

Studies on the Stability of the Hydrosulphide Hydrosol of Antimony in the Light of some recent Developments

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The stability of negative Sb_2S_3 sol of mean particle diameter 87.5 Å has been ascertained in the presence of K^+ , Ba^{2+} , Al^{3+} and Th^{4+} . The electrophoretic measurements of the sol permitted the calculation of its zeta potential (assumed to be equal to the electrostatic potential) as a function of ionic strength. From the knowledge of ζ potential the energy of repulsion, V_R , was calculated; the attraction energy, V_A , was estimated from physico-chemical data. Combination of the two energies yielded the profiles of interaction from which stability ratio could be calculated. Stability factor, F , was also estimated from the Derjaguin equation, but it was not satisfactory presumably owing to the exclusion of V_A .

The flocculation powers of cations were in the order $\text{Al}^{3+} > \text{Ba}^{2+} > \text{Mn}^{2+} > \text{Th}^{4+} > \text{K}^+ > \text{Na}^+$. Thorium behaves anomalously perhaps due to hydrolysis. In general, the interaction between the Sb_2S_3 particles could be interpreted in the light of the D.V.O. theory.

The survey of literature reveals that much work, mainly of qualitative nature, has already been done on the Sb_2S_3 sol¹⁻⁹. There appears, however, lack of quantitative data specially in the light of some recent developments on the stability of lyophobic colloids. It is, therefore, proposed in the present paper to apply the modern theory of the subsidence of lyophobic sols due to Derjaguin,^{10,11} Verwey and Overbeek¹² (D.V.O. theory) to the flocculation results of the hydrosulphide sol of antimony using three important variables, namely, particle radius a , surface potential ψ , and the Debye-Hückel reciprocal length K .

EXPERIMENTAL

(a) *Materials*: Sodium chloride, potassium chloride, barium chloride, manganese chloride and thorium nitrate used for coagulation studies were all of Analar grade. Potassium antimony tartrate and aluminium chloride were of B.D.H. quality and were

1. Schulze, *J. Chem. Soc.*, (2) 1883, 27, 320.
2. Ivanitzkaja and Orlova, *Koll. Beihfte*, 1923, 18, 1.
3. Linder and Picton, *J. Chem. Soc.*, 1892, 61, 123.
4. Sen, Ganguly and Dhar, *J. Phys. Chem.*, 1924, 28, 313
5. Ghosh and Dhar, *ibid*, 1926, 30, 628; 1927, 31, 187, 449; *Koll. Zeit.*, 1925, 29, 435, 658; and *Koll. Zeit.*, 1925, 36, 129.
6. Wintgen, *Koll. Beihfte*, 1915, 7, 251.
7. Bhatnagar and co-workers, *J. Indian Chem. Soc.*, 1925, 2, 11; 1927, 4, 209; *J. Phys. Chem.*, 1924, 28, 730; 1924, 28, 392.
8. Ganguly and Dhar, *J. Phys. Chem.*, 1922, 31, 16.
9. Prasad and co-workers, *Koll. Zeit.*, 1925, 37, 101.
10. Derjaguin, *Trans. Farad Soc.*, 1940, 36, 203, 730; *J. Expt. Theor. Phys.*, USSR, 1941, 11, 802.
11. Derjaguin and Landau, *Acta. Physico Chim.*, 1941, 14, 633.
12. Verwey and Overbeek, "Theory of stability of lyophobic colloids", Elsevier, Amsterdam (1948)

not purified further. Ordinary distilled water was redistilled before use from all-pyrax apparatus and was of the specific conductance $\approx 1.10^{-6}$ ohm $^{-1}$ cm $^{-1}$. All other glasswares were of pyrex.

(b) *Preparation of the sol*: Antimony trisulphide sol was prepared by bubbling a slow stream of hydrogen sulphide gas through 500 ml redistilled water in which 500 ml aqueous solution of 1 per cent potassium antimony tartrate was added dropwise. The speed of drops and stream of hydrogen sulphide were adjusted in such a manner that the addition of each drop of aqueous tartrate solution was followed by 5-7 bubbles of H_2S gas. The excess of H_2S was removed by passing a current of purified hydrogen gas for half-an-hour. The intense red-yellow sol so obtained was then dialysed in a parchment bag against running distilled water for two and a half days.

(c) *Electrophoretic mobility measurements*: To measure the electrophoretic mobility, the experiments were carried out in a modified apparatus¹³ of Burton tube fitted with two wide side tubes. During the measurements constant current was supplied and the potential drop across the two pt. electrodes in the U-tube was measured using a potentio-vacuum tube voltmeter. Measurements were made at the sharp descending boundary between the colloidal solution and an equi-conducting aqueous solution of acetic acid. All the readings were taken between 35 and 45 minutes after the addition of electrolyte. The mean of three readings was taken to calculate mobility. The reproducibility of the electrophoretic mobility was $\pm 4\%$.

