evidence about the adsorption of the stabilizing ions, the observations of electrophoretic mobility of the coagulating particles, the effects of ionic antagonism, the relationship between the coagulation value and the coefficient of the activity of the electrolyte, and others. To make an observation of all of these relations in a well defined set of experimental systems possible, the reasons were given why the sols of silver halogenides in *statu nascendi* have been chosen. Some results already obtained with such sols are discussed pointing the way to a theoretical approach. The coagulation mechanism is interpreted as a result of a change in the dynamical equilibrium which exists between the stabilizing ions fixed on the wall of the particle and the counter ions. It was assumed that the coagulation is the result of the lower probability for the formation of the ionic pairs between stabilizing and coagulating ions against the similar association-dissociation equilibria in the solution in bulk. The influence of the density and the arrangement of the stabilizing ions as compared to the configuration of the ions in the kinetical-statistical lattice of the electrolytic solution has been emphasized in particular by pointing out the possibility of the simple ratio between the logarithm of the critical concentration for the coagulation and the critical distance $_cd$. This distance is taken as the thickness of the shell of the coulombic interactions of the ionic distribution spheres representing the simple model of the structure of an electrolytic solution.

Although there are many extensive theories of the stability and coagulation of the hydrophobic sols, it is difficult for an experimental worker to find the necessary correlation between the theoretical predictions and some empirical facts. The difficulties arose principally from the complexity of the factors involved in the mathematical treatment in the theories of Verwey and Overbeek¹) and Levine²) and others. It is true, there is a large number of various factors in colloidal systems, *e. g.*, the number and size of the particles, their charges, the electrical and chemical interactions between the surface and the ionic component of the media, the influence of the dielectric constant, the rôle of the potentials of the London-van der Waals type, the kinetic factors etc., which should be taken into account in every attempt to describe the systems of this

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¹) E. J. W. Verwey and J. Th. Overbeek, Theory of the Stability of Lyophobic Colloids, New-York — Amsterdam, 1948.

²) S. Levine, Trans. Faraday Soc., **42**, 102 (1946); **44**, 833 (1948).

kind. The uncertainties, however, in the determination of their exact values will make all such theories — which try to embrace nearly all of these factors — of a very limited use. The step by step procedure from one experimental result to the other seems to be nowadays a simpler, and, probably, a safer way in the circumstances where our knowledge of the structure of the interfaces and of the solutions shows such a great number of vacant points.

We shall therefore endeavour to find out the principal elements of the coagulation mechanism by investigating the simple coagulating systems in a way that only small and systematic variations of the working conditions are applied. The electrolytic coagulation itself as a typical, very sensitive and abrupt process will be used for the determination of the correspondence of state of such systems. For the correlation of the experimental results, an attempt has already been made³) to draw a simple picture of the configuration of the boundary state using the most elementary conceptions of spacial distribution. In general it seems that the process of coagulation may be a very useful indicator of the conditions in the boundary region where the states of both phases beyond the boundaries could also be indirectly guessed through the special conditions determined by the structure of the space between them.

Nevertheless, by investigating the interdependence of the coagulation and the gradual change of the conditions under which nearly all of the coagulation phenomena occur, much of those elements may be found which are of the greatest importance in settling the open questions in the important neighbouring fields. Thus the process of coagulation may serve as an internal signal of the correspondence of the state of the boundary layers and the electrolytic solutions for which other experimental methods are rather insensitive.

GENERAL EXPERIMENTAL EVIDENCE

There is a great number of attempts to characterize the process of coagulation by various phenomena which are — more or less nearly — related to the esential part of the coagulating mechanism itself. To mention all of them it would be necessary to review the history of a great deal of colloid science, and therefore only the main relations will be given here in brief. This review aims especially at emphasizing the need that the

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³) B. Težak, Z. physikal. Chem., **191 A**, 270 (1942); Arhiv kem. **19**, 19 (1947).

actual theory of the coagulation should be capable to give for all of the following findings a justifiable frame.

The rule of Schulze and Hardy. The classical investigations of Schulze[4]), Linder and Picton[5]), and Hardy[6]), have clearly shown the electrical character of the electrolytic coagulation of hydrophobic sols. The effectiveness of the ions which have a charge which is opposite to the charge of the colloid particles increases enormously with the increase in valency (rule of Schulze and Hardy). For instance, in the case of the coagulation of negative arsenic trisulphide sol, the coagulation values of 49.5, 0.691 and 0.093 mM were found for potassium, barium and aluminium chloride respectively. Since the formulation of this rule, there was a great many number of investigations with various sols such as ferric, aluminium, chromic, manganese, vanadium and other oxides, copper ferrocyanide, silver iodide and bromide, sulphur, gold, silver, parafin, palmitic acid, mastic, and others. Many of those systems are very complex and the coagulations were performed under conditions where many foreign factors could intervene. Especially, the adsorption effects in purified systems of high sol concentrations may prevent us to obtain net results. Thus it was found that the coagulating power of an electrolyte depends on the quality of the sol. The purer the sol the less is the valency effect[7]). Other deviations from the rule were found with ions of higher valency and of very large ionic size where the adsorption effects must be taken into account. But in spite of all these mostly undefined influences, the relations concerning the valency effect are in general consistent.

The influence of the dimension of the coagulation ion. A review of the relation between the radius and the coagulating value of an ion has been given by Wo. Ostwald[8]). Ostwald gives many examples from the colloid chemical literature that the coagulation value of an ionic series, especially in some experiments with negative sols, follows the rule according to the simple hyperbolic equation

$$(1 - f_k)(r + a) = b$$

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[4]) H. Schulze, J. pr. Chem., (2) 25, 431 (1882); 27, 320 (1883); 32, 390 (1885).

[5]) S. Linder and H. Picton, J. Chem. Soc., 61, 114 (1892); 67, 64 (1895).

[6]) W. B. Hardy, Proc. Roy. Soc., 66, 110 (1889); J. Physical Chem., 4, 255 (1900).

[7]) N. R. Dhar and V. Gore, J. Indian Chem. Soc., 6, 31 (1929).

