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IMPORTANT SIGNIFICANCE OF S-SHAPED CURVES DURING SLOW COAGULATION OF LYOPHOBIC SOLS

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The points of inflection in the S-shaped curves of slow coagulation may be assumed to denote the same kinetic state of aggregation when the sol is coagulated with different concentrations of the electrolyte, because at this stage $d^2x/dt^2 = 0$ for all cases. The times corresponding to the points of inflection for different concentrations of the electrolyte, KNO_3 (Kruyt and Troelstra's extinction data), added to the sol of AgI, satisfies the linearity of the equation

$$\frac{1}{C-a} = \frac{n}{m}.t+\frac{1}{m}$$

which follows from the empirical relation given by

$$C = a + \frac{m\left(\frac{1}{t}\right)}{n+\frac{1}{t}}.$$

In a previous paper on the verification of the above equation by different techniques (*J. Colloid Sci.*, 1956, **11**, 124) it was shown that the relation between the concentration of the electrolyte and the time of coagulation as given by the equation,

$$C = a + \frac{m\left(\frac{1}{t}\right)}{n+\frac{1}{t}}$$

(where C is the concentration of the electrolyte, t is the time for the same degree of aggregation or coagulation, and a, m and n are the parametric constants), was supported by the experimental data obtained from the variations in (*i*) viscosity, (*ii*) light transmission, (*iii*) extinction coefficient and (*iv*) counting of the number of particles and tyndallometric data. The data in respect of the variations of the foregoing properties were taken from the observations of Gann (*Koll. Chem.-Beih.*, 1916, **8**, 64), Mukerjee (*J. Chem. Soc.*, 1924, **125**, 785), Kruyt and Troelstra (*Kolloid Beih.*, 1945, **54**, 225) and Tezak (*J. Phys. Coll. Chem.*, 1951, **55**, 1557). The same stage of coagulation, or more correctly the same degree of aggregation, was obtained, *a fortiori*, by drawing a line parallel to the time axis to cut the characteristic curves for the different concentrations of the added electrolyte. This line would cut the family of curves (one curve for each different concentration of the electrolyte) and, hence, it could be reasonably assumed that the same value of viscosity, light extinction or transmission, or number of particles would mean the same state of coagulation or degree of aggregation. The constant 'a' was determined by extrapolation of $C-(1/t)$ curves as explained before, and the linearity of the relation between $1/(C-a)$ and t was found to hold good in the light of the equation.

It was emphasised further by us (*Kolloid Z.*, 1955, **141**, 95 ; 1956, **148**, 136) that the points of inflection in the autocatalytic viscosity—time curves of As_2S_3 and $Fe(OH)_3$ sols denoted the same kinetic stage of slow coagulation for the different concentrations of an electrolyte added to the sol. The times corresponding to the points of inflection in the viscosity—time curves, when plotted against the respective values of $1/(C\text{-}a)$, gave a straight line, which proved the validity of the equation.

Kruyt *et al.* (*loc. cit.*) studied the coagulation of silver iodide sol by measuring the changes in the extinction of light and obtained autocatalytic curves when the % extinction was plotted against the concentration of the coagulating electrolyte (potassium nitrate) for different times of coagulation (Kruyt, "Colloid Science", 1952, p. 299). The values of the %extinction obtained at the points of inflection of these S-shaped curves, reported in this communication, also confirm the linearity of the relation between $1/(C\text{-}a)$ and t.

Method of Verification.—In order to obtain the values of t, C and the constant a, the concentration 'C' corresponding to the inflection points of the curves was read. The time during which coagulation had proceeded was given; C was then plotted against $1/t$. The curve on extrapolation cuts the C-axis when $1/t = 0$ (Fig. 1). The intercept on the C axis gives the value of a. Then $1/(C\text{-}a)$ was plotted against t and a straight line was obtained (Fig. 2).

TABLE I

a = 120 mM/litre. m = 41.7 mM/litre. n = 29.19 min.$^{-1}$

C.	t.	$1/t$.	$C-a$.	$1/(C\text{-}a)$.
132.4 m M/litre	8 mins.	0.125	12.4	0.08065
136.3	5	0.200	16.3	0.06135
142.2	3	0.333	22.2	0.04505
146.1	2	0.500	26.1	0.03831
152.0	1	1.000	32.0	0.03125

FIG. 1

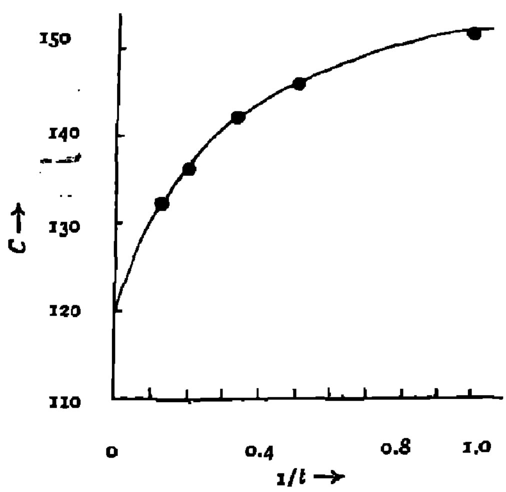
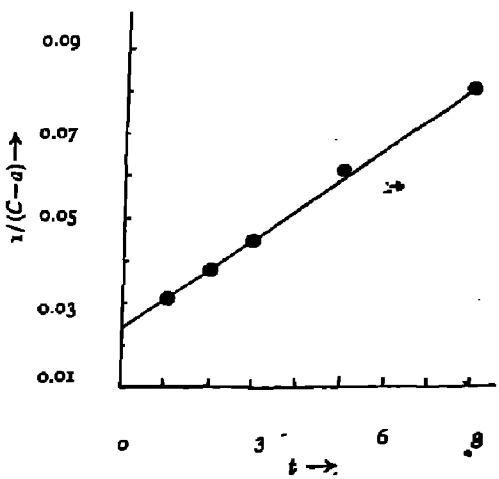


FIG. 2



In the light of our observations previously communicated (*loc. cit.*) and the results derived from the extinction curves, it may be emphasised, *a priori*, that the points of inflection in the S-shaped curves of slow coagulation with different concentrations of an electrolyte denote the same characteristic state in the kinetics of the process, where d^2x/dt^2 becomes zero. It may be visualised therefore that at this stage of aggregation, the system is governed by such conditions as to reduce the acceleration of the change to zero. To reach this state under the influence of varying concentrations of the electrolyte, different times will be required, which fit in the equation under reference very satisfactorily. This fact was evidenced by our study of the slow coagulation of As_2S_3 and $Fe(OH)_3$ sols by viscosity measurements, and it was again supported by the data obtained from the extinction curves of AgI sol, given by Kruyt and Troelstra (*loc. cit.*).

In view of the above observations it may be concluded that the inflection points of the S-shaped curves of slow coagulation indicate a very characteristic state in the mechanism of slow coagulation and serve as a strong evidence to prove the validity of the equation referred to above.

The constants *a*, *m* and *n* of the equation were evaluated graphically as explained previously (this *Journal*, 1952, **29**, 759) and their values have been shown in Table I.

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