The ζ -potential (zeta potential) was calculated by the Hückel's¹⁴ equation and the correction for relaxation and the Henry effect were made using the Overbeek's¹⁵ formulae for symmetrical and unsymmetrical electrolytes respectively.

$$U = \frac{e\zeta}{6\pi\eta} \left[f_1(ka) - v^+ \left(\frac{e\zeta}{KT} \right)^2 f_2(ka) - \frac{\rho_+ + \rho_-}{2e} \frac{eKT}{6\pi\eta\epsilon} \left(\frac{e\zeta}{KT} \right)^2 f_4(ka) \right] \quad (1)$$

and

$$U = \frac{e\zeta}{6\pi\eta} \left[f_1(ka) - (v_+ - v_-) \left(\frac{e\zeta}{KT} \right)^2 f_2(ka) - \frac{\rho_+ v_+ + \rho_- v_-}{(v_+ + v_-)e} \cdot \frac{eKT}{6\pi\eta\epsilon} \left(\frac{e\zeta}{KT} \right)^2 f_4(ka) \right] \quad (2)$$

where U is the electrophoretic mobility of the particles. $f_1(ka)$ is identical with the Henry function and the $f_2(ka)$, and $f_3(ka)$ and $f_4(ka)$ have been tabulated by Overbeek¹⁶. ϵ is the dielectric constant of the medium, η , the viscosity of the medium, T , the absolute temperature, a , the radius of the particle, k , the Debye-Hückel reciprocal length, K , Boltzmann's constant and e , the electronic charge. v_+ and v_- are the valences and ρ_+ and ρ_- the frictional constants of the cations and anions respectively. These are calculated taking the ionic conductance of Cl^- , Na^+ , K^+ and Be^{2+} to be 76.3, 50.1, 73.5 and 63.6 respectively and that of Mn^{2+} , Al^{3+} and Th^{4+} to be 70 ohm $^{-1}$ cm $^{-2}$. All work was carried out in a thermostat at $30 \pm 0.5^\circ C$.

13. Bhatnagar and Bhattacharya, *Koll. Zrit.*, 1960, 179, 29.

14. Hückel, *Zrit Physik.*, 1924, 23, 204.

15. Overbeek, *Koll. Beihfte.*, 1943, 54, 287.

16. Overbeek, "Advances in Colloid Science", Vol. III, Interscience, London 1950, page 115.

(d) *Measurements of the size of the colloidal particles with the help of electron microscope*: A sample of the colloidal solution under investigation was diluted 10 times. Specimen for electron micrograph was prepared by allowing a small drop of specimen in liquid suspension to dry on 200 mesh copper grid support which had earlier been covered with a thin film of collodion. The electron photograph was taken on Siemens Elmiskop I electron microscope at 100 KV.

THEORETICAL

(a) *The stability theory and its application to the present system*: According to the well known theory of the stability of lyophobic colloids developed independently by Derjaguin and Verwey and Overbeek (*loc. cit.*) colloidal particles are subject to forces of repulsion owing to the interaction of electrical double layers which are generally present around the particles and forces of attraction of the London-van der Waals type. Coagulation occurs if the attraction forces predominate over the repulsive forces, otherwise the sol is stable. More precisely, a combination of energies of the London attraction forces with double layer repulsion forces leads to potential energy curves and if the potential energy barrier V is high enough (*viz.*, $V \gg 15 KT$) the colloid is stable. The energy barrier opposes collision of the particles and a portion of colliding particles can surmount it only if the potential barrier has a lower value. It is, therefore, the net interaction between the colloidal particles which will determine its stability. This interaction will consist of (i) potential energy of repulsion and (ii) potential energy of attraction.

In the frame work of the D.V.O. theory the potential energy of repulsion, V_R and potential energy of attraction, V_A between two equal small spherical particles of radius a , electrical potential Ψ , smallest interparticle distance H_0 , are respectively given by following simple approximate equations,

$$V_R = [a \epsilon \Psi^2 \exp(-Tu)] / u + 2 \quad (\text{for small value of } T) \quad \dots (3)$$

and

$$V_A = -A/12 u \quad (u \ll 1) \quad \dots (4)$$

where ϵ is the dielectric constant of the medium of the colloidal solution, $u = H_0/a$, $T = Ka$ and A the van der Waals or Hamaker constant. K is the Debye-Hückel parameter denoting the reciprocal thickness of the double layer. Here the electrical potential, Ψ , has been assumed to be equal to the electrokinetic potential (ζ) as the latter quantity is important from the standpoint of stability. The correction for the retardation of the London-van der Waals forces given by Schenkel and Kitchner¹⁷ has been neglected as in the present system the range of interest is within the validity of the formula.

