"Zonal Effect" in the Slow Coagulation of Colloid Arsenious Sulphide.

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The results of numerous viscosity measurements reported in previous publications⁽¹⁾ suggested that the progress of a slow coagulation, contrary to the mechanism contemplated in Smoluchowski's classical theory,⁽²⁾ for the kinetics of coagulation is not time continuous but zonal. Subsequent work on the behaviour of colloid manganese dioxide studied by the familiar opacity method⁽³⁾ and that dependent on the determination of μ_D the refractivity⁽⁴⁾ during numerous coagulations has confirmed the above deduction. That this zonal effect in slow coagulations is not merely an instance of the somewhat abnormal behaviour of colloid MnO_2,⁽⁵⁾ but obtains more widely, is shown by results on the electrolytic coagulations of aqueous sodium oleate⁽⁴ᵉ⁾ and different oil suspensions⁽⁴ᵍ⁾ on the coagulations of other systems. Similar results are obtained with colloidal solutions of gold, antimony trisulphide and ferric oxide, which will be published shortly. The present paper reports the occurrence of the zonal effect in colloid As_2S_3.

Experimental. The colloid was prepared and its strength estimated as described by Joshi and Kulkarni.⁽⁴ᵃ⁾ The course of coagulation was followed by measuring the variation of μ_D the refractive index for the sodium line by means of a Pulfrich refractometer. The general experimental procedure, the precautions observed during these measurements

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(1) Joshi and Viswanath, *J. Indian Chem. Soc.*, **10** (1933), 329; Joshi and Menon, *ibid.*, **10** (1933), 599; Joshi and Nanjappa, *ibid.*, **11** (1934), 133; Joshi and Iyengar, *ibid.*, **11** (1934), 55, 573; Joshi and Panikkar, *ibid*, **11** (1934), 797; *J. chim. phys.*, **32** (1935), 455; *Proc. Acad. Sci.* (United Provinces Agra Oudh, India), **5** (1935), 41.

(2) Smoluchowski, *Z. physik. Chem.*, **92** (1917), 129.

(3) Joshi and Purushottam, *Current Sci.*, **4** (1936), 870; Joshi and S. J. Rao, *J. Indian Chem. Soc.*, **13** (1936), 311.

(4a) Joshi and Kulkarni, *ibid.*, **13** (1936), 441.

(4b) Joshi and S. J. Rao, *ibid.*, **13** (1936), 141.

(4c) Joshi and Panikkar, *ibid.*, **13** (1936), 309.

(4d) Joshi and S. J. Rao, *Kolloid-Z.*, **76** (1936), 145.

(4e) Joshi and S. J. Rao, *Fettchem. Umshau*, **43** (1936), 36.

(4f) Joshi and Purushottam, *Current Sci.*, **4** (1936), 481.

(4g) Joshi and Sarkar, *J. Bombay Univ.*, **4** (1935), 140.

(5) Joshi and T. S. Narayan, *Kolloid-Z.*, **49** (1932), 335; *J. Indian Chem. Soc.*, **7** (1930), 883; Joshi and V. L. Narayan, *ibid.*, *Sir P. C. Ray Comm. Vol.*, 1933, p. 41.

have been described previously.(4b) The measurements were continued until the coagulating mixture in the refractometer cell remained sensibly homogeneous, that is, free from local and random turbidities due to the coagulam. Although a large number of coagulations were studied in regard to change of μ_D, only two μ_D-time curves are shown in Fig. 1 to indicate the generality of the results. The coagulant used was a suitably diluted solution of H_2SO_4, so as to produce a measurable change in μ_D during a moderate period. The concentration of the coagulant and of the colloid as indicated in Fig. 1 refer to their values in the coagulating mixture. The temperature was maintained constant at 25° ± 0.1°. The least changes in μ_D refer to 0.5 minute, which could be definitely measured with the instrument, and which corresponds to a change of about 0.00004 in μ_D.

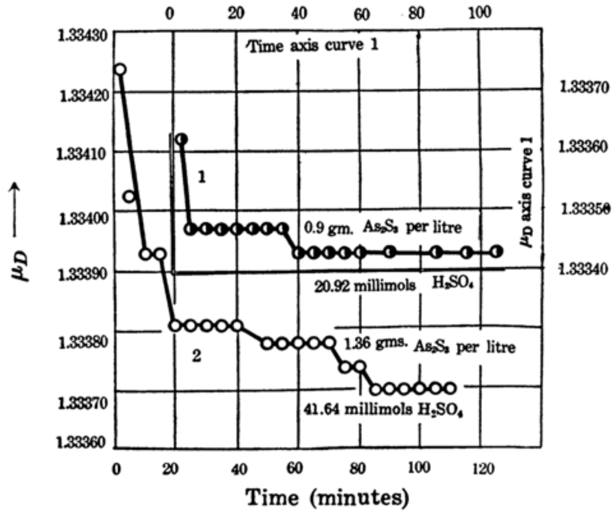

Fig. 1.

Discussion. The two typical curves in Fig. 1 show definitely that the progress of coagulation as recorded by change of μ_D is not time-continuous, but discontinuous or zonal. It was observed that for a given concentration of the colloid, the net change in μ_D during the coagulation and the number of discontinuities or the zonal effect tends to diminish for very large and small values of the concentration of the coagulant. Similar, though not indentical is the influence of the change of colloid content at constant concentration of the coagulant. This is in complete accord with the results obtained previously.(1) It was observed, for example, that a viscosity-time curve corresponding to a moderately high concentration of the coagulant showed a slight initial fall and then a continuous rise. With a lower concentration, the coagulation curve consisted of a definitely greater number of breaks or discontinuities. A satisfactory theory for the refractivity of a colloid is fundamental to the elucidation of the turbidity phenomena, which are the chief characteristic (for evidence indicating limitation of the validity of this familiar notion, compare Joshi and Kulkarni$^{(4a)}$) of the coagulation phenomena; it must analyse the influence of such factors as the micellar charge, the nature of the surrounding Helmholtz layer, the refractivity of the continuous and the micellar material, the size and perhaps the shape of the particles; these determine the magnitude of the path in unit time of a light beam passing through the system, and therefore, its refractivity. These quantities are manifestly subject to change during coagulation. During the process, the coalescence of the particles increases the proportion of the medium viz. water in the light path. μ_D is expected to approach its value and therefore, diminish, since the refractivity of the dispersed material is ordinarily greater than that of water. That this change, concomitant with coagulation proceeds zonally is an interesting and hitherto practically an ignored feature of the phenomenon of coagulation in the slow region, and observed perhaps for the first time in colloid arsenious sulphide which has had about the longest and widest usage in studies of the coagulation phenomena.

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