BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 551—553 (1969)

Studies on the Coagulation of Silver Sol: Effect of Dialysis, Non-electrolytes and Ageing on the Constants of Bhattacharya's Equation

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(Received April 20, 1968)

Bhattacharya *et al.*[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 and obtained hyperbolic curves in the majority of cases, although straight lines were obtained in some cases. The relation established by them is,

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

where a, m and n are constants. The equation on simplifying assumes the form:

$$1/(C-a) = (n/m)t + 1/m \tag{2}$$

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

In this communication, an attempt has been made to study the variations of the constants, *i. e.*, a, m and n at different periods of dialysis of the sol. The values of the constants have also been evaluated in the presence of different non-electrolytes to throw light on the stabilising or sensitising power of the non-electrolytes used. The effect of ageing on the above constants for the dialysed silver sol using $NaNO_3$, $Ba(NO_3)_2$ and $Al(NO_3)_2$ as coagulating electrolytes, has also been incorporated in this paper.

Experimental

Silver sol was prepared by adding just sufficient ammonia to 20 ml of 5% silver nitrate solution to dissolve silver hydroxide formed; the solution was then made upto one litre. 2% solution of tannic acid was then added to the solution, drop by drop with constant stirring, until a dark brown sol was obtained. It was dialysed against running distilled water until free from electrolytes.

Three different samples of the sol were prepapred. One sample was used for the study of the effect of dialysis,the second for the effect of ageing and the third for the study of non-electrolyte effect.

Time of coagulation of the sol, using $NaNO_3$, $Ba(NO_3)_2$ and $Al(NO_3)_3$ as coagulating electrolytes was determined by light extinction method, using a Gallenkamp Photoelectric Colorimeter. For each concentration of the coagulating electrolyte, the extinction 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.

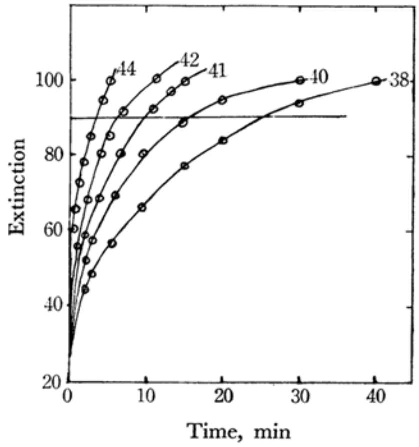

Fig. 1. Coagulation of silver sol- with $NaNO_3$ of various concentrations (mM/l)

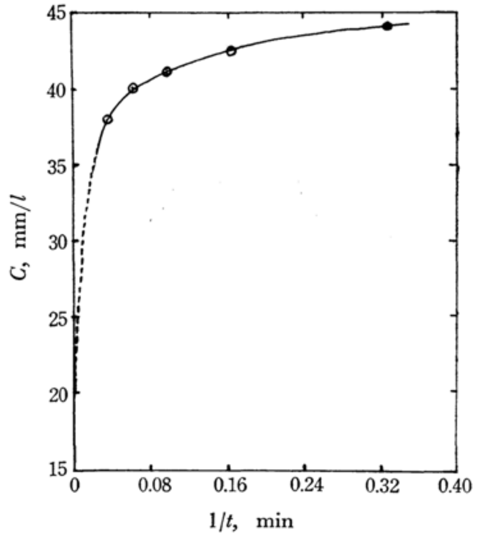

Fig. 2. Relation between the electrolyte concentration and inverse of the coagulation time.

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[1] A. K. Bhattacharya *et al.*, *J. Ind. Chem. Soc.*, **28**, 179, 638 (1951); **29**, 687, 759 (1952); *J. Colloid Sci.*, **10**, 551 (1955).

TABLE 1. EFFECT OF DIALYSIS

Sol dialysed for (days)	Sp. cond. $\times 10^4$ (mhos) at 30°C	$NaNO_3$			$Ba(NO_3)_2$			$Al(NO_3)_3$		
		a (mM)	m (mM)	n (min^{-1})	a (mM)	m (mM)	n (min^{-1})	a (mM)	m (mM)	n (min^{-1})
1	3.70	50.0	25.0	0.0312	0.22	0.114	0.0974	0.035	0.023	0.0596
2	2.17	45.0	23.81	0.020	0.71	0.150	0.0638	0.030	0.0212	0.057
3	1.50	40.0	26.31	0.0183	0.16	0.125	0.0642	0.025	0.018	0.0472
5	0.70	30.0	25.0	0.0132	0.14	0.135	0.0554	0.020	0.0169	0.0432
7	0.28	20.0	24.32	0.0123	1.03	0.111	0.0454	0.015	0.020	0.0413
9	0.24	10.0	27.0	0.0110	0.12	0.120	0.0321	0.005	0.0185	0.0355