For the present system of lyophobic colloid in which, except electrostatic repulsion and van der Waals attraction, other energies can be neglected, the total energy of interaction, V is simply the sum of the repulsive and attractive energies, i.e.,

$$V = a \epsilon \Psi^2 \exp(-Tu) / u + 2 - A/12 u \quad \dots (5)$$

This potential energy of interaction for slow coagulation, according to Fuchs's¹⁸ treatment, is related to the stability ratio, W as follows,

$$W = 2 \int_0^{\infty} \exp \frac{1}{kT} (a e^{\Psi^2} \exp (-T u)/u + 2 - A/12 u) \frac{du}{(u+2)^2} \quad \dots (6)$$

Unfortunately integration of the right-hand expression cannot be done directly and, therefore, value of W has to be obtained by graphical integration using the plots of $\exp (V/kT)/s^2$ against s .

An approximate equation¹⁹ as given below may also be used for the value of stability ratio of lyophobic colloids.

$$W = \exp (V_m/kT)/2 K a \quad \dots (7)$$

Here V_m is the maximum in the potential energy curves.)

Derjaguin (*loc. cit.*) has also described a formula for the stability of lyophobic colloidal particles, which is as follows,

$$F = a c \Psi^{1/2} kT \quad \dots (8)$$

where F is the stability factor and the other terms have the usual meanings.

For the theoretical calculation of van der Waals attraction constant, A , use may be made of the Hamaker²⁰ equation :

$$A = \pi^2 q^2 \lambda \quad \dots (9)$$

where q is the number of atoms (molecules) in cm^3 of the substance composing the particles, and λ is the London constant which can be calculated from the following equations, (see Srivastava²¹)

$$\text{Slater-Kirkwood}^{22} \text{ equation : } \lambda_{S-K} = 11.25 \times 10^{-24} v^{1/2} P^2/k \quad \dots ((10)$$

$$\text{Slater-Kirkwood and Moolwyn-Hughes}^{23} \text{ equation : } \lambda_{S-K-M} = 7.8 \times 10^{-24} v^{1/2} P^2/k \quad \dots (11)$$

$$\text{Nengebauer}^{24} \text{ equation : } \lambda_N = -1.62 \times 10^{-25} P k \quad \dots (12)$$

where v is the number of valency electrons in the outer shell, P the polarizability and k the diamagnetic susceptibility.

However, the value of A obtained from equation (9) is for interaction between two solid Sb_2S_3 particles in vacuum. Therefore, to calculate the interaction between Sb_2S_3 solid particles in water a correction has been made and interaction was calculated from the expression (*loc. cit.*)

18. Fuchs, *Z. Physik*, 1934, 89, 734.

19. Kravt "Colloid Science", Elsevier, Amsterdam, 1952, Vol. I, page 285.

20. Hamaker, *Physica*, 1937, 4, 1038.

21. Srivastava, *Indian J. Chem.*, 1965, 3, 376.

22. Slater and Kirkwood, *Phys. Rev.*, 1931, 37, 682.

23. Moolwyn-Hughes, "Physical Chemistry", Pergamon, London, 1957, page 383.

24. Nengebauer, *Z. Physik*, 1937, 107, 785.

$$A = (A^1Sb_2S_3 - Sb_2S_3 - A^1H_2O - H_2O)^* \quad (13)$$

Here it may be mentioned that in the calculation of A certain physico-chemical data such as susceptibility and polarizability will be needed which are applicable for pure crystalline antimony sulphide particles. The colloidal particles are, however, not stoichiometric units and are aggregated molecular species with adsorbed ions. Therefore, the data of the crystalline species may be applied to colloidal particles as a first approximation only.

RESULTS

Size of the particle of Sb_2S_3 sol: A typical electron micrograph of Sb_2S_3 sol particles is given in Fig. 1 and from the particle size distribution curve the mean particle radius was found to be 43.75\AA .



Fig. 1 Electron micrograph of Sb_2S_3 sol. $\times 160,000$

The zeta potentials: The concentration and pH of the 50% diluted sol which was dialysed for two and a half days against slow running distilled water were 1.1×10^{-3} gms/ml and 3.4 ± 0.05 respectively. The experimental value obtained for the mobility of the above antimony trisulphide sol was $5.6 \mu/\text{sec}/\text{volt}/\text{cm}$. The zeta potential calculated from this value was 99.7 mV at 30°C .

The mobility and the ζ -potentials of Sb_2S_3 particles as a function of log molar concentration of different electrolytes, viz., $NaCl$, KCl , $MnCl_2$, $BaCl_2$, $AlCl_3$, and $Th(NO_3)_4$, are given in Figs. 2 and 3 respectively. In general, it is seen that the mobility and the ζ -potential decrease as the concentration of electrolytes increases. With $NaCl$ and KCl the fall of the ζ -potential is almost linear throughout, but with $MnCl_2$, $BaCl_2$, and $AlCl_3$, it is comparatively slow at the initial stages and then becomes sharp. $Th(NO_3)_4$ shows altogether different behaviour; its mobility (as also ζ -potential) first increases with increase of electrolyte concentration and then falls steeply after a certain concentration.

