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Verification of Bhattacharya's Equation for Slow Coagulation by Spectrophotometric Measurements in Copper Ferrocyanide and Zinc Ferrocyanide Sols

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The copper ferrocyanide and zinc ferrocyanide sols have been prepared, and their precipitation values have been studied by using KCl, $BaCl_2$ and $AlCl_3$ and by employing the spectrophotometric method in the light of the equation:

$$C = a + \frac{m \cdot 1/t}{n + 1/t}$$

It has been found that the values of a and m remain the same at all stages of coagulation, while the value of n depends to a great extent on the coagulation stage.

Bhattacharya and Kumar[1] established the relation between the electrolyte concentration, C, and the inverse of the corresponding time of coagulation, $1/t$, in the zone of slow coagulation, they obtained hyperbolic curves in the majority of cases, although straight lines were obtained in some cases. The relation established by them was:

$$C = a + \frac{m \cdot 1/t}{n + 1/t} \qquad (1)$$

where a, m and n are constants. The equation, upon simplification, assumes the following form:

$$1/(c-a) = \frac{n}{m} \cdot t + \frac{1}{m} \qquad (2)$$

Accordingly, the equation can be verified from the coagulation data if the plots between $1/(c-a)$ and t provide a straight line.

In this communication, attempts will be made to verify this equation by means of studies on the slow coagulation of copper ferrocyanide and zinc ferrocyanide sols by spectrophotometric measurements.

Experimental

The sols were prepared as has been described earlier.[2,3] The spectrophotometer (Hilger Uvispek) was first adjusted to a suitable wavelength (700 mμ for the copper ferrocyanide sol and 610 mμ for the zinc ferrocyanide sol) for the mixture of sol and water to be placed in the tube. A mixture of water, an electrolytes, and the sol was then taken into the same tube, and the specific absorbance $(1/L)\log_{10}(I_0/I)$ was noted against the time. The experiments were repeated with varying amounts of water and electolytes, keeping the total volume of the mixture and the volume of the sol constant.

Results

For each concentration of the coagulating electrolyte, the specific absorbance was plotted against the time (Fig. 1) then a straight line parallel to the time axis was drawn so as to cut all the curves at different points, referring to the same state of aggregation in all the different cases.

The inverses of the coagulation time thus obtained were plotted against the electrolyte concentration, and the value of a was determined as the concentration extrapolated to $(1/t) \rightarrow 0$, as is shown in Fig. 2. Finally, $1/(c-a)$ was plotted against t; straight lines, as Fig. 3 shows, were obtained, as was to be expected from Eq. (2). The values of m and n can be obtained from these straight lines. Similar figures, Figs. 4—8, were obtained for copper and zinc ferrocyanide sols with KCl, $BaCl_2$, and $AlCl_3$. The parameters thus obtained

1) A. K. Bhattacharya and R. Kumar, *J. Indian Chem. Soc.*, **28**, 179, 658 (1951); **29**, 687, 759 (1952); *J. Coll. Soc.*, **11**, 124 (1956).
2) D. N. Chaturvedi and O. P. Bansal, *J. Indian Chem. Soc.*, **40**, 1029 (1963).
3) O. P. Bansal *et al.*, *Koll. Z. Polymers*, **189**, 147 (1963).

are shown in Table 1 for copper ferrocyanide and in Table 2 for zinc ferrocyanide.

Discussion

On examining critically the variations in the values of a (the critical stability concentration),

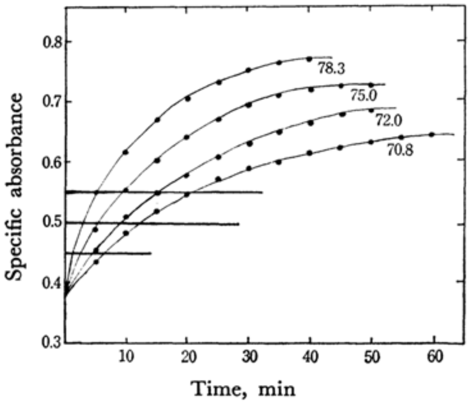

Fig. 1. Coagulation of copper-ferrocyanide sol with KCl of various concentration (mM/l).

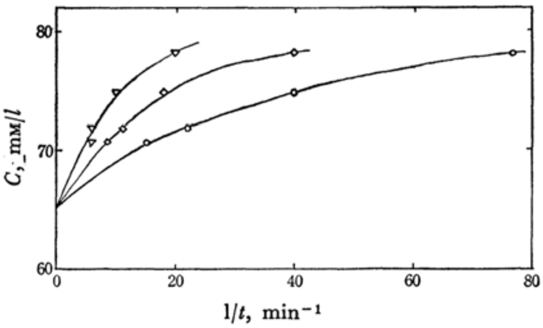

Fig. 2. Relation between the electrolyte concentration and the inverse of coagulation time for various specific absorbance copper ferrocyanide sol with KCl.
-○- 0.45 abs. -□- 0.50 abs. -△- 0.55 abs.

