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Stability of Hydrosol of Arsenic Trisulphide in the Light of D. L. V. O. Theory

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The stability of negative As_2S_3 sol of mean particle diameter 90 Å has been studied in presence of different valent cations *viz.* Na^+, Ba^{2+}, $UO_2{}^{2+}$, Al^{3+} and Th^{4+} using D. L. V. O. theory. The zeta potential (assumed to be equal to the surface potential) of the sol particles was calculated from the electrophoretic measurements as a function of ionic strength. The knowledge of zeta potential permitted the calculation of repulsive energy V_R, and the energy of attraction V_A was estimated from physico-chemical data. The stability ratio, W, was calculated from interaction profiles which were made from the combination of the two energies. Stability factor, F, was also estimated from the Derjaguin equation, but it was not satisfactory presumably owing to the exclusion of V_A. In general, the interaction between As_2S_3 particles could be interpreted in the light of D. L. V. O. theory. The flocculation powers of cations were in the order of $Al^{3+} > Th^{4+} > UO^{2+} > Ba^{2+} > Na^+$. The anomalous behaviour of thorium is perhaps due to its hydrolysis.

From the survey of literature it appears that sufficient data are available on As_2S_3 sol.[1-10] However, there is a lack of quantitative data especially in the light of some recent developments on the stability theory of lyophobic colloids. In the present work, therefore, an attempt has been made to apply the modern theory of the subsidence of lyophobic sols due to Derjaguin, Landau,[11,12]

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[1] S. S. Bhatnagar and D. L. Srivastava, *J. Phys. Chem.*, **28**, 730 (1924).

[2] S. N. Mukherjee, *Kolloid. Z.*, **53**, 159 (1930).

[3] B. N. Ghosh and N. R. Dhar, *J. Phys. Chem.*, **29**, 668 (1925).

[4] B. N. Ghosh, *J. Chem. Soc.*, **1929**, 2693.

[5] J. N. Mukherjee *et al.*, *J. Indian Chem. Soc.*, **2**, 296 (1925); **4**, 493 (1927); **5**, 735 (1928).

[6] S. S. Joshi and A. J. Rao, *ibid.*, **10**, 237, 247 (1933).

[7] B. P. Yadava and A. C. Chatterji, *ibid.*, **21**, 227 (1944).

[8] J. N. Mukherjee, S. P. Roychowdhury and S. G. Rajkumar, *ibid.*, **10**, 27 (1933).

[9] H. R. Kruyt *et al.*, *Z. Physikal. Chem.*, **130**, 170 (1927).

[10] H. Freundlich, *Z. Physik. Chem.*, **44**, 129 (1903); **73**, 385 (1910).

[11] B. Derjaguin, *Trans. Faraday Soc.*, **36**, 203, 730 (1940).

[12] B. Derjaguin and L. D. Landau, *Acta Phys. Chim. USSR*, **14**, 633 (1941).

Verwey and Overbeek[13] (D. L. V. O. theory) to the flocculation results of the hydrosol of arsenic trisulphide. The use of the three important variables namely particle radius a, surface potential ψ_0 and Debye-Hückel reciprocal length κ has been made while applying the D. L. V. O. theory in order to calculate interaction energies, stability factor and flocculating concentrations.

Theoretical

The Stability Theory and Its Application to the Present System. According to the well known theory of the stability of lyophobic colloids the stability depends upon the total energy of interaction between two colloidal particles consisting of a long range electrical repulsion and van der Waals attraction. If the resultant potential energy barrier is high enough, *viz.* $V \geqslant 15\,\boldsymbol{k}T$, the colloidal system is stable, otherwise a portion of colliding colloidal particles can surmount it, leading to flocculation. The potential energies of repulsion and attraction and the total attraction are given below.

Potential Energy of Repulsion V_R. The potential energy of repulsion between two spherical particles of radius a, electrical potential ψ_0, interparticle distance H_0 is given by a simple approximate equation (*loc. cit.*),

$$V_R = \frac{\varepsilon a \psi_0^2}{u+2} e^{-\tau u} \qquad (1)$$

which is valid only for the small value of τ, where ε is the dielectric constant of the medium, $u = H_0/a$ and $\tau = \kappa a$.