The minimum ζ -potential that could be conveniently measured was about 60 mV below which there was visible flocculation of the sol particles.

Calculation of van der Waals constant: To calculate van der Waals constant, one requires the value of London constant which was calculated using the susceptibility of one

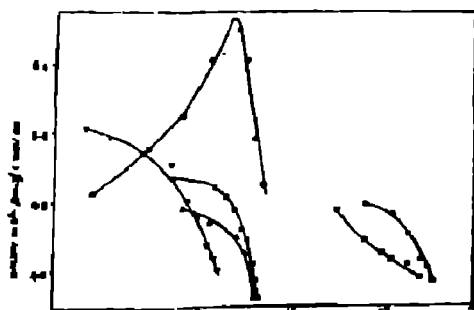


Fig. 1. Variation of magnetic susceptibility with temperature for Sb_2S_3 .

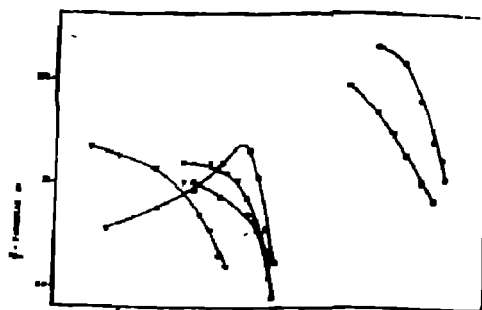


Fig. 2. Variation of magnetic susceptibility with temperature for Sb_2S_3 .

gram formula wt.²⁶ = 8.6×10^{-3} , $v = 28$ and $P = 2.335 \times 10^{-23}$ (calculated from Clausius-Mosotti equation using refractive index data of Sb_2S_3 ²³). With the proper choice of units, the values of the London constant calculated from equations (10), (11) and (12) are as follows,

$$\lambda_{S-K}^{Sb_2S_3} = 0.717 \times 10^{-27} \quad \text{ergs cm}^6,$$

$$\lambda_{S-K-M}^{Sb_2S_3} = 24.64 \times 10^{-27} \quad \text{ergs cm}^6, \text{ and}$$

$$\lambda_N^{Sb_2S_3} = 5.401 \times 10^{-27} \quad \text{ergs cm}^6$$

Now by finding q (8.226×10^{21}) from the density (4.64), the use of equation (9) permits the calculation of van der Waals constant for Sb_2S_3 from each of the three equations. Similarly, the corresponding constant for water is given by Verwey and Overbeek (*loc. cit.*) (see also Watillon²⁷) and hence the net attraction constant of Sb_2S_3 particles in water can be estimated from equation (13). The results are summarised in Table I.

TABLE I

Value of the van der Waals constant calculated from different equations using $M = 339.7$, $P = 2.335 \times 10^{-23}$ cc/mol., $q = 8.226 \times 10^{21}$ molecules/cc.

Equation used	$\Lambda_{Sb_2S_3-Sb_2S_3} \times 10^{13}$ (vac.) (erg)	$\Lambda_{H_2O-H_2O} \times 10^{13}$ (vac.) (erg)	$\Lambda_{Sb_2S_3 \text{ in } H_2O} \times 10^{13}$ (erg)
S-K	4.489	5.95	1.816
S-K-M	16.46	7.70	10.11
N	3.61	5.61	1.324

25. "Hand-book of Chem. and Phys.", 43rd., edition, Chemical Rubber Publishing Co., 1961-62, p. 2683.

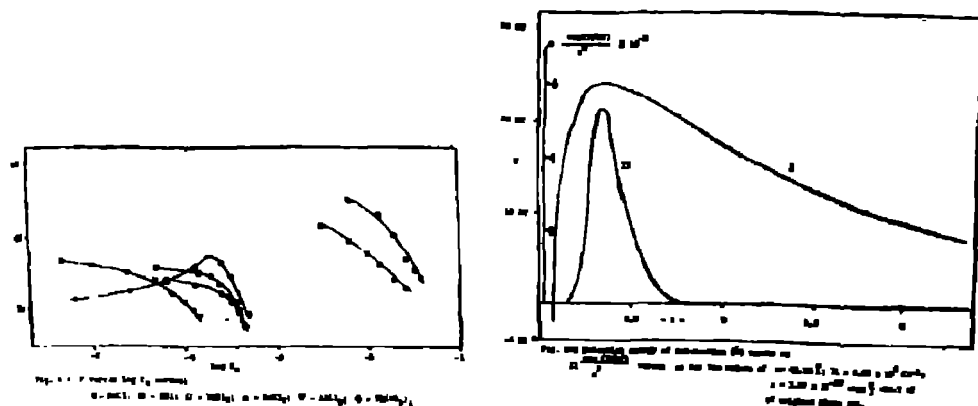
26. *International Critical Tables*, Vol. VII, page 19.