TABLE 2. EFFECT OF AGEING

Concentration of the sol = 0.203 g silver/l

Period of ageing (days)	$NaNO_3$			$Ba(NO_3)_2$			$Al(NO_3)_3$		
	a (mM)	m (mM)	n (min^{-1})	a (mM)	m (mM)	n (min^{-1})	a (mM)	m (mM)	n (min^{-1})
0	8.0	40.0	0.101	0.08	0.156	0.055	0.019	0.0078	0.0312
10	6.0	25.0	0.0291	0.04	0.180	0.042	0.018	0.0081	0.0300
20	5.0	18.18	0.080	0.03	0.135	0.0325	0.017	0.0085	0.0282
30	2.0	9.09	0.0591	0.010	p.100	0.0261	0.014	0.009	0.0253

TABLE 3. EFFECT OF NON-ELECTROLYTES

Concentration of the sol = 0.3296 g silver/litre

		$NaNO_3$			$Ba(NO_3)_3$			$Al(NO_3)_3$		
		a (mM)	m (mM)	n (min^{-1})	a (mM)	m (mM)	n (min^{-1})	a (mM)	m (mM)	n (min^{-1})
Ethanol	(0.1 ml)	24.5	12.5	0.0270	0.12	0.133	0.053	0.022	0.0071	0.046
Ethanol	(0.2 ml)	19.5	10.0	0.0232	0.11	0.080	0.0230	0.021	0.0062	0.036
Ethanol	(0.3 ml)	17.0	8.7	0.0217	0.10	0.075	0.0200	0.020	0.0053	0.032
Ethanol	(0.4 ml)	14.5	8.0	0.0120	0.09	0.065	0.0182	0.0190	0.0050	0.030
Ethanol	(0.5 ml)	13.0	6.0	0.0080	0.08	0.050	0.0140	0.0180	0.0043	0.020
Acetone	(0.1 ml)	25.0	10.53	0.0210	0.14	0.120	0.0460	0.021	0.008	0.040
Acetone	(0.2 ml)	20.0	11.76	0.0160	0.135	0.100	0.0420	0.020	0.0077	0.038
Acetone	(0.3 ml)	18.0	9.00	0.010	0.125	0.100	0.0380	0.0195	0.0077	0.0307
Acetone	(0.4 ml)	15.0	7.70	0.0083	0.120	0.092	0.030	0.0190	0.0069	0.0280
Acetone	(0.5 ml)	13.0	8.00	0.0062	0.110	0.073	0.0261	0.0180	0.0059	0.0250
Formamide	(0.1 ml)	24.0	12.05	0.0120	0.120	0.125	0.048	0.022	0.0075	0.0458
Formamide	(0.2 ml)	22.0	13.16	0.0110	0.10	0.110	0.045	0.021	0.0070	0.0420
Formamide	(0.3 ml)	22.0	13.16	0.0110	0.095	0.100	0.041	0.020	0.0067	0.0382
Formamide	(0.4 ml)	22.0	13.16	0.0110	0.090	0.100	0.0372	0.0195	0.0064	0.0345
Formamide	(0.5 ml)	22.0	13.16	0.0110	0.085	0.0909	0.0312	0.0190	0.0062	0.0321
Pure sol	—	26.0	15.87	0.0276	0.150	0.1136	0.0556	0.0260	0.00363	0.052
Urea-5M	(1.0 ml)	28.0	18.52	0.0278	—	—	—	—	—	—
Urea-5M	(1.5 ml)	30.0	19.23	0.0281	0.155	0.1786	0.091	0.030	0.040	0.056
Urea-5M	(2.0 ml)	—	—	—	0.160	0.2272	0.098	0.040	0.05	0.0621

The inverse of the coagulating time thus obtained were plotted against the electrolyte concentration, and the value of a was determined as the concentration extrapolated to $(1/t) \to 0$, as is shown in Fig. 2. Finally, $1/(C-a)$ was plotted against t; straight lines, as Figs. 3 and 4 show, were obtained, as was to be expected from Eq. (2). The values of m and n can be obtained from these straight lines.²⁾ The values of the constants obtained for the same stage of coagulation given by the same extinction value for the sol at the different stages of dialysis and ageing, and also in the presence of different amounts of various non-electrolytes have been recorded in Tables 1, 2 and 3.