Potential Energy of Attraction V_A. The potential energy of attraction can be put into the simple form[14]

$$V_A = \frac{-A}{12u} \qquad (\text{Provided } u \ll 1) \qquad (2)$$

Here A is the van der Waals or Hamaker constant.

Total Potential Energy of Interaction V *and the Stability Ratio* W. The total energy of interaction V, for the present system where other energies can be neglected, is simply the sum of the repulsive and attractive energies. For slow flocculation, the theory is developed by Fuchs[15] who found that the effective collisions were reduced by a factor W which is termed the stability ratio. This ratio is related to the potential energy of interaction V as follows,

$$W = 2\int_2^\infty \exp \frac{1}{\boldsymbol{k}T}\left(\frac{\varepsilon a \psi_0^2}{u+2} e^{-\tau u} - \frac{A}{12u}\right) \times \frac{\mathrm{d}u}{(u+2)^2} \qquad (3)$$

Here the value of W has to be obtained by graphical integration using the plots of $\exp(V/\boldsymbol{k}T)/s^2$ against s.

An approximate equation[16] as given below may also be used for the value of stability ratio of lyophobic colloid.

$$W = \exp\,(V_{max}/\boldsymbol{k}T)/2\kappa a \qquad (4)$$

where V_{max} is the maximum in the potential energy curves.

Derjaguin (*loc. cit.*) has also described a formula for the stability of lyophobic sols as given below,

$$F = \frac{\varepsilon a \psi_0^2}{2\boldsymbol{k}T} \qquad (5)$$

in which attraction force has been neglected. Here F is the stability factor and other terms have the usual significance.

Theoretical Calculation of van der Waals Constant $\boldsymbol{A}$. To calculate London - van der Waals attraction constant A, Hamaker (*loc. cit.*) has given an equation (*cf.* Srivastava[17])

$$A = \pi^2 q^2 L \qquad (6)$$

where q is the number of atoms (molecules) in 1 ml of the substance composing the particles and L is the London constant which is calculated from the following equations.

(i) The Slater-Kirkwood[18] (S-K) equation.

$$L_{\text{S-K}} = 11.25 \times 10^{-24}\, \nu^{1/2} P^{3/2} \qquad (7)$$

(ii) The Slater-Kirkwood equation modified by Moelwyn-Hughes[19] (S–K–M)

$$L_{\text{S-K-M}} = 7.8 \times 10^{-24}\, \nu P^{3/2} \qquad (8)$$

(iii) Neugebauer[20] (N) equation

$$L_{\text{N}} = -1.62 \times 10^{-6}\, \kappa P \qquad (9)$$

where ν is the number of valency electrons in the outer shell, P is the polarizability and κ is the diamagnetic susceptibility. Polarizability is calculated from the classical Clausius-Mosotti equation.

However, the value of A obtained from Eq. (6) is for the interaction between two As_2S_3 solid particles in vacuum. Therefore, to calculate the interaction between As_2S_3 solid particles in water a correction has been made and interaction was calculated from the expression (*loc. cit.*)

$$A = (A^{1/2}{}_{\text{As}_2\text{S}_3\text{-As}_2\text{S}_3} - A^{1/2}{}_{\text{H}_2\text{O-H}_2\text{O}})^2 \qquad (10)$$

Experimental Procedure

Materials. All the chemicals were of B. D. H. Analar grade. All glassware was of Pyrex and was thoroughly cleaned before use. Ordinary distilled

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[13] E. J. W. Verwey and J. Th. G. Overbeek, "Theory of Stability of Lyophobic Colloids," Elsevier Publishing Co., Amsterdam (1948).

[14] H. C. Hamaker, *Physica*, **4**, 1058 (1937).

[15] N. Fuchs, *Z. Physik.*, **89**, 736 (1934).

[16] H. R. Kruyt, "Colloid Science," Vol. I, Elsevier, Amsterdam (1952), p. 285.

[17] S. N. Srivastava, *Indian J. Chem.*, **3**, 376 (1965).

[18] J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, **37**, 682 (1931).

[19] E. A. Moelwyn-Hughes, "Physical Chemistry," Pergamon Press, London (1957), p. 383.