27. Watillon and Joseph-Petit, III. *Inter. Cong. Surf. sci.*, Cologne 1960, 1, 145.

It is found that the value of the London constant calculated from S-K-M formula yields a comparatively high value. Therefore, in the present calculations the value of A_{S-K-M} has been neglected and for further calculations the mean value from the remaining two formulae ($=1.57 \times 10^{-12}$ ergs) has been used.

An estimate of the stability factor, F from Darjagin equation: The value of the factor was calculated from equation (8) for different electrolytes and the results have been depicted graphically in Fig. 4.

Potential energy curves. In Fig. 5 curve I shows the net potential energy of interaction of the Sb_2S_3 sol corresponding to ζ -potential = 99.7 mV. This has an energy maxi-



Log W against log C_e

Stability ratio was calculated by graphical integration of equation (6), as well as from an approximate equation (7). In Fig. 5 a typical curve II of $\exp(V/kT)/s^2$ against s has

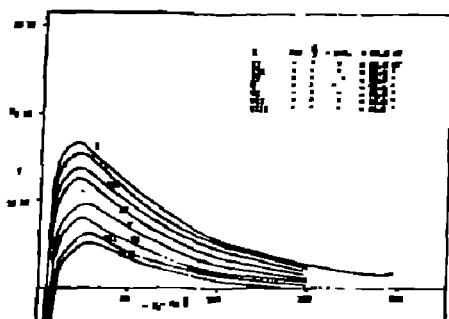


Fig. 5 - Curves for potential energy of adsorption (V) as the function of s , curve 1_{10} .

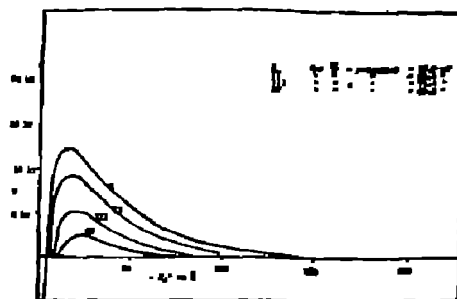


Fig. 6 - Curves for potential energy of adsorption (V) as the function of s , curve 1_{10} .

been drawn to calculate the stability factor W in the absence of electrolytes, which comes out to be 2.5×10^8 ; the value of W calculated from approximate equation (7) is 4.25×10^{10} .

In Figs. 10 and 11, the curves for $\log W$ against $\log C_e$ are given for varying concentrations of the electrolytes.