[8]) Wo. Ostwald, Kolloid-Z., 85, 34 (1938).

where f_k is the coefficient of activity for the coagulating ion, r the ionic radius in Å, while a and b are constants characteristic for the experimental system. The constants a and b vary between 16 to 0.6 and 3·345 to 0·109, respectively, for an univalent ion, between 5·8 to 0·25 and 1·28 to 0·35, respectively, for a bivalent ion, and between 8·7 to 1·5 and 2 to 0·3, respectively, for a trivalent coagulating ion. There also exists a simple relationship between the constants a and b. Generally, for the sols where the hydrophobic behaviour is less marked, there is a greater influence of the ionic size on the coagulation. It is interesting to note that Ostwald in discussing the relation between the size of the coagulating ion and its coagulating value has pointed out the possibility that the ionic radius could be determined from the coagulation data. As a proof he gave a series from Freundlich's investigations of the coagulating power of great organic ions[9]), where all (except of strychninnitrate) have found their reasonable place in the series.

The rule of Burton and Bishop[10]). The problem of the purity of the sol[11]) arose primarily after the formulation of the sol concentration effects[12]). We quote Burton's formulation of the rule: »For univalent ions the concentration of the ion necessary to produce coagulation increases with decreasing concentration of the colloid — this increase being very marked with low concentration of the colloid. For bivalent ions the concentration of the ion necessary to produce the coagulation is almost constant, i. e. independent of the concentration of the colloid. For trivalent ions the concentration of the ion necessary to produce coagulation varies almost directly with the concentration of the colloid.«[13])

Apart from the validity or invalidity of the rule of Schulze and Hardy, examinations of the validity of the rule of Burton and Bishop have proved to be of primary importance for the interpretation of many theories. The great number of experimental results in connection with Burton's rule are given by Ostwald's, Kruyt's and Weiser's

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[9]) H. Freundlich, Kapillarchemie, 4 Ed., II Vol., Leipzig 1932, p. 122.

[10]) E. F. Burton and E. Bishop, J. Physical Chem., 24, 701 (1920).

[11]) R. C. Judd and C. H. Sorum, J. Amer. Chem. Soc., 52, 2598 (1930); E. D. Fisher and C. H. Sorum, J. Physical Chem., 39, 283 (1935); 44, 62 (1940).

[12]) H. R. Kruyt and J. van der Spek, Kolloid-Z., 25, 1 (1919).

[13]) E. F. Burton, The Physical Properties of Colloidal Solutions, 3 ed., London — New York, 1938, p. 192.

schools. The experiments of Ostwald, Kauffmann[14], [15]) and others confirmed the rule; the results of Kruyt and his collaborators[16]) show direct counter effects, while Weiser and Milligan[17]) summarize their investigations with a conclusion that only fortuitous combination of circumstancies can give coagulation value — sol concentration curves that are in accord with Burton and Bishop's rule. Hazel[18]) observed proportionate stability with all electrolytes upon dilution of the sol of manganese oxide and arsenic trisulphide. This inconsistency of results in spite of the similarity of the material systems points out very impressively the complexity of the investigated field.

The adsorption of ions. After settling the important questions of the neutralizing adsorption, the exchange adsorption, and the direct adsorption of coagulating ions[19]), the central points to be still settled are: the determination of the extent of adsorption of the stabilizing (potential determining) ion; the detection of the distribution of that ion on the surface of the colloid particles; and the determination of the proportion of these ions which are in a free, dissociated state. The first of these points was solved in respect of silver iodide[20]) and bromide[21]); the experimentally determined amounts of the adsorbed stabilizing iodide and bromide ions correspond to about 2% and 0.5% of the colloid surface respectively. Concerning the distribution, Kruyt and Verwey[20]) believe that the stabilizing ions are attached only on corners, edges and spots of the imperfections of the crystalline particles. As to the proportion between the ions in the free and the associated state, the complex results of electrokinetic and other phenomena allow only guesses.

The electrophoretic mobility. There are many findings of the parallelism between stability and the electrokinetic potential or the values connected with it[22]), but there is also a great

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[14]) Wo. Ostwald, Kolloid-Z., **75**, 39 (1936).

[15]) H. Kauffmann, Kolloid-Z., **92**, 343 (1940); **93**, 86 (1940).

[16]) H. R. Kruyt and M. A. M. Klompé, Kolloid-Beih., **54**, 484 (1943).

[17]) H. B. Weiser and W. O. Milligan, J. Amer. Chem. Soc., **62**, 1924 (1940).

[18]) F. Hazel, J. Physical Chem., **45**, 738 (1941).

[19]) H. Freundlich, K. Joachimsohn and G. Ettisch, Z. physikal. Chem., **41** A, 249 (1929).

[20]) E. J. W. Verwey and H. R. Kruyt, Z. physikal. Chem. **167** A, 137 (1933).

[21]) A. Basiński, Rec. trav. chim., **59**, 331 (1940).

[22]) H. Eilers and J. Korff, Trans. Faraday Soc., **36**, 229 (1940).

deal of evidence on the electrophoretic mobility of the coagulating particles[23]) which is not in agreement with the simple conceptions of the rôle of the zeta potential in stability. It has been shown that the electrophoretic velocity of colloidal particles increases with time in the presence of coagulating concentrations of the electrolyte. This effect is the more marked the higher the valency of the coagulating ions. When the purity of the sol is comparatively greater, the valency effect on the electrophoretic mobility disappears. This behaviour is analogous to the decreasing valency effect on the coagulating power of electrolytes in the case of extremely pure sols.

The ionic antagonism. The sensitivity of the coagulating mechanism is specially manifested in the variation of the coagulation values when mixtures of electrolytes of different coagulation values are applied. These influences may give an additivity, a sensibilization or an antagonism effect. The phenomena of ion antagonism have been found on various complex[24]) and simple[25]) sols, and depend primarily on the presence of a relatively greater concentration of the accompanying ion in relation to the coagulating ion. In some cases the phenomena of ion antagonism are conditioned by the charge of the colloid particles.

The influence of the media. It has been generally observed that with a lower dielectric constant of the media, the coagulation values are regularly lowered. A review of those investigations is given by Ostwald, Kokkoros and Hoffmann[26]) together with an adequate discussion.

The coefficient of electrolyte activity. In numerous papers Wo. Ostwald and his collaborators[27]) have attempted to show the preponderant rôle of the coefficient of activity of the dominating ion. It is of interest to mention that the systematic investigations of the relatively simple systems are rather scarce in Ostwald's reviews. The majority of the coefficients of activity of the coagulating electrolytes were calculated for complex and concentrated sols. There are many reasons to assume

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[23]) J. N. Mukherjee, S. G. Chaudhury and K. Bhabak, J. Indian Chem. Soc., **13**, 372 (1936).

[24]) H. Freundlich and J. Tamchyna, Kolloid-Z., **53**, 288 (1930); H. B. Weiser, J. Physical. Chem. **30**, 29 (1926); F. Hazel, J. Physical. Chem. **45**, 747 (1941).

