# Ionic Association and Coagulation*

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The ion exchange theory of coagulation is verified by quoting
experimental results on coagulation values of K^+, Ba^{2+}, and La^{3+}
for negative AgBr sols in mixed solvents, according to which the
proportionality constant of the Schulze-Hardy rule is a linear
function of $1/D$ (D = dielectric constant). As critical in the Bjer-
rum's theory of association the minimum distance between two
ions is suggested in which they are separated by only one water
molecule.

The recently proposed ion exchange theory[1,2] of coagulation was deduced
from the results on adsorption-desorption equilibria[7] of the coagulating counter
ions on coagulated AgI. The equality of the experimental slopes of the linear
functions: »logarithm coagulation value-valency« and »logarithm concentration
(50% adsorption)-valency« is a direct confirmation for the correctness of this
theory. In the present paper the results of a paper by Matijević, Kratohvil, and
Orhanović[3] on the influence of the dielectric constant of the electrolyte upon
the coagulation values of ions of different valencies are shown to confirm the
same theory.

The equilibrium on which the ion exchange theory[1,2] of coagulation is based
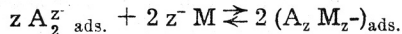can be represented by the reaction:

$$z\,(A_2^{z-} \cdot z^- H_2O)_{ads.} + 2\,z^-\,M \rightleftarrows 2\,(A_z\,M_z\text{-})_{ads.} + zz^-\,H_2O$$
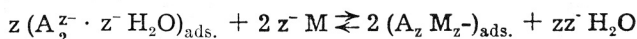
The mass action law equation valid for the above process is:

$$'A_z = 'K_z^{-1} = (x\,\gamma)^2\,a_{H_2O}^{zz-}/[(1-x)\,\gamma]^z\,c^{2z-} \qquad (1)$$

(The notation is given at the end of the paper.)

The analogous classical association process can be written as:

$$z\,A_2^z{}_{ads.} + 2\,z^-\,M \rightleftarrows 2\,(A_z\,M_z\text{-})_{ads.}$$

with the corresponding classical association constant:

$$A_z = K_z^{-1} = 'K_z^{-1}/a_{H_2O}^{zz-} = (x\,\gamma)^2/[(1-x)\,\gamma]^z\,c^{2z-} \qquad (2)$$

The coagulation value-valency relation (Schulze-Hardy rule) according to
the ion exchange theory was represented by the equation[1]:

$$-\log c_{coag} = \log {}^0D/(x_{coag}\,\gamma)^{1/z-} + z\,a \qquad (3)$$

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From equations (2) and (3) the following a-A$_z$ relation may be obtained:

$$a = -1/2\; zz^- \log A_z + \log [(1 - x_{coag})\; \gamma]^{1/2\; z^-}/^0D \qquad (4)$$

In fig. 1 the results taken from a paper by Kratohvil, Orhanović, and Matijević[3] are inserted. For each point the mean of four coagulation values of AgBr $(2 \cdot 10^{-4}\,M)$ was plotted against 1/D. The four values were measured in isodielectric mixtures of water and methanol, n-propanol, i-propanol, and
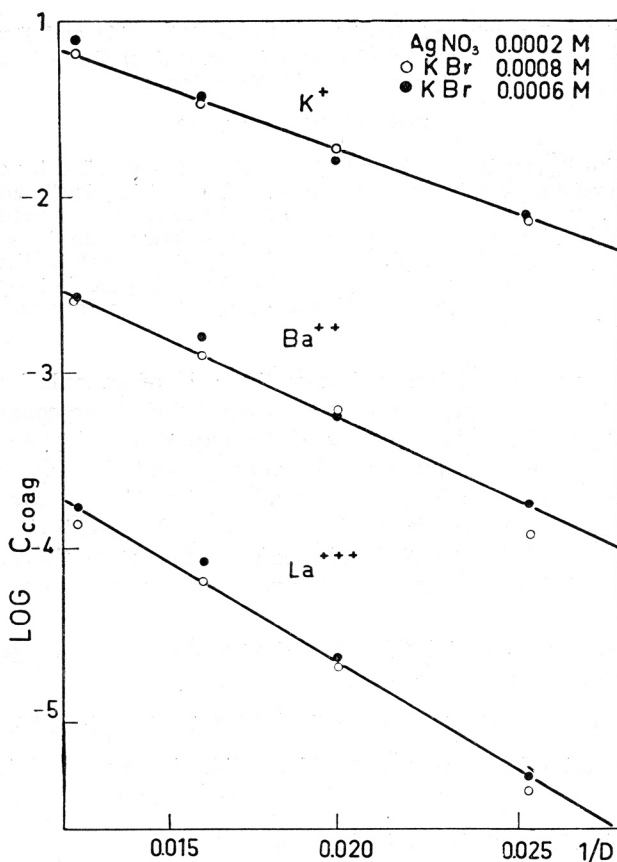

Fig. 1. Influence of the dielectric constant upon the coagulation values of Na$^+$, Ba^{2+}, and La^{3+} in water — methanol, — ethanol, — n-propanol and — isopropanol. Ordinate: logarithm coagulation concentration; Abscissa: 1/D (D dielectric constant) (AgNO$_3$: 2.10^{-4} M; KBr. 8.10^{-4} and 6.10^{-4} M after Matijević et al ref. 3.

ethanol at total concentrations $8 \cdot 10^{-4}$ and $6 \cdot 10^{-4}\,M$ KBr.