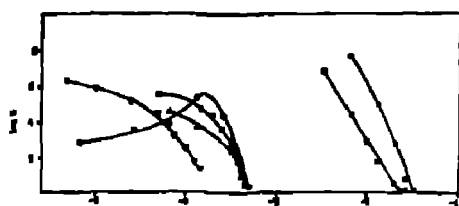


Fig. 10 - $\log W$ versus $\log C_e$
(1 - $NaCl$; 2 - KCl ; 3 - $LiCl$; 4 - $CaCl_2$; 5 - $MgCl_2$; 6 - $AlCl_3$; 7 - $FeCl_3$; 8 - $Th(NO_3)_4$; 9 - $Th(NO_3)_4$; 10 - $Th(NO_3)_4$; 11 - $Th(NO_3)_4$; 12 - $Th(NO_3)_4$; 13 - $Th(NO_3)_4$; 14 - $Th(NO_3)_4$; 15 - $Th(NO_3)_4$; 16 - $Th(NO_3)_4$; 17 - $Th(NO_3)_4$; 18 - $Th(NO_3)_4$; 19 - $Th(NO_3)_4$; 20 - $Th(NO_3)_4$; 21 - $Th(NO_3)_4$; 22 - $Th(NO_3)_4$; 23 - $Th(NO_3)_4$; 24 - $Th(NO_3)_4$; 25 - $Th(NO_3)_4$; 26 - $Th(NO_3)_4$; 27 - $Th(NO_3)_4$; 28 - $Th(NO_3)_4$; 29 - $Th(NO_3)_4$; 30 - $Th(NO_3)_4$; 31 - $Th(NO_3)_4$; 32 - $Th(NO_3)_4$; 33 - $Th(NO_3)_4$; 34 - $Th(NO_3)_4$; 35 - $Th(NO_3)_4$; 36 - $Th(NO_3)_4$; 37 - $Th(NO_3)_4$; 38 - $Th(NO_3)_4$; 39 - $Th(NO_3)_4$; 40 - $Th(NO_3)_4$; 41 - $Th(NO_3)_4$; 42 - $Th(NO_3)_4$; 43 - $Th(NO_3)_4$; 44 - $Th(NO_3)_4$; 45 - $Th(NO_3)_4$; 46 - $Th(NO_3)_4$; 47 - $Th(NO_3)_4$; 48 - $Th(NO_3)_4$; 49 - $Th(NO_3)_4$; 50 - $Th(NO_3)_4$; 51 - $Th(NO_3)_4$; 52 - $Th(NO_3)_4$; 53 - $Th(NO_3)_4$; 54 - $Th(NO_3)_4$; 55 - $Th(NO_3)_4$; 56 - $Th(NO_3)_4$; 57 - $Th(NO_3)_4$; 58 - $Th(NO_3)_4$; 59 - $Th(NO_3)_4$; 60 - $Th(NO_3)_4$; 61 - $Th(NO_3)_4$; 62 - $Th(NO_3)_4$; 63 - $Th(NO_3)_4$; 64 - $Th(NO_3)_4$; 65 - $Th(NO_3)_4$; 66 - $Th(NO_3)_4$; 67 - $Th(NO_3)_4$; 68 - $Th(NO_3)_4$; 69 - $Th(NO_3)_4$; 70 - $Th(NO_3)_4$; 71 - $Th(NO_3)_4$; 72 - $Th(NO_3)_4$; 73 - $Th(NO_3)_4$; 74 - $Th(NO_3)_4$; 75 - $Th(NO_3)_4$; 76 - $Th(NO_3)_4$; 77 - $Th(NO_3)_4$; 78 - $Th(NO_3)_4$; 79 - $Th(NO_3)_4$; 80 - $Th(NO_3)_4$; 81 - $Th(NO_3)_4$; 82 - $Th(NO_3)_4$; 83 - $Th(NO_3)_4$; 84 - $Th(NO_3)_4$; 85 - $Th(NO_3)_4$; 86 - $Th(NO_3)_4$; 87 - $Th(NO_3)_4$; 88 - $Th(NO_3)_4$; 89 - $Th(NO_3)_4$; 90 - $Th(NO_3)_4$; 91 - $Th(NO_3)_4$; 92 - $Th(NO_3)_4$; 93 - $Th(NO_3)_4$; 94 - $Th(NO_3)_4$; 95 - $Th(NO_3)_4$; 96 - $Th(NO_3)_4$; 97 - $Th(NO_3)_4$; 98 - $Th(NO_3)_4$; 99 - $Th(NO_3)_4$; 100 - $Th(NO_3)_4$.)



Fig. 11 - $\log W$ versus $\log C_e$
(1 - $NaCl$; 2 - KCl ; 3 - $LiCl$; 4 - $CaCl_2$; 5 - $MgCl_2$; 6 - $AlCl_3$; 7 - $FeCl_3$; 8 - $Th(NO_3)_4$; 9 - $Th(NO_3)_4$; 10 - $Th(NO_3)_4$; 11 - $Th(NO_3)_4$; 12 - $Th(NO_3)_4$; 13 - $Th(NO_3)_4$; 14 - $Th(NO_3)_4$; 15 - $Th(NO_3)_4$; 16 - $Th(NO_3)_4$; 17 - $Th(NO_3)_4$; 18 - $Th(NO_3)_4$; 19 - $Th(NO_3)_4$; 20 - $Th(NO_3)_4$; 21 - $Th(NO_3)_4$; 22 - $Th(NO_3)_4$; 23 - $Th(NO_3)_4$; 24 - $Th(NO_3)_4$; 25 - $Th(NO_3)_4$; 26 - $Th(NO_3)_4$; 27 - $Th(NO_3)_4$; 28 - $Th(NO_3)_4$; 29 - $Th(NO_3)_4$; 30 - $Th(NO_3)_4$; 31 - $Th(NO_3)_4$; 32 - $Th(NO_3)_4$; 33 - $Th(NO_3)_4$; 34 - $Th(NO_3)_4$; 35 - $Th(NO_3)_4$; 36 - $Th(NO_3)_4$; 37 - $Th(NO_3)_4$; 38 - $Th(NO_3)_4$; 39 - $Th(NO_3)_4$; 40 - $Th(NO_3)_4$; 41 - $Th(NO_3)_4$; 42 - $Th(NO_3)_4$; 43 - $Th(NO_3)_4$; 44 - $Th(NO_3)_4$; 45 - $Th(NO_3)_4$; 46 - $Th(NO_3)_4$; 47 - $Th(NO_3)_4$; 48 - $Th(NO_3)_4$; 49 - $Th(NO_3)_4$; 50 - $Th(NO_3)_4$; 51 - $Th(NO_3)_4$; 52 - $Th(NO_3)_4$; 53 - $Th(NO_3)_4$; 54 - $Th(NO_3)_4$; 55 - $Th(NO_3)_4$; 56 - $Th(NO_3)_4$; 57 - $Th(NO_3)_4$; 58 - $Th(NO_3)_4$; 59 - $Th(NO_3)_4$; 60 - $Th(NO_3)_4$; 61 - $Th(NO_3)_4$; 62 - $Th(NO_3)_4$; 63 - $Th(NO_3)_4$; 64 - $Th(NO_3)_4$; 65 - $Th(NO_3)_4$; 66 - $Th(NO_3)_4$; 67 - $Th(NO_3)_4$; 68 - $Th(NO_3)_4$; 69 - $Th(NO_3)_4$; 70 - $Th(NO_3)_4$; 71 - $Th(NO_3)_4$; 72 - $Th(NO_3)_4$; 73 - $Th(NO_3)_4$; 74 - $Th(NO_3)_4$; 75 - $Th(NO_3)_4$; 76 - $Th(NO_3)_4$; 77 - $Th(NO_3)_4$; 78 - $Th(NO_3)_4$; 79 - $Th(NO_3)_4$; 80 - $Th(NO_3)_4$; 81 - $Th(NO_3)_4$; 82 - $Th(NO_3)_4$; 83 - $Th(NO_3)_4$; 84 - $Th(NO_3)_4$; 85 - $Th(NO_3)_4$; 86 - $Th(NO_3)_4$; 87 - $Th(NO_3)_4$; 88 - $Th(NO_3)_4$; 89 - $Th(NO_3)_4$; 90 - $Th(NO_3)_4$; 91 - $Th(NO_3)_4$; 92 - $Th(NO_3)_4$; 93 - $Th(NO_3)_4$; 94 - $Th(NO_3)_4$; 95 - $Th(NO_3)_4$; 96 - $Th(NO_3)_4$; 97 - $Th(NO_3)_4$; 98 - $Th(NO_3)_4$; 99 - $Th(NO_3)_4$; 100 - $Th(NO_3)_4$.)