[20] Th. Neugebauer, *Z. Physik.*, **107**, 785 (1937).

water redistilled from an all Pyrex apparatus and having the specific conductance $\approx 1\times10^{-6}$ ohm^{-1}cm^{-1} was used for all experimental work.

Preparation of the As_2S_3 Sol. To prepare the arsenic trisulphide sol a very slow stream of hydrogen sulphide gas was bubbled through 250 m*l* redistilled water in which 250 m*l* aqueous solution 0.4% arsenic trioxide was added dropwise. The speed of the drops and stream of hydrogen sulphide were adjusted in such a manner that the addition of each drop of aqueous solution of arsenic trioxide was followed by 3—4 bubbles of H_2S gas. The excess of H_2S gas was then removed by passing a current of purified hydrogen gas till the H_2S gas completely removed. The light yellow sol of As_2S_3 so obtained was then dialysed in a parchment paper bag against slow running distilled water for one and a half day. The conductance of the As_2S_3 sol thus obtained was 3.2×10^{-5} ohm^{-1} cm^{-1}.

Electrophoretic Mobility Measurements. The mobility measurements were made by moving boundary method. To measure the elcctrophoretic mobility of the sol, the experiments were carried out in a modified apparatus[21] of Burton tube fitted with two wide side tubes. Constant current was supplied to the platinum foil electrodes in wide tubes and the potential drop across the two Pt electrodes in U-tube was measured with a vacuum tube voltmeter. Measurements were made at sharp descending boundary between the colloidal solution and an equiconducting aqueous solution of acetic acid.

The zeta potential was calculated by the Overbeek[22,23] formulae for symmetrical and unsymmetrical electrolytes from the following equations (*cf.* Hückel[24])

$$U=\frac{\varepsilon\zeta}{6\pi\eta}\left[f_1(\kappa a)-v^2\left(\frac{e\zeta}{\boldsymbol{k}T}\right)^2 f_3(\kappa a)\right.$$
$$\left.-\frac{\rho_+ + \rho_-}{2e}\cdot\frac{\varepsilon\boldsymbol{k}T}{6\pi\eta e}\left(\frac{e\zeta}{\boldsymbol{k}T}\right)^2 f_4(\kappa a)\right] \qquad (11)$$

$$U=\frac{\varepsilon\zeta}{6\pi\eta}\left[f_1(\kappa a)-(v_- - v_+)\left(\frac{e\zeta}{\boldsymbol{k}T}\right)f_2(\kappa a)\right.$$
$$\left.-\frac{\rho_+ v_+ - \rho_- v_-}{(v_+ + v_-)e}\cdot\frac{\varepsilon\boldsymbol{k}T}{6\pi\eta e}\left(\frac{e\zeta}{\boldsymbol{k}T}\right)^2 f_4(\kappa a)\right] \qquad (12)$$

Here $f_1(\kappa a)$ is identical with the Henry function and the $f_2(\kappa a)$, $f_3(\kappa a)$ and $f_4(\kappa a)$ have been tabulated by Overbeek.[23] v_+ and v_- are the valencies of the cations and anions respectively. ρ_+ and ρ_- are the frictional constant of the cations and anions respectively of the used electrolyte. Other terms have their usual meaning.

Electron Microscopic Size of the Colloidal As_2S_3 Particles. A Sample of the colloidal solution under investigation was diluted 10 times. A specimen for electron microscopy 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 thin film of collodion. The electron photograph was taken on Siemens Elmiskop I electron microscope at 100kV (due to courtesy of Dr. K. Bahadur, Officer in-charge of electron microscopy Division, Defence Science Laboratory, Delhi).

Results and Discussion

Size of the Particles of As_2S_3 Sol. A typical electron micrograph of As_2S_3 sol particles is given in Fig. 1 and the particles size distribution curve obtained from this is given in Fig. 2. The mean particle radius was found to be 45 Å.

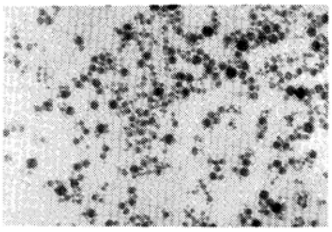

Fig. 1. Electron micrograph of negative As_2S_3 sol under the magnification of 1.2×10^5.