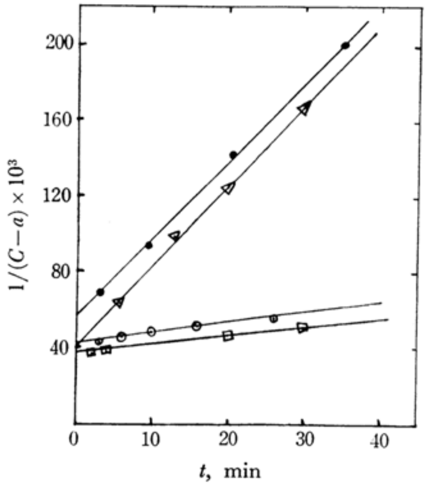

Fig. 3. Coagulation with $NaNO_3$.
⊙ Sol dialysed for 7 days.
⊡ Sol dialysed for 9 days.
△ Sol aged for 10 days.
● Sol aged for 20 days.

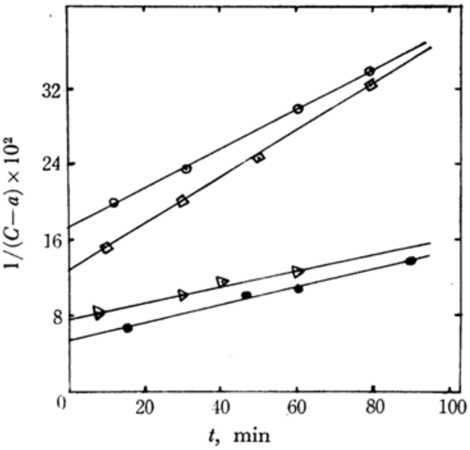

Fig. 4. Coagulation with $NaNO_3$.
⊙ In the presence of ethanol
⊡ In the presence of acetone
△ In the presence of formamide
● In the presence of urea.

Discussion

Bhattacharya's equation, in the form of Eq. (2), shows that the plots, $1/(C-a)$ against t should be a straight line and this has actually been observed in all cases of the present studies (Representative Figs. 3 and 4) confirming the applicability of the equation for the coagulation of the sol by electrolytes, in the partially dialysed state and also in the presence of non-electrolytes.

If $1/t$ is made large as compared to n, Eq. (1) takes up the form, $C=a+m$. This means that m is the excess of the electrolyte that should be added above the critical stability concentration, a, in order to cause the immediate coagulation of the sol. It may be said that at $C=a+m$, the region of slow coagulation merges into that of rapid coagulation. From Table 1 it is evident that the value of $(a+m)$ decreases with progressive dialysis of the sol indicating that the region of slow coagulation merges into that of rapid coagulation earlier in the dialysed sol. From this, it is evident that the sol becomes increasingly sensitive with progressive dialysis.

The values of the constants, a, $(a+m)$ and n show a decrease in the presence of ethanol, acetone and formamide but the presence of urea causes an increase. Ethanol, acetone and formamide sensities the sol against mono, di and tri-valent ions, since in the presence of these non-ionic substances the region of slow coagulation merges into that of rapid coagulation earlier as evidenced by the low values of $(a+m)$. Urea stabilises the sol. The extent of stabilisation or sensitisation increases with the increased non-ionic addition.

Ageing results in aggregation of particles which renders the sol unstable and since a, $(a+m)$ and n are connected with the stability, the values of these constants should decrease with the ageing of the sol, and this fact has also been confirmed experimentally.

On examining critically the variations in the values of a, it is found that the variations in the values of a with the valency of the precipitating ion support the law that the coagulating power of the ion increases with the increase in its valency. This law has been stated originally for the lowest electrolyte concentration, $(a+m)$ required for the rapid coagulation, but here the law is applied better to the maximum electrolyte concentration, a, at which even the slow coagulation is expected not to occur.

Thanks are due to Dr. A. K. Bhattacharya, D. Sc., F.R.I.C. (London), Prof. of Chemistry, University of Jammu and Kashmir and Dr. A. Kumar for their valuable suggestions in this work.

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2) A. K. Bhattacharya *et al.*, *J. Colloid Sci.*, **11**, 124 (1956); *Agra Univ. J. Res. Sci.*, **12**, 101 (1963).