[25]) A. Basiński, Rocz. Chem., **15**, 430 (1935).

[26]) Wo. Ostwald, H. Kokkoros and K. Hoffmann, Kolloid-Z., **81**, 48 (1937).

[27]) Wo. Ostvald, J. Physical. Chem., **42**, 981 (1938); Kolloid-Z., **88**, 1 (1939); **94**, 169 (1941).

that Ostwald's postulates $f_k \cong$ const., and f_k = const., where f_k is the coefficient of activity of the coagulating ion, cannot be directly applied because of the superposition of the adsorption to the simple ionic effect. Only in the region of very small sol concentrations, where the adsorption effects are quite negligible, the physical meaning of the activity coefficient may be understood. But in these systems of lower sol concentrations the values of the coefficient are usually different for ions of various valency. According to Kauffmann's[14]) and our results[28]), the plots of the coefficient of activity *vs.* concentration of the sol show a falling order from ions of higher to those of lower valency. In exceptional cases only, where the density of charges on the colloid particles is very low, this order may be reversed.

Other relations. There are a great many other observations concerning the coagulation. Some are of a physical, others of a chemical or of a mixed character. For illustration the influence of the size of the colloid particles may be mentioned[29]), as it was manifested by fractionated coagulation of sulphur sols. There are, further, the effects of temperature, of stirring, and of other factors which are not of such an importance as those direct or derived observations which are presented for discussion under our subheadings.

THE SPECIAL EXPERIMENTAL SYSTEM AND METHOD

It is clear that so far the experimental data for a comprehensive theory of the stability of lyophobic sols were insufficient. All the simple conceptions of the rôle of neutralization of the particle charges (Linder and Picton), of the exchange of the ions (Duclaux), of the critical electrokinetic potential (Powis), of the adsorption effects of the coagulating ions (Freundlich), have proved inadequate. With regard to the complexity of the problems involved it will be almost impossible to discuss the experimental material profitably without some limitations regarding the system, the method of observation and the theoretical approach. Our discussion and conclusions will, therefore, be given not from a general but from our standpoint.

A full description of the pure physical factors such as the size and the number of colloidal particles, or the state of the composite electrolytic solution, presents such difficulties that

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[28]) B. Težak, E. Matijević and K. Schulz, Arhiv kem., **20**, 1 (1948).

[29]) S. Odén, Nova Acta Soc. Sci. Upsal., IV, 3, 4 (1913).

it is impossible to start an investigation with the system actually defined in all details. For this reason it is natural that attempts are made to find the most effective part of the coagulating mechanism, and, after this has been disclosed, to turn back for an examinination and explanation of the other parts according to the order of the magnitude of their actual or probable influences.

According to this direction it would be necessary to use a special system and an adequate experimental method by means of which the most sensitive points of the coagulating mechanism could not only be detected but also quantitatively and systematically followed.

Requirements concerning the system. The starting point must be a system which can be well defined experimentally. It is also necessary to use in its preparation the smallest number of possible steps. As the specificity and the sensibility of a colloid system is influenced mostly by their preparation and subsequent purification, the sols *in statu nascendi* shoud be preferred. Further, as we are examining the influence of electrolytes, simple ionic crystals must be chosen as the colloid particles in preference to other inorganic and organic substances for which the difficulties in defining the surface structure and reactions are much greater.

The other requirements for a standard system are: the general feature of the coagulation phenomenon should be nearly the same in spite of the changed conditions under which the experiments are performed, and the gradual and systematic changes of the greatest possible number of the most effective factors should easily be observed.

It seems to us that in all these respects the most favorable systems are the coagulating systems of silver halides *in statu nascendi* prepared from a mixture of electrolytes.

Requirements concerning the method. There is a great number of possible experimental techniques for the registration of the coagulation, but the limitations for the standard systems as given above may prove the tyndallometrical measurements to be the most convenient. To avoid the superposition of two or more effects such as »pure« ionic and other, e. g., adsorption processes, it will be necessary to use very diluted systems. For dilute systems, under ordinary working conditions, the tyndallometry is certainly more sensitive than the absorbometry.

In order to follow the coagulating process in all its characteristic features, the number and the size of the coagulating particles should be observed from the beginning to the end of the coagulation. To meet this requirement, at least approximately, each system was observed in fixed time intervals through a period from 30 seconds up to one or twenty four hours. For a rough determination of the size of the particles, the so called tyndallometrical dispersion quotients, DQ_T, have been used. The DQ_T-method consists in a measurement of the intensity of light scattered in two spectral regions, e. g. blue and red; the ratios of these intensities, being a function of the particle radii, allow an estimation of their size. In such a way an approximate determination of particle size is accomplished very quickly and easily. The DQ_T-values are, namely, nearly linear functions of the particle sizes between 50 and 400 mμ[30]), which represent the main region of the coagulation processes.

Actual experiments. We have prepared systems of sparingly soluble silver salts, such as chloride, bromide, iodide and others, by mixing the reacting components allways in the same manner. The reacting solutions contained various electrolytes, the influence of which had to be observed. The formation of the precipitate through all the stages, from the initial crystallization to the coagulation, and the sedimentation, was followed in regular time intervals by measuring the intensity of tyndall light by means of a Pulfrich photometer through blue, green and red light filters. From a series of such measurements the coagulation values have been determined.

The systems belonging to one series of experiments have been prepared always in a serial order of 8 to 16 samples which have been treated successively in exactly the same manner. The precipitating systems have been obtained by mixing equal volumes (usually 5 ml) of solutions, from which the one contained silver nitrate, and the other the halide component in a concentration exceeding that of the silver ion. In order to study the effects of other ions, various electrolytes were added to the solution which contained the halide component. In this way the possibilities of a very large number of variations have been opened.

We prepared, usually, something like a concentration gradient by using a series of 8 to 16 test tubes containing solutions in which the investigated electrolyte was varied stepwise. Thus,

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[30]) B. Težak, Kolloid-Z., **74** 16 (1936); Z. physikal. Chem., **175 A**, 219 (1935).

the coagulation values have been determined by taking that concentration of the electrolyte, where under the same conditions in respect to all other circumstances, the greatest change of the tyndallometric values in the course of two to twenty minutes could be observed.

For convenience, instead of a great number of graphical analysis of the results in diagrams: tyndallometric value *vs.* time (time-tyndallograms) for various concentrations of electrolyte, the four or ten minute curves in the diagram: tyndallometric value *vs.* logarithm of the concentration of the neutral electrolytes (concentration-tyndallograms) have been used for determination of the concentration limits between rapid and slow coagulating processes. Such a concentration in an experimental series where the changes in velocity of precipitation are most abrupt is taken as the coagulation value.