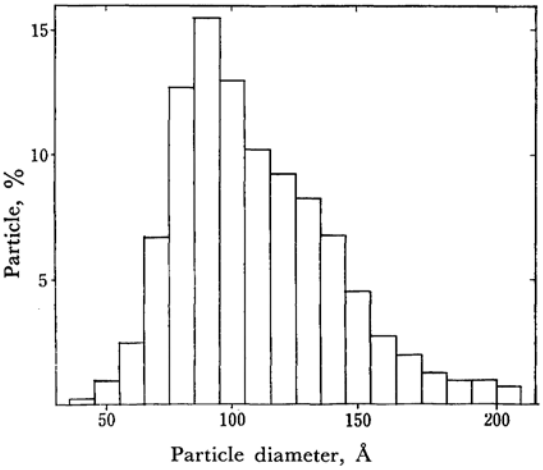

Fig. 2. Particle size distribution of negative arsenic trisulphide sol.
Number of particles counted = 400
Mean diameter of the particles = 90 Å

The Zeta Potentials. The concentration and pH of the 50% diluted sol were 1.2×10^{-3} g/m*l* and 4.0 ± 0.05. The experimental value obtained for the mobility of the above arsenic trisulphide sol was 5.4 (μ/sec)/(V/cm) at 26°C. The zeta potential calculated from this value was 102.6 mV.

The mobility and zeta potential of As_2S_3 sol particles as a function of log molar concentration of different electrolytes are given in Figs. 3 and 4 respectively. In general, it is seen that the mobility and the zeta potential decrease as the concentration of electrolytes increases. With NaCl the fall of the zeta potential is almost linear throughout but with $BaCl_2$, $UO_2(NO_3)_2$, $AlCl_3$ and $Th(NO_3)_4$, it is comparatively slow in the initial stages and then becomes sharp. The minimum zeta potential that could be conveniently measured was about 60 mV below which there was visible flocculation of the sol particles.

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[21] P. D. Bhatnagar and A. K. Bhattacharya, *Koll. Zeit.*, **170**, 29 (1960).
[22] J. Th. G. Overbeek, *Koll. Beheifte*, **54**, 287 (1943).
[23] J. Th. G. Overbeek, "Advances in Colloid Science," Vol. III, Elsvier, London (1950), p. 115.
[24] E. Hückel, *Physik. Z.*, **25**, 204 (1924).

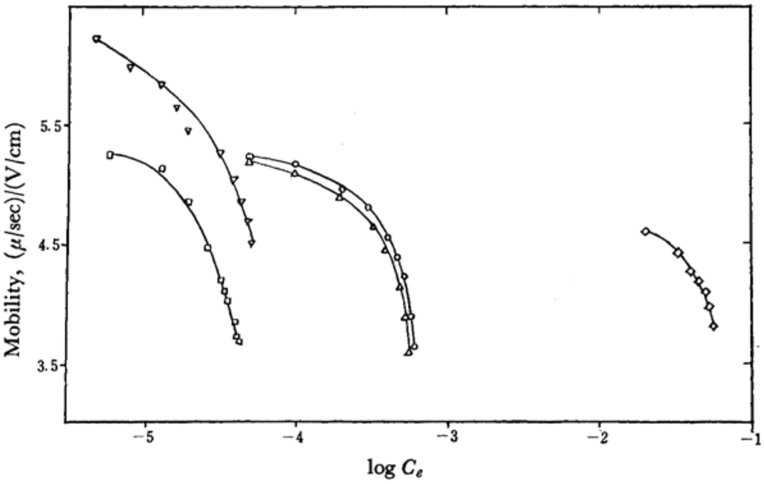

Fig. 3. Mobility *versus* log C_e (C_e=molar concentration of electrolyte) curves.
◇ NaCl; ○ $BaCl_2$; △ $UO_2(NO_3)_2$; □ $AlCl_3$; ▽ $Th(NO_3)_4$