In general all the curves have similar shapes and almost the same slopes in the lower part of the slow coagulation range. The only exception is the curve obtained with $Th(NO_3)_4$, where the stability ratio first increases with the increase of thorium nitrate concentration and after certain concentration the nature of the curve assumes the general form. The resultant stability ratio obtained by the two different methods shows that values of W obtained from the method of approximate equation are higher than those calculated from graphical integration.

To calculate the coagulation concentration of various salts which are used to coagulate the Sb_2S_3 sol the extrapolation of the linear portion of $\log W$ versus $\log C_e$ curve was made to $\log C_e$ axis^{20,21} where $\log W = 0$, assuming the validity of the equation^{20,21}:

28. Ottewill and Watanabe, *Koll. Zeit.*, 1960, 170, 38; 1960, 173, 122.

29. Ottewill and Wilkins, *Trans. Faraday Soc.*, 1960, 170, 132; 1962, 58, 608; *III Intern. cong. surf. sci.* Cologne, 1960, 11, 653.

30. Pain, *Koll. Beihfte*, 1912, 4, 34.

31. Reerink and Overbeck, *Dix. Faraday Soc.*, 1954, 18, 74.

$\log W = K_1 - K_2 \log C_0$. The values obtained in this manner are given in table II. A comparison of the coagulation concentrations given in table II shows that the value is slightly higher when calculated by the approximate equation (7) than that by the graphical integration. The flocculating concentrations so obtained were confirmed from the turbidity data³². The coagulating concentrations obtained from the turbidity measurements are given in table III. Here the values obtained from $\log dt/dE$ versus $\log C_0$ curves are the values for rapid flocculation and those from E versus $\log C_0$ curves are the values at the threshold for rapid flocculation. These flocculation results have been discussed in detail elsewhere³².

TABLE II

Coagulation data for Sb_2S_3 sol

Electrolyte	Coagulation concentration moles/litre		$-\log W/d \log C_0$	
	for W from eqn. (7)	for W from graphical integration	for W from eqn. (7)	for W from graphical integration
NaCl	3.4×10^{-3}	3.0×10^{-3}	15.2	12.5
KCl	2.5×10^{-3}	2.3×10^{-3}	9.0	7.8
$BaCl_2$	4.9×10^{-4}	4.6×10^{-4}	22.0	16.6
$NaCl_2$	5.0×10^{-4}	4.7×10^{-4}	22.5	16.6
$AlCl_3$	2.2×10^{-4}	2.1×10^{-4}	12.5	7.8
$Th(NO_3)_4$	5.5×10^{-4}	5.2×10^{-4}	16.1	15.2

TABLE III

The flocculating concentration from the turbidity measurement for negative Sb_2S_3 sol.

Electrolyte	Flocculating concentration in moles per litre.	
	from $\log dt/dE$ vs. $\log C_0$ curves	from E vs. $\log C_0$ curves
NaCl	6.60×10^{-4}	3.90×10^{-4}
KCl	5.2×10^{-4}	3.1×10^{-4}
$MnCl_2$	1.1×10^{-3}	4.4×10^{-4}
$BaCl_2$	8.0×10^{-4}	3.5×10^{-4}
$AlCl_3$	1.4×10^{-4}	6.0×10^{-5}
$Th(NO_3)_4$	1.2×10^{-3}	5.0×10^{-4}

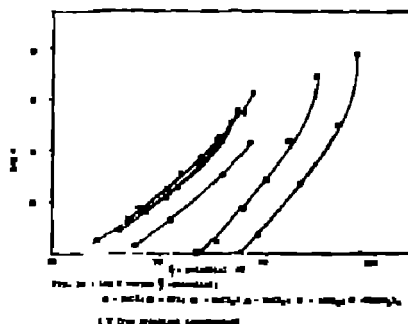
The values of $\log W$ are plotted against ζ -potentials for different electrolytes in Fig. 12. The general shape of the curves is according to the trend expected theoretically.