RESULTS AND THEIR INTERPRETATION

As model systems we have chosen silver chloride and bromide *in statu nascendi*. The conditions which such systems should fulfill are: (a) the crystallization stage should not interfere with the coagulation phenomena, (b) the adsorption effects should be negligible; and (c) the coefficient of activity of the electrolytic solutions in one correlated experimental series should not change greatly.

Experimental results with systems of silver chloride and bromide. Only the experiments can answer whether these conditions are satisfied or not, but for the beginning it would be worth while to start with the assumption that our systems really correspond to our requirements. This assumption seems to be justified by some experimental results which we are going to present here in the connection with our interpretation of the coagulating mechanism. The final decision as to the correctness of our assumptions we must leave until a much greater number of experiments is collected, which should either confirm or invalidate our working hypothesis.

By precipitation of silver chloride from 1×10^{-4} N solutions of silver nitrate and various concentrations of potassium, barium and aluminium chloride, the coagulation values for these cations were obtained. Similar series with lithium, sodium, potassium, rubidium and caesium chloride were also made[2]). These coagulation values are shown in Table I.

Table I

System: silver nitrate 1×10^{-4} N — Me-chloride (water solution, 20°C)

Electrolyte	Coagulation value (in normalities)
$LiCl$	$8{\cdot}7\times10^{-2}$ N
$NaCl$	$7{\cdot}4\times10^{-2}$ N
KCl	$5{\cdot}7\times10^{-2}$ N
$RbCl$	$5{\cdot}2\times10^{-2}$ N
$CsCl$	$4{\cdot}6\times10^{-2}$ N
$BaCl_2$	$3{\cdot}0\times10^{-3}$ N
$AlCl_3$	$1{\cdot}7\times10^{-4}$ N

For systems of silver bromide similar results were obtained[31]. The difference in preparation of the systems consisted in the use of a constant concentration of the bromide ion; the only variable concentration in one experimental series was that of the neutral electrolyte (potassium, barium and lanthanum nitrate). The results are given in Table II.

Table II

System: silver nitrate: 1×10^{-4} N — hydrobromic acid 4×10^{-4} N — Me-nitrate (water solution, 20°C)

Electrolyte	Coagulation value (in normalities)
KNO_3	$5{\cdot}6\times10^{-2}$ N
$Ba(NO_3)_2$	$3{\cdot}1\times10^{-3}$ N
$La(NO_3)_3$	$1{\cdot}2\times10^{-4}$ N
$Th(NO_3)_4$	$5{\cdot}0\times10^{-6}$ N

In both series of experimental results the coagulation values were in the order corresponding to the rule of Schulze and Hardy.

The distribution of the stabilizing ions. We have mentioned the experimental results concerning the amount of adsorption of the stabilizing ion on silver iodide and bromide[20], [21]. For the silver chloride it may be suposed that the maximum of the adsorption for the stabilizing ion is reached when 0·5 per cent of the free surface of the colloid particles is covered. In respect to the distribution, it is assumed that the stabilizing ions are not adsorbed specifically on certain spots but that they are distributed in a neary uniform manner throughout the exposed surface. Thus the distances between the neighbouring stabilizing ions are about 40 and more Å. U. For such a distribution it is possible to consider that the interaction between the stabilizing ion and the ion in solution is a separate elementary process,

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[31] B. Težak and E. Matijević, Arhiv. kem., 19, 29 (1947).

uninfluenced by the similar interactions in the neighbourhood. Many of the processes of the association-dissociation equilibria related to the ion-pair formation in the solution must be, therefore, fully reflected in slightly modified circumstances where one of the partners of the ion-pair is fixed on the wall. This is our basic conception for building up the configuration of the boundary region.

The chemical potential and activity of the coagulating ion. In order to interprete the results of the Tables I and II an attempt will be made to use the chemical potential and the activity coefficient by dividing in the usual way the chemical potential, μ_i, on one part of the coulombic interactions, $\mu_{i(coul)}$, and the other without the electric potential, $\mu_{i(o)}$. Thus the μ_i of the expression

$$\mu_i - \mu_i^0 = k\,T\,ln\ a_i \tag{1}$$

where μ_i and μ_i^0 are the chemical potentials of an ion in actual and in some standard state, k is the Boltzmann constant, T absolute temperature, and a_i activity of an ionic constituent, may be given by

$$\mu_i = \mu_{i\,(coul)} + \mu_{i\,(o)} \tag{2}$$

If the coagulation is the result of the coulombic interactions between the stabilizing and the coagulating ions which lead to the dynamical equilibria of the association-dissociation ratio for the ion-pair formation, the ions with the coulombic potential may be replaced by other species without the electrical charge under the condition that they will undergo mutual interactions with the stabilizing ions owing to their thermal and other potentials, and with the same frequency as charged ions do. To achieve this situation it will naturally be necessary that the concentration of our uncharged species will be much greater than that of the charged ones, while the concentration of both should be a specific function of the concentration of the stabilizing ions fixed on the wall. The chemical potential of the uncharged species will be denoted with $\mu_{i\,(fix)}$, and according to *(2)* is

$$\mu_{i(fix)} = - \mu_{i(coul)} + \mu_{i(o)}, \tag{3}$$

where $\mu_{i(o)}$ is the chemical potential of the uncharged species which are in the same concentration as the charged ions causing the coagulation. The $\mu_{i(fix)}$ must be of the same value for all cases regardlessly of the valency of ions represented by $\mu_{i(coul)}$ and $\mu_{i(o)}$

Thus

$$\overset{\text{II}}{\mu}_{i(coul)} = -\mu_{i(fix)} + \overset{\text{II}}{\mu}_{i(o)} \tag{4}$$

$$\overset{\text{I}}{\mu}_{i(coul)} = -\mu_{i(fix)} + \overset{\text{I}}{\mu^{i}}_{(o)} \tag{5}$$

where superscript gives the valency of the counter ions against univalent stabilizing ion.