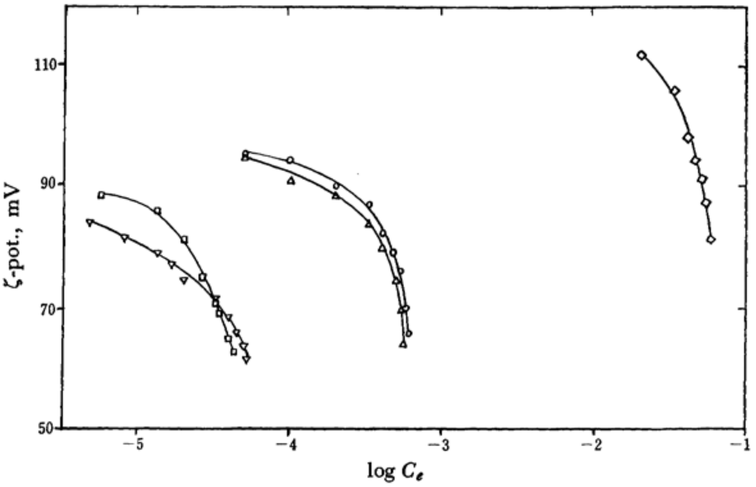

Fig. 4. Zeta potential against log C_e curves.
◇ NaCl; ○ $BaCl_2$; △ $UO_2(NO_3)_2$; □ $AlCl_3$; ▽ $Th(NO_3)_4$

Calculation of van der Waals Constant. The value of the London constant is required to calculate van der Waals constant which was calculated using the susceptibility of one gram formula wt.[25)] $=-7.00\times10^{-5}$, $\nu=28$ and $P=2.16\times10^{-23}$ (calculated from Clausius-Mosotti equation using refractive index data of As_2S_3.[26)] With the proper choice of units the London constant, calculated from Eqs. (7), (8) and (9) are as follows

$$L_{\text{S-K}}^{As_2S_3}=6.0\times10^{-57}\ \text{erg cm}^6$$

$$L_{\text{S-K-M}}^{As_2S_3}=22.02\times10^{-57}\ \text{erg cm}^6$$

and

$$L_{\text{N}}^{As_2S_3}=4.08\times10^{-57}\ \text{erg cm}^6$$

Now the use of Eq. (6) permits the calculation of van der Waals constant for As_2S_3 from each of the three equations by finding $q(=8.4\times10^{21})$ and density (=3.43). Similarly, the corresponding constant for water is given by Verwey and Overbeek (*loc. cit.*) (see also Watillon[27)]) and hence the net attraction constant of As_2S_3 particles in water can be estimated from Eq. (10). The results are summarized in Table 1.

It is found that the value of the van der Waals constant calculated from S-K-M formula yields comparatively high value. Therefore, in the

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25) "Handbook of Chem. and Phys.," 43rd ed. Chemical Rubber Publishing Co. (1961—1962), p. 2683.

26) "International Critical Tables," Vol. I, p. 174.

27) A. Watillon and A. M. Joseph-Petit, "Proceedings, Third International Congress on Surface Activity," Butterworths Scientific Publication (London), **1**, 145 (1960).

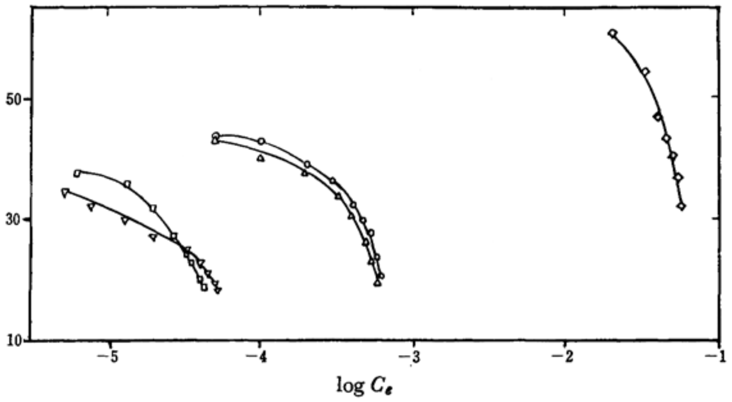

Fig. 5. *F versus* log C_e.
◇ NaCl; ○ $BaCl_2$; △ $UO_2(NO_3)_2$; □ $AlCl_3$; ▽ $Th(NO_3)_4$