DISCUSSION

The order of flocculation power as ascertained from the stability results as well as from electrophoresis data is: $Al^{3+} > Ba^{2+} > Mn^{2+} > Th^{4+} > K^+ > Na^+$. From Schulze-Hardy rule the flocculating concentrations of different electrolytes would be expected to be in the ratio of $1 : (\frac{1}{2})^6 : (\frac{1}{3})^6 : (\frac{1}{4})^6$, where the denominator is the valency of the counter ion;

32. Daluja and Srivastava, (to be published).

hence taking the monovalent ion as 100, the ratio should be 100:1.6:0.13:0.024. Experimentally the ratio for Na^+ , K^+ , Mn^{++} , Ba^{++} , Al^{3+} and Th^{4+} was found to be 100:76.6:1.56:153:0.7:1.79. Thus, a marked deviation from Schulze-Hardy rule occurs particularly with thorium. The nature of thorium ion in solution is complicated and it appears



that the ion present in the pH range 3 to 4 was not a simple tetravalent species but contaminated with ions of different valencies as a result of hydrolysis^{33,34}.

Reversal of charge with polyvalent ions as usually expected with colloids is absent in the present work. This is in conformity with the work of Troelstra^{35,36} who showed that in acid solutions when pH is low the reversal of charge was absent or at least difficult. This was also pointed out by Matijevic and co-workers³⁷ who showed that the reversal of charge is obviated owing, in all probability, to the presence of the insoluble hydroxide of thorium formed as a result of hydrolysis.

The stability of the colloid has been first estimated by Derjaguin's formula (equation 8 and fig. 4). According to theoretical expectation F should be higher than 10 for a colloid to be stable. But for the present system the value of F is not less than 15 even for a reasonably flocculated sol examined within 50 minutes after preparation. This is inconsistent with the Derjaguin theory. In the application of Derjaguin's equation (8) only one approximation is used, which is not expected to affect the results so much. So the reason for this discrepancy seems to lie in the neglect of the van der Waals attractive forces and Debye-Hückel parameter which also plays an important part in the stability as discussed before.

The potential energy barrier of the original Sb_2S_3 sol is 24.1 kT which is a reasonably high value to show that the sol is stable. The potential energy profiles as given in figures 6 to 9 for four different electrolytes (viz., KCl , BaCl_2 , AlCl_3 and $\text{Th}(\text{NO}_3)_4$) are in good agreement with the theoretical expectation. The value of V_m in each case shows the range of slow flocculation till the V_m decreases to a sufficiently low value which is a threefold of rapid coagulation.

33. Chauvenet and Tonnet, *Bull. Soc., Chim., France*, 4, 1930, 47, 701.

34. Chauvenet and Mme. Souteyrand-Franck, *ibid.*, 4, 1930, 47, 1128.

35. Troelstra, *Thesis, Utrecht*, 1941, pages 125, 132.

36. Kruyt and Troelstra, *Koll. Beheft.*, 1943, 34, 284, 277.

37. Matijevic, Abramson, Schulze and Kerker, *J. Phys. Chem.*, 1960, 64, 1157.

The stability factor, W , of the initial sol is 2.5×10^3 . The other limit approaches nearly zero on the addition of electrolytes. The values of the stability factors in the zone of slow coagulation are comparable with those obtained by Ottewill and co-workers (loc. cit.) on AgI and arachidic acid systems. Except for thorium the general shape of the log W and ξ curves for slow coagulation is in keeping with the theory. It is obvious from the curves that the higher the value of T , the higher is the ζ -potential at which flocculation can occur.

The first approximation that has to be made in the calculation of the electrostatic repulsive energy is the identification of Ψ with ζ and the combination of large potentials with small T , but as pointed out by Overbeek (loc. cit.) the errors introduced may not be serious. Another parameter which has to be accurately known in order to apply the D.V.O. theory correctly to any system is the Hamaker constant, A , the value of which, calculated here from physico-chemical data, is 1.57×10^{-12} ergs, and is well within the range suggested by Overbeek.

In conclusion it may be asserted that the D.V.O. theory for small spherical colloidal particles seems to be applicable reasonably well to the present system in so far as it gives a satisfactory interpretation of the interaction between the Sb_2S_3 colloidal particles. The value of the stability factor of the sol as deduced on the basis of the D.V.O. theory is in accordance with the high value of zeta potentials and low value of the particle radius.

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