Since

$$\mu_{i(fix)} = \mu^0 + kT\, ln\, C_{i(fix)}$$

and

$$\mu_{i(o)} = \mu^0 + kT\, ln\, C_i,$$

where C denotes a concentration in normalities, it is

$$\mu_{i(coul)} = -kT\, ln \frac{C_{i(fix)}}{C_i} \tag{6}$$

Supposing that there exists a dynamical equilibrium of the interionic interactions in the layer adjacent to the surface of the colloid particle and in the solution in bulk, and that the critical condition for coagulation is connected with Bjerrum's ion-pair formation between stabilizing-coagulating ions, the kT may be replaced for the case of uni-univalent electrolyte by $\frac{e^2}{2D_a\delta}$, where ${}_a\delta$ is the interionic distance. Accordingly equation *(6)* can be written

$${}_a\delta = -\frac{e^2}{2D\,\mu_{(coul)}}\, ln \frac{C_{i(fix)}}{C_i} \tag{7}$$

Taking $\mu_{i(coul)} = kT\, ln\, f$, and $ln\, f = -\frac{e^2}{2DkT}\varkappa$ we obtain

$${}_a\delta = \frac{1}{\varkappa}\, ln \frac{C_{i(fix)}}{C_i} \tag{8}$$

In the case of ideal distribution of the univalent stabilizing ions in respect to the distribution of the ions in the lattice of the solution, it may be supposed that the whole configuration of the ions near the surface corresponds to such a packing that the critical coefficient of activity of the coagulating ion, f_c, is constant at the critical concentration for the coagulation, ${}_cC_i$, in spite of the change of valency or of the size of coagulation ion. In such circumstances $\frac{1}{\varkappa}$ becomes a standard distance, ${}_s\delta$, which is specific for the system under observation.

The model of the ionic distribution. To afford a visualized conception of the relations encountered in methoric spaces or in solutions of electrolytes in general, it will be assumed that the ions of the electrolytic solution occupy positions of a 'lattice' of the kind similar to Ghosh's interpretation[32]) but modified in the sense of the modern approach. According to the kinetic theory of liquids and liquid mixtures developed by Bernal[33]), Lennard-Jones[34]), Kirkwood[35]), Scatchard[36]), Born[37]), Eyring[38]), Stewart[39]), Huggins[40]), and others, as well as to the results of X-ray, Raman and infra-red investigations of liquid systems, it may be assumed that in solutions of electrolytes in general there are some arrangements similar to those of the heavy polyvalent ions, which show by X-ray reflection photography a 'spacing' that increases with the dilution (Prins[41])). Thus an ordinary diluted solution of an electrolyte should have also a kind od Prins' superarrangement of ions relative to one another, as well as a subarrangement of solvent molecules round a particular ion. In short periods of time there is, therefore, the probability to construct for each ion of the solution a statistical 'cage' as a function of the dilution and of the type of the 'lattice'. In the simplest case the distribution will correspond to the cubic packing of the spheres, the approximate volume of which is obtained by dividing the whole volume of the solution with the total number of ions. The chemical potential of an ion, $\mu = \frac{\partial G}{\partial n}$, may be represented in such a circumstance with the 'density' of the ionic distribution within the particular sphere. The probability that an ion could be found in the neighbourhood

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[32]) J. Ch. Ghosh, J. Chem. Soc., **113**, 449, 627, 707; **117**, 1930 (1920).

[33]) J. D. Bernal, Trans. Faraday Soc., **33**, 27 (1937).

[34]) J. Corner and J. E. Lennard-Jones, Proc. Roy. Soc., **A 178**, 401 (1941).

[35]) J. G. Kirkwood and E. M. Boggs, J. Chem. Physics, **10**, 394 (1942); J. G. Kirkwood, J. Chem. Physics, **14**, 180 (1946).

[36]) G. Scatchard, J. Chem. Physics, **9**, 34 (1941); Chem. Rev., **44**, 7 (1949).

[37]) M. Born and H. S. Green, Proc. Roy. Soc., **188**, 10 (1946); H. S. Green, Proc. Roy. Soc., **189**, 103 (1947); M. Born and H. S. Green, Proc. Roy. Soc., **190**, 455 (1947); **191**, 168 (1947).

[38]) R. B. Parlin and H. Eyring, Chem. Rev., **44**, 47 (1949); A. E. Stearn, E. M. Irish and H. Eyring, J. Physical Chem., **44**, 981 (1940).

[39]) G. W. Stewart, Trans. Faraday Soc., **33**, 238 (1937); J. Chem. Phys., **7**, 869 (1939); **11**, 72 (1943).

[40]) M. L. Huggins, J. Physical. Chem., **52**, 248 (1948).

[41]) J. A. Prins, J. Chem. Phys. **3**, 72 (1933); Trans. Faraday Soc., **33**, 110 (1937).

of the periphery of one sphere will be given by its 'oscillations', resulting in 'self-diffusion' and 'mutual-diffusion' in the sense of Yang's definitions[42]). To account for the great potentials which are influencing the mutual diffusion and the Bjerrum's associations owing to the coulombic interactions, it may be convenient to introduce the effect of Debye-Hückel atmosphere in a simple way by constructing for each ionic distribution sphere a corresponding association shell, the thickness of which for a symmetrical electrolyte is $\frac{1}{2} \frac{z^2 e^2}{2DkT}$.

For each electrolytic solution, characterized with a definite coefficient of activity, the ratio between the shell thickness and the radius of the sphere must be a constant, representing through the corresponding volume ratio the probability that the ion is found in the associated state against the probability that it will be found in its spheric 'cage' at all.

With such a model there exists in ideal case the ratio $\frac{{}_s\delta}{{}_sd} = \frac{{}_a\delta}{{}_cd}$ which may be used in our expression *(8)* giving the standard thickness, ${}_sd$, and the critical thickness of the association shell, ${}_cd$, which is the critical distance of the coulombic interactions between stabilizing and coagulating ions, while $\mu_{i(coul)}$ is given as the volume of the corresponding shell. Thus our equation *(8)* becomes

$$ {}_cd = {}_sd \ ln \frac{C_{i(fix)}}{C_i} \qquad (9) $$

and the values of ${}_cd$ and ${}_sd$ express the main characteristics of the stabilizing and coagulating ions of the particular sol while their variation for the system under the same experimental conditions could be attributed directly to the interactions of the stabilizing and coagulating ions. The ${}_sd$-value would be connected chiefly with the density of the stabilizing ions on the surface of the particles, while the ${}_cd$-value could be expressed as approximately equal to $\left(\frac{e^2}{2DkT} - r_i\right) z$, where r_i is the crystallographic radius of the coagulating ion.