TABLE 1. VALUE OF THE VAN DER WAALS CONSTANT CALCULATED FROM DIFFERENT EQUATIONS USING $M=246.1$, $P=2.16\times10^{-23}$ m*l*/mol, $q=8.4\times10^{21}$

Equation used	$A_{As_2S_3\text{-}As_2S_3}$ $\times10^{12}$ erg in vacuum	$A_{H_2O\text{-}H_2O}$ $\times10^{13}$ erg in vacuum	$A\times10^{12}$ erg As_2S_3 in water
S-K	4.18	5.95	1.62
S-K-M	15.32	7.70	9.23
N	2.84	5.61	0.87

present calculations, the value of $A_{S\text{-}K\text{-}M}$ has been neglected and for further calculations the mean value of the remaining two ($=1.25\times10^{-12}$ erg) formulae has been used.

An Estimate of the Stability Factor *F*, from the Derjaguin Equation. The stability of the colloid has been first estimated by Derjaguin's Eq. (5) and results have been depicted in Fig. 5. 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 45 min after preparation. This is inconsistent with the Derjaguin theory. In the application of Derjaguin's Eq. (5) only one approximation ($\psi_0\approx\zeta$) is used which is not expected to effect the results so much. Therefore, the reason for this discrepancy seems to be in the neglect of the van der Waals attraction forces and Debye-Hückel parameter which also play an important part in the stability as discussed before.

Potential Energy. In Fig. 6, Curves I, II and III show the repulsive energy V_R, attractive energy V_A and net potential energy of interaction $V(=V_R+V_A)$ of the As_2S_3 sol corresponding to zeta potential=102.6 mV. This has an energy maximum, $V_{max}=33.4\,\boldsymbol{k}T$ (using van der Waals constant $A=1.25\times10^{-12}$ erg) which is a sufficiently high value to show that the sol is stable.

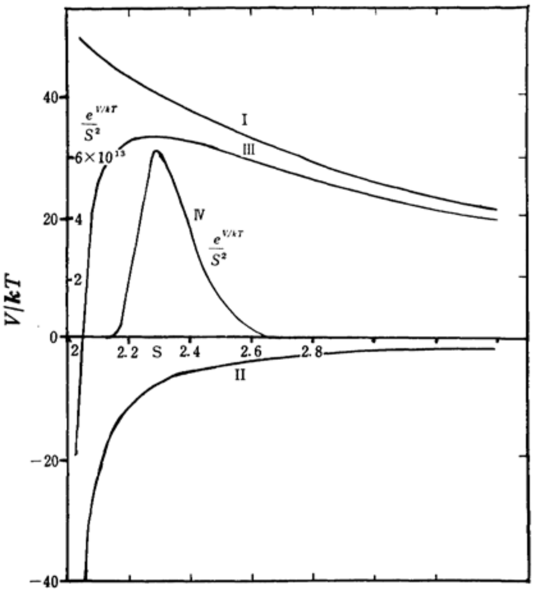

Fig. 6. Curves of potential energy of (I) repulsion, (II) attraction (III) interaction and (IV) of the quantity $\exp(V/\boldsymbol{k}T)/s^2$ *versus* *s* for the values of $a=45$ Å, $\kappa=4.52\times10^5$ cm^{-1}, $A=1.25\times10^{-12}$ erg and $\zeta=(\psi_0)=102.6$ mV of 50% diluted As_2S_3 sol.

Potential energy curves of colloidal particles as a function of distances between their surfaces are shown in Figs. 7—10 respectively in the presence of NaCl, $UO_2(NO_3)_2$, $AlCl_3$ and $Th(NO_3)_4$ which are in good agreement with theoretical prediction. The value of V_{max} in each case shows the range of slow flocculation till V_{max} decreases to a sufficiently low value which is the threshold of rapid coagulation. In Fig. 8 a dotted curve without relaxation correction to zeta potential=98.8 mV (after correction zeta potential=95 mV) has also been given. This gives an idea of the magnitude of error likely to be introduced if relaxation is not taken into account.