By the least square method the following linear regressions were obtained from the measured points for the three plots:

$$\text{K}^+ \;:\; \log_1 c_{coag} = -(75.3 \pm 3.39)/D - (0.21 \pm 0.063) \qquad (5a)$$

$$\text{Ba}^{++} \;:\; \log_2 c_{coag} = -(102.3 \pm 6.62)/D - (1.25 \pm 0.12) \qquad (5b)$$

$$\text{La}^{+++} \;:\; \log_3 c_{coag} = -(121.1 \pm 6.90)/D - (2.16 \pm 0.13) \qquad (5c)$$

The F, resp. the F_k values[4] are $_1F = 492$, $_2F = 239.1$, $_3F = 307.6$, $F_k = 18.51$ (P = 0.05, $n_1 = 1$, $n_2 = 2$). The linear regression is in all the three cases highly significant since $F \gg F_k$. Therefore the conclusion can be made that plot log c_{coag} vs. 1/D is linear.

From the above linear equations the following equations for the a value can be obtained which are, for the same reason, highly significant too:

$$K^+ - Ba^{++}: \quad a = -27.1/D - 1.04 \qquad (6a)$$

$$Ba^{++} - La^{+++}: a = -18.7/D - 0.91 \qquad (6b)$$

$$\text{mean:} \qquad a = -22.9/D - 0.98 \qquad (6c)$$

The relatively high a values for the $K^+ - Ba^{++}$ pair are caused by the relatively high logarithm coagulation values for K^+ which, when corrected in the activity values would be in water for about 0.15 lower. The a value for $K^+ - Ba^{++}$ would be then practically equal to the a values for the $Ba^{++} - La^{+++}$ pair. For Ba^{++} and La^{+++} the necessary corrections are negligible (< -0.05).

The association constant — dielectric constant (D) relation, based on Bjerrum's ion pair formation theory can be given in the form[5,6] (p. 388):

$$\log A_z = -\log K_z = B + C/D \qquad (7)$$

Since according to experimental evidence a is a linear function of 1/D, the term $\log [(1 - x_{coag}) \gamma]^{1/2\, z^-}/^0D$ in equation (4) — for theoretical as well as empirical reasons — can be a linear function of 1/D only. Then the experimentally established linearity of the plots a vs. 1/D and log c_{coag} vs. 1/D can be considered as a confirmation of the correctness of the assumption that association-dissociation equilibria between the coagulating ions and the stabilising particles in the double layer are the basic processes causing stability or coagulation as well as a confirmation of the correctness of the exchange theory of coagulation.

Since a linear relation a vs. 1/D is postulated by the ion exchange theory and by Bjerrum's ion pair formation theory, this latter results can be considered as a confirmation of the essential correctness of both theories. However, according to Fuoss[5] the main insufficiency of the ion pair formation theory is the arbitrarily chosen critical Bjerrum's distance at $r = c^2/2\, DkT$ and the theoretically undetermined distance of the closest approach. In fact, the value of this distance was deduced from theory to give the best accordance between theory and experiment[6] (p. 381). Such an accordance could also be obtained with other pairs of values for these two distances.

For distances between associating ions, which are great compared with the size of solvent (water) molecules the mathematical treatment of the solvent medium as a continuum is certainly justified. When in the meantime these distances become comparable with the size of the solvent molecules, the continuous decrease of the distances between ions becomes impossible. Finally, the ions can be separated only by one or none water molecule. In this last case it can be only stated that the ion pair is formed.

From the ion exchange theory of coagulation it follows as the necessary consequence that the stability is characterized by the double layer with an excess of hydrated adsorbed potential determining ions, while the coagulation is characterized by an excess of associated ion pairs formed between them and

between the coagulating counter ions. In this way a clear cut definition of the associated and dissociated state was given causing coagulation or stability. The coagulation value is then a characteristic value of the variable concentration at which in the double layer a discontinuity in the properties causes a change of the repulsion to attraction forces or the annihilation of the repulsion forces between the particles.

Since in Bjerrum's theory the criterion for the distinction between the associated and dissociated state is insufficient, the same criterion, as applied in the recent coagulation theory, could be applied here: As critical the distance between two oppositely charged ions by which they are separated with only one water molecule could be taken. Two ions with no water molecules separating them form an ion pair.

Symbols used:

a	slope of the linear Schulze-Hardy rule and of the linear adsorption rule
a_{H_2O}	activity of water
A_z	association constant
A^{z-}	constituent anion of valency z^-
B and C	constants in the equation for the $A_z - D$ relation according to Bjerrum's theory
c	concentration of a cation of valency z^+
D	dielectric constant
^0D	constant distribution coefficient of a hypothetical cation of zero valency
K_z	dissociation constant
M	coagulating cation of valency z^+
x	fraction of the maximal adsorbed amount γ of cations

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IZVOD

Ionska asocijacija i koagulacija

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Eksperimentalno utvrđena linearna zavisnost logaritma koagulacionih vrijednosti jedno, dvo i trovalentnih kationa o recipročnoj vrijednosti dielektrične konstante smjesa : voda — metanol; voda — etanol; voda — n-propanol i voda iso-propanol solova negativnog AgBr potvrđuje na temelju Bjerrum-ove teorije ionskih parova

ispravnost pretpostavke da su asocijaciono — disocijacione ravnoteže između protu-iona i adsorbiranih konstitucionih iona temeljni procesi koji uvjetuju stabilnost ili koagulaciju solova. Time je također potvrđena ispravnost teorije ionske izmjene u koagulaciji.

Predlaže se kao kritična udaljenost za razlikovanje između asociranog ionskog para i slobodnih iona prema Bjerrum-ovoj teoriji udaljenost, koja je određena veli-činom vodenih molekula. Ionski par nastaje kad molekule vode ne razdvajaju više dva protivno nabijena iona.

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