It must be emphasized, however, that all these relations can in reality be found only under our simplified conditions of which may be noticed especially: (1) the concentration of the sol particles should enable us to consider the adsorption effects as

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[42]) L. M. Yang, Proc. Roy. Soc., A 198, 94, 471 (1949).

negligible, (2) the density of the stabilizing ions should be comparatively low (e. g., one charge on more than 500 Å^2), (3) the ionic configuration in the solution should correspond to the distribution of the stabilizing ions on the wall according to the cubic 'lattice', (4) the stabilizing ions, being uniformly distributed on the wall, should not change greatly the critical distance between them and the counter ions as compared with the similar distances between ions in the solution in bulk, (5) the dielectric constant should be taken as equal to that of macroscopic value, and (6) the ratio between the coefficients of 'self-diffusion' and 'mutual diffusion' of the ions should not change with the concentration.

The best proof of our view on the architecture of the methoric space in case of the coagulating particles can be given as a result of a great number of experiments with the same well defined systems. On the ground of the relations discussed, it is to be expected that with systems, where only small changes are allowed, the coagulation performed under the same conditions except the coagulating electrolyte may be used to indicate the influence of the ionic size and valency according to the expressions given.

Of course, in reality many of our relations are far from being maintained, but the general picture, however, may be of some use as a means for the orientation in this complex field of investigation.

The schematic presentation of the boundary state. In Figgs 1, 2, 3 and 4 the critical conditions for the coagulation of silver chloride and bromide sols *in statu nascendi* are illustrated according our concepts.

Fig. 1 represents the relationship between coulombic parts of the univalent and bivalent counter ions against the logarithm of their coagulating concentration according to equations *(4)*, *(5)* and *(6)*:

$$\overset{II}{\mu}_{i(coul)} - \overset{I}{\mu}_{i(coul)} = -kT\,ln\,\frac{C_{i(fix)}}{C_i^{II}} + kTln\,\frac{C_{i(fix)}}{C_i^{I}} =$$

$$= kTln\,C_i^{II} - kTln\,C_i^{I} \qquad (10)$$

The concentration values are given from Table I.

Using our model for the ionic distribution, instead of coulombic parts, $\overset{I}{\mu}_{i(coul)}$ and $\overset{II}{\mu}_{i(coul)}$, of the interactions between the stabilizing and coagulating ions, the critical thicknesses of the cor-

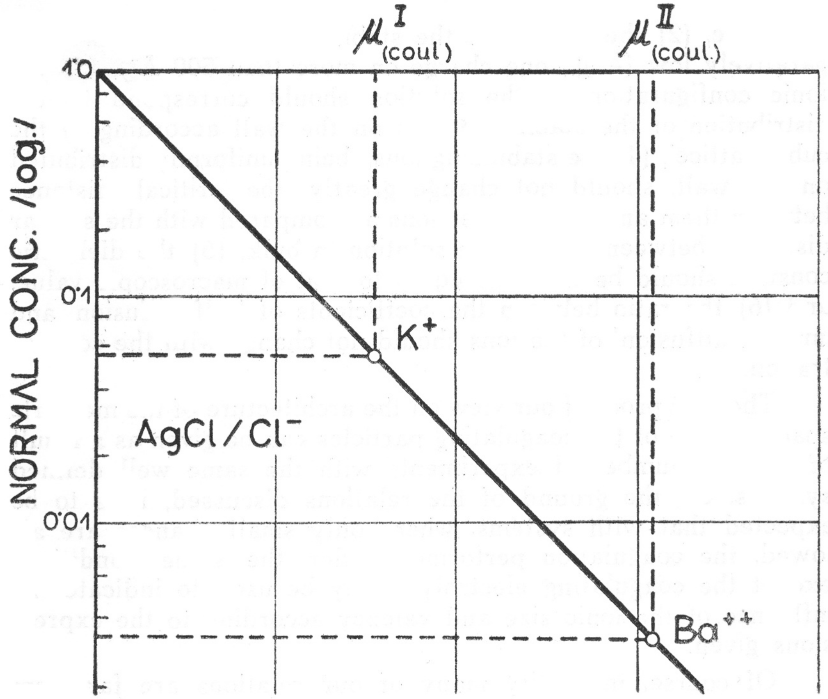

Fig. 1. Relationship between coulombic part of the chemical potentials and logarithm of coagulation values of K- and Ba-chlorides for AgCl-sol.

responding shells can be taken (Fig. 2). The critical distances $_{c}d$ and $_{c}d^{II}$ are given according to the expression (9). The value of $C_{i(fix)}$ was taken as equal to 1. Assuming that the diference between the critical distances of barium and potassium ion is 3·8 Å (for $D = 80; \frac{e^2}{2DkT} = 3{\cdot}6$ Å), the abscissae values in ångtröms have been, namely, obtained, and thus the possibility to follow the influence of the radius of the coagulating ion is given. This relationship is simply expressed for our experimental systems of silver chloride *in statu nascendi* as

$$z(2{\cdot}52 + r_i^{+}) = -3{\cdot}06 \log_c C_i^{+} \qquad (11)$$

while for the results of the coagulating systems of silver bromide (Table II) it is

$$z(2{\cdot}38 + r_i^{+}) = -2{\cdot}98 \log_c C_i^{+} \qquad (12)$$

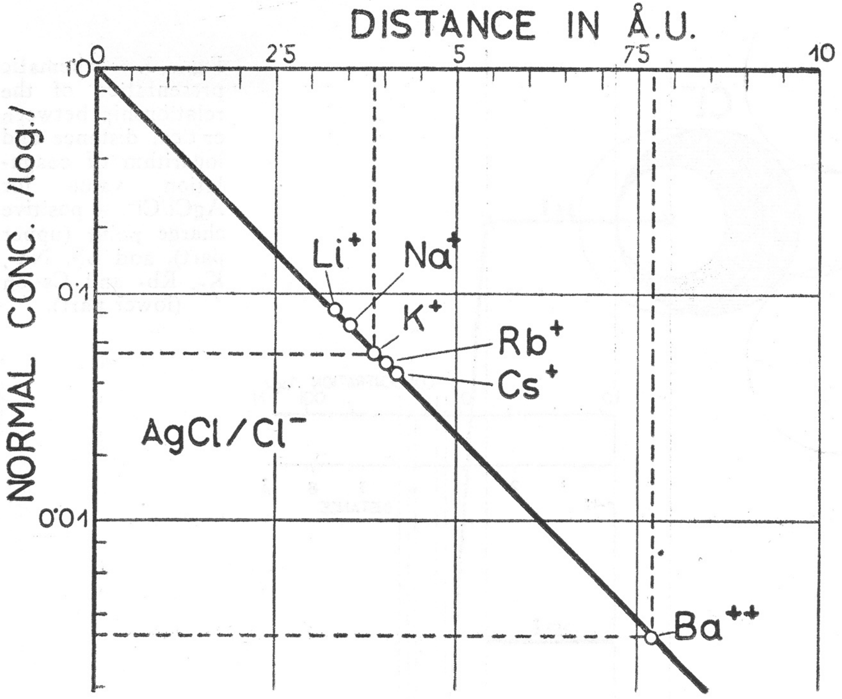

Fig. 2. Relationship between critical distances and logarithm of coagulation values of Li-, Na-, K-, Rb-, Cs- and Ba-chlorides for AgCl-sol.