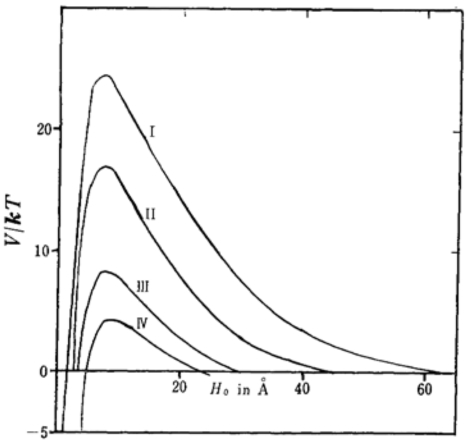

Fig. 7. Curves for potential energy of interaction (V), in the presence of NaCl against H_0.

Curve I	for zeta pot. = 112.0 mV
Curve II	for zeta pot. = 106.0 mV
Curve III	for zeta pot. = 94.5 mV
Curve IV	for zeta pot. = 87.4 mV

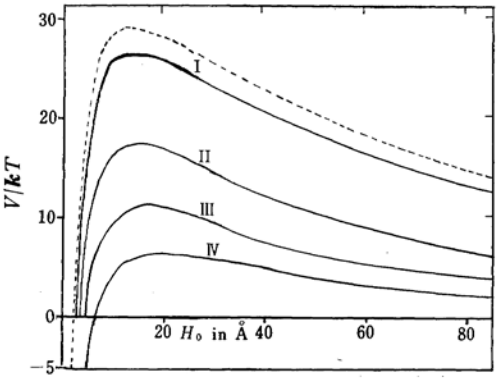

Fig. 8. Curves for potential energy of interaction (V), in the presence of $UO_2(NO_3)_2$ against H_0.

Curve I	for zeta pot. = 95.0 mV
Curve II	for zeta pot. = 84.3 mV
Curve III	for zeta pot. = 74.4 mV
Curve IV	for zeta pot. = 64.0 mV
Curve dotted	for zeta pot. = 98.8 mV

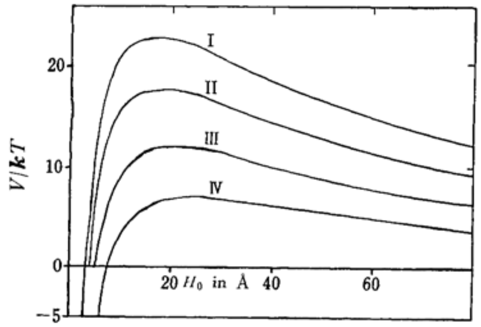

Fig. 9. Curves for potential energy of interaction (V), in the presence of $AlCl_3$ against H_0.

Curve I	for zeta pot. = 88.7 mV
Curve II	for zeta pot. = 81.5 mV
Curve III	for zeta pot. = 71.0 mV
Curve IV	for zeta pot. = 62.8 mV

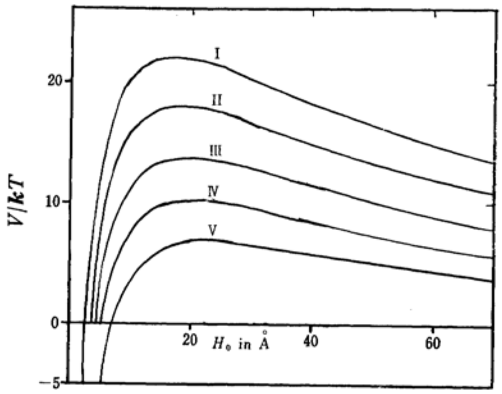

Fig. 10. Curves for potential energy of interaction (V), in the presence of $Th(NO_3)_4$ against H_0.

Curve I	for zeta pot. = 87.2 mV
Curve II	for zeta pot. = 81.5 mV
Curve III	for zeta pot. = 74.7 mV
Curve IV	for zeta pot. = 68.6 mV
Curve V	for zeta pot. = 61.3 mV

Stability Factor *W*. Stability factor was calculated by graphical integration of Eq. (3), as well as from an approximate Eq. (4) and the results are reported in Table 2. In Fig. 6 a typical Curve IV