TABLE 1. VALUES OF PARAMETRIC CONSTANTS OF BHATTACHARYA'S EQUATION IN THE COPPER FERROCYANIDE SOL (0.925 g/l)

Electrolyte	Stage of coagulation (specific absorbance)	a	m	n
KCl	0.45	65	20	0.520
	0.50	65	20	0.284
	0.55	65	20	0.170
$BaCl_2$	0.45	0.18	0.434	0.4204
	0.50	0.18	0.434	0.2242
	0.55	0.18	0.434	0.1441
$AlCl_3$	0.45	0.05	0.540	0.498
	0.50	0.05	0.540	0.427
	0.55	0.05	0.540	0.250

TABLE 2. VALUES OF PARAMETRIC CONSTANTS OF BHATTACHARYA'S EQUATION IN THE ZINC FERROCYANIDE SOL (0.802 g/l)

Electrolyte	Stage of coagulation (specific absorbance)	a	m	n
KCl	0.45	134	166.7	1.351
	0.50	134	166.7	0.683
	0.55	134	166.7	0.433
$BaCl_2$	0.45	0.20	0.666	1.671
	0.50	0.20	0.666	0.553
	0.55	0.20	0.666	0.335
$AlCl_3$	0.45	0.10	0.714	0.697
	0.50	0.10	0.714	0.348
	0.55	0.10	0.714	0.214

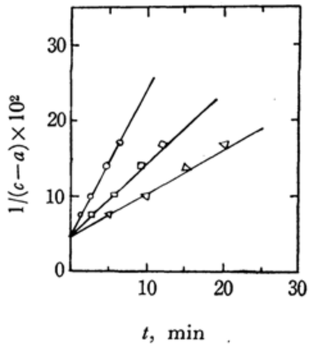

Fig. 3. Copper ferrocyanide sol with KCl.
-○- 0.45 abs. -□- 0.50 abs.
-△- 0.55 abs.

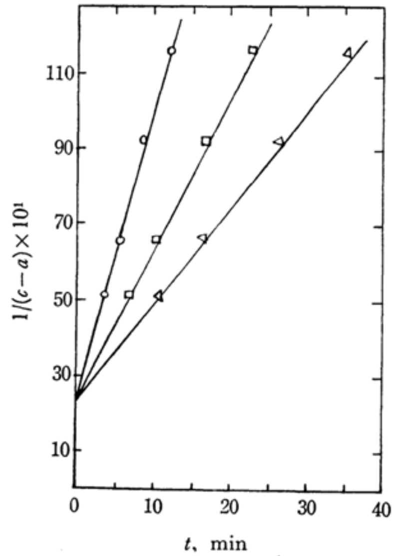

Fig. 4. Copper ferrocyanide sol with $BaCl_2$.
-○- 0.45 abs. -□- 0.50 abs.
-△- 0.55 abs.

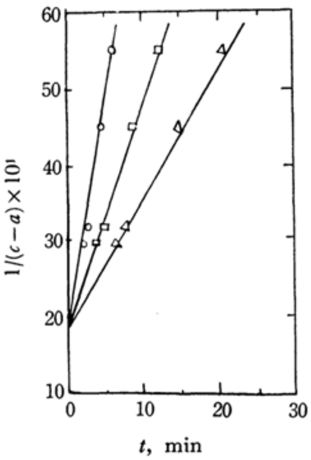

Fig. 5. Copper ferrocyanide sol with $AlCl_3$.
-○- 0.45 abs. -□- 0.50 abs.
-△- 0055 abs.

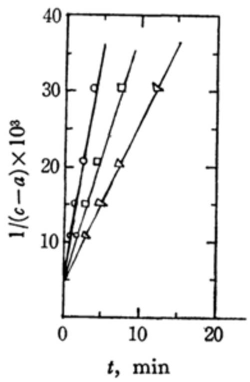

Fig. 6. Zinc ferrocyanide sol with KCl.
-○- 0.45 abs. -□- 0.50 abs.
-△- 0.555 abs.

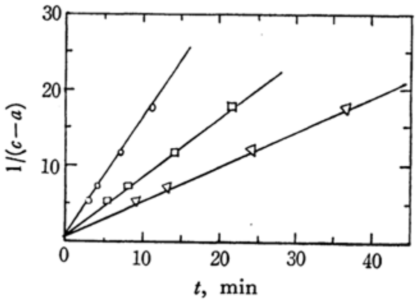

Fig. 7. Zinc ferrocyanide sol with $BaCl_2$.
-○- 0.45 abs. -□- 0.50 abs.
-△- 0.55 abs.

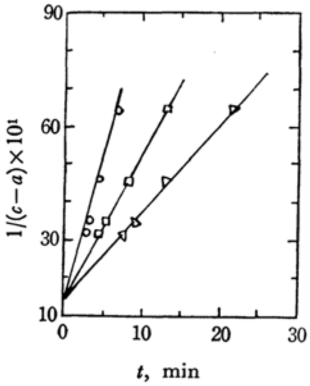

Fig. 8. Zinc ferrocyanide sol with $AlCl_3$.
-○- 0.45 abs. -□- 0.50 abs.
-△- 0.55 abs.

it is found that the variations in the values of a with the valency of the cation of the electrolyte used supports the idea that the coagulating power of the cation increases with an increase in the valency, as is demanded by the Schulze-Hardy law. The law was stated originally for the lowest electrolyte concentration required for rapid coagulation $(a+m)$, but here the law is applied better to the electrolyte concentration a, at which not even a slow coagulation is expected to occur.

The values of a and m remain the same for all stages of coagulation, determined at different absorbance values, for the same electrolyte and sol. However, the values of n depend greatly on the coagulation stage and are found to decrease with the process of aggreagation.

Figures 3—8 clearly show that Bhattacharya's equation agrees well with the experimental data at all the stages of coagulation determined by the spectrophotometric studies.

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