where z is the valency and r_i^+ the crystallographically determined radius of the coagulating ion; C_i^+ being its coagulation value. As it may be expected, for each experimental system the numerical coefficients are specific. Among many factors which are exerting their influence the following may be mentioned: (1) the 'density' of the stabilizing ion and its 'concentration' (the function of the number and size of the colloidal particles), (2) the size and the hydration of the coagulating ion, (3) the 'lattice' of the electrolytic solution, (4) the variation of the dielectric constant of the media generally and in close neighbourhood of an ion specially, (5) the relation of the size of the distribution sphere of an ion in solution to the distribution of the stabilizing ions on the wall, etc. In spite of the complexity of all these factors the mere simplicity of our expressions *(11)* and *(12)* seems to justify the further steps in constructing some of the structural elements of our critical boundary state.

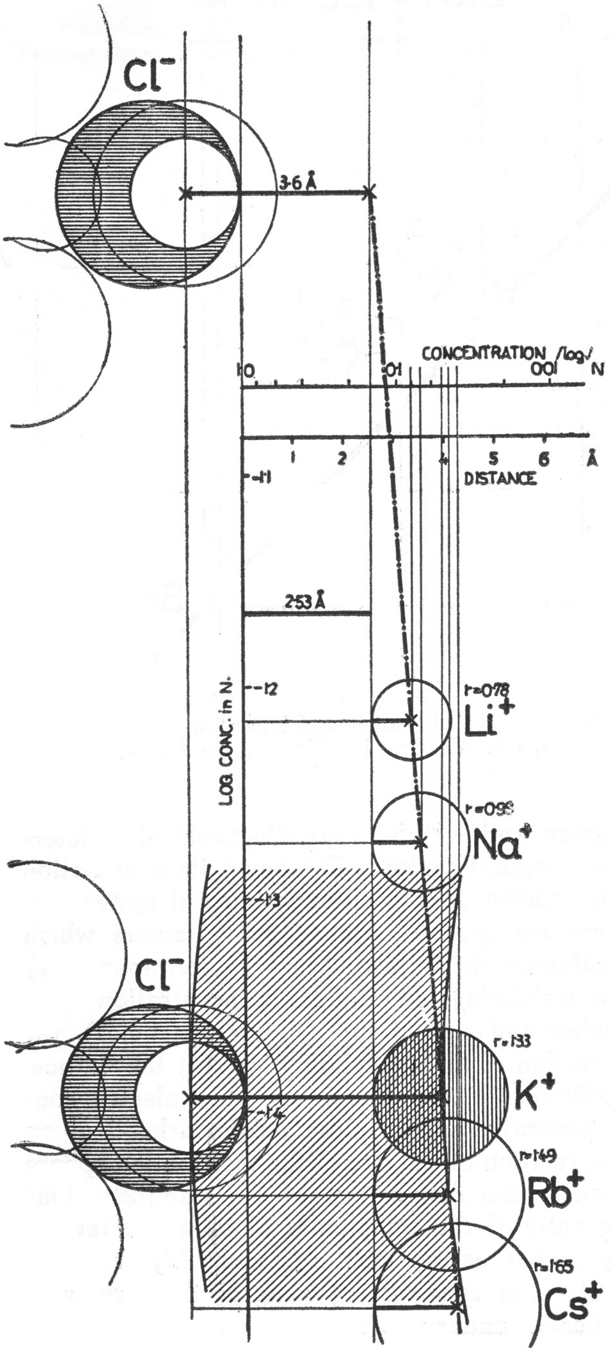

Fig. 3. Schematic presentation of the relationship between critical distance and logarithm of coagulation value for AgCl/Cl⁻ — positive charge point (upper part), and Li-, Na-, K-, Rb- and Cs-ion (lower part).

In Fig. 3 there is a schematic presentation of the relations between the adsorbed chloride ion as the stabilizing ion, and lithium, sodium, potassium, rubidium and caesium as coagulating ion, respectively.

In cases where the chloride ion is adsorbed on the crystal lattice of silver chloride and the counter ion is an univalent positive charge point (upper part), the critical distance, ${}_cd$, could be simply given by $\frac{e^2}{2\,DkT} = 3{\cdot}6$ Å. U. calculating from the centre of the negative ion to the positive charge point. The actual distance of the positive charge point to the stabilizing ion is $({}_cd^I - r_{Cl^-}) = 2{\cdot}53$ Å. U. Taking the real counter ion, the critical distance becomes greater for the actual distance of one ionic radius, r_i^+. In the lower part of Fig. 3 there is a series of alcaline ions with their crystallographically determined radii. Their position is such as to give in a graphical presentation the increase of the critical distance in respect to the various ionic sizes.

For the illustration of the influence of valency of the counter ion, and of our concept of the distribution sphere and the association shell, Fig. 4 may be used, where the situation for the

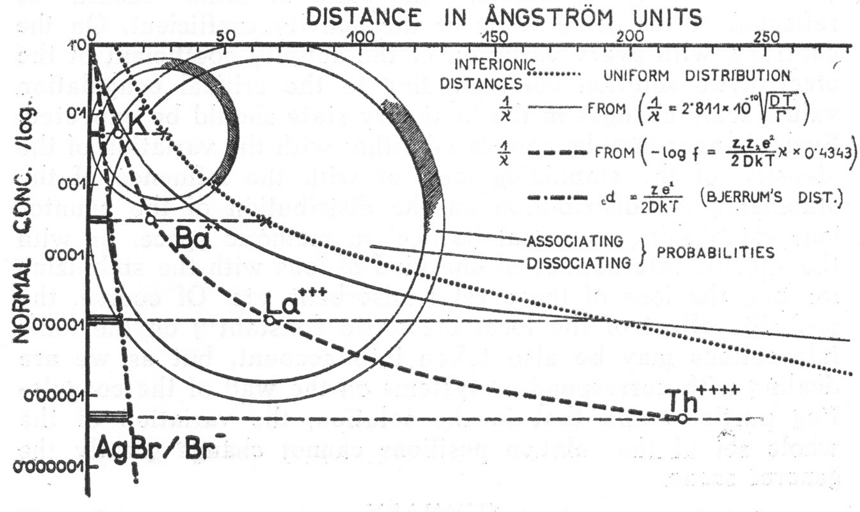

Fig. 4. Schematic presentation of the relationship between critical distances (—.—.— line), thicknesses of ionic atmosphere (— — — — — — curve), and distances between ions when uniformly distributed in solution (. . . . . curve), against logarithm of coagulation value for ions of various valencies. The circles represent the ionic distribution spheres, while the partially shaded shells give the coulombic parts of the chemical potentials for K- and Ba-ions in critical state for coagulation.

results of Table II is schematically presented. There is the diagram: logarithm of coagulation value — distance between the stabilizing ion fixed on the crystal lattice and the potassium, barium, lanthanum and thorium ion respectively. The critical distances according to *(12)* are given with one, two, three or four lines, respectively, so as to symbolize the corresponding valencies. However, in respect to the actual distances between the stabilizing ion and the dissolved counter ion the probability of mutual positions must be found. Supposing a statistically uniform distribution of the ions, their distances between are given with a dotted curve, which may be used for the construction of our distribution spheres. Such a sphere, the radius of which is given by interionic distance, with the corresponding shell, the thickness of which is the critical distance, ${}_c d$, must have its corresponding system in the dissociation-association mechanism between the ions in the solution in bulk. Thus *the correspondence of state given with the conditions for coagulation signifies such an arrangement between stabilizing-coagulating ion-pair which may be directly compared with the similar process of dissociation-asociation equilibria of the ions in electrolytic solution.* If the conditions on the wall for various coagulating ions are strictly comparable between themselves, this state of affair should be reflected in the same value of the activity coefficient. On the contrary, with every variation of the activity coefficient of the electrolytic solution corresponding to the critical coagulation value, some changes in the boundary state should be expected. Such changes may be connected either with the variation of the 'density' of the stabilizing ions, or with the influence of the stabilizing ion distribution on the distribution of the counter ions establishing a special 'lattice' in methoric space, or with the specific interactions of one kind of ions with the stabilizing ion and the ions of the crystal adsorbent, etc. Of course, the probable effect of the local dielectric constant[43]) on the ionic interactions may be also taken into account, but as we are dealing with corresponding systems on the wall of the coagulating particles and that in the solution, the variation of the whole set of the relative positions cannot change greatly the general scene.

SUMMARY

The critical state, when the processes of association-dissociation of the stabilizing-coagulating ion-pair are not at the same level as the analogous processes of the ion-pair formation in the

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[43]) H. S. Frank, J. Amer. chem. Soc., 63, 1789 (1941).

solution in bulk, is considered as the primary impulse for coagulation, thus giving the probability for a greater association between stabilizing and coagulation ion. With this one-sided disturbance of the equilibria, the coagulation may proceed as a result of a process of shrinking of the complex 'lattice' of the colloid particles and the surrounding ionic atmosphere, in spite of the charges on the micelles, and — as Langmuir[43]) appropriately points out — without the necessity to have an additional attractive force postulated by Hamaker, Verwey and Overbeek and others.

We agree completely with the statement of Wo. Ostwald, that the first principle of the coagulation processes must lie in the conditions given by the state of the electrolytic solution, but from our point of view the caution must be added that this statement should apply also to the functional relationship between the state of the electrolytic solution and the ionic arrangement in the methoric space. Both sides, the solution and the constants connected with the methoric space and especially the 'density' of the stabilizing ions, are equally important, and we have in the critical conditions for the coagulation a correspondence of state which can be used as a means for the investigating them both. When the equilibria between the ionic interactions in methoric space and electrolytic solution are disturbed, it is possible to have either a peptization or a coagulation phenomenon, each of which have many specific features. We have supposed that the lower degree of the association between the stabilizing-coagulating ion-pair against the similar process of pair formation in electrolytic solution could be made responsible for the initial stage of coagulation of lyophobic sols; for further stages we are aware that they represent a series of problems of a different kind than those we have hitherto considered, and although they are important for course of the coagulation, there role is however of the second order.

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[44]) I. Langmuir, J. Chem. Physics, 6 (1938) 837.

METORIKA KOAGULACIONIH PROCESA. I.
MEHANIZAM KOAGULACIJE HIDROFOBNIH SOLOVA

Božo Težak

Radi potrebe da teorija obuhvati sve poznate eksperimentalne nalaze o koagulaciji liofobnih solova, dan je kratak pregled najvažnijih činjenica i empirijskih pravila s obzirom na fenomenologiju koagulacije. Posebno je spomenuto: (1) pravilo Schulze-a i Hardy-a, (2) odnos između veličine jona i njegove koagulacione vrijednosti, (3) pravilo Burton-a i Bishop-ove, (4) nalazi o adsorpciji stabilizacionih jona, (5) rezultati elektroforetskih promatranja čestica, koje su u stanju koagulacije, (6) antagonistički efekti jona, (7) utjecaj promjene dielektrične konstante koagulacionog medija, (8) odnos između koagulacione vrijednosti i koeficienta elektrolitnog aktiviteta i dr.

Iznešeni su razlozi, zašto su izabrani solovi srebrnih halogenida in statu nascendi kao eksperimentalni sistemi, na kojima se mogu promatrati svi ti odnosi.

Diskutirani su neki rezultati, koji su već dobiveni s ovakovim solovima i kod toga je pokazan put za teoretsku interpretaciju. Koagulacioni mehanizam je predstavljen kao rezultat promjene u dinamičkoj ravnoteži, koja postoji između stabilizacionih jona i protujona. Predpostavljeno je, da je koagulacija posljedica veće vjerojatnosti stvaranja jonskih parova (u Bjerrum-ovom smislu) između stabilizacionih i koagulacionih jona nasuprot sličnim procesima asocijacije-disocijacije jona u unutrašnjosti tekućine. Osobito je naglašen utjecaj gustoće i rasporeda stabilizacionih jona usporedivši ih s konfiguracijom jona u kinetičko-statističkoj mreži jona elektrolitne otopine. Kod toga je pokazana mogućnost, da se nađe jednostavan odnos između logaritma kritične koncetracije za koagulaciju i posebne kritične udaljenosti, koja je označena s ${}_cd$. Ta udaljenost je uzeta kao debljina ljuske, koja pokazuje vjerojatnost coulombskih utjecaja kod jonskih distribucionih sfera, s kojima je predstavljen jednostavni model za strukturu elektrolitne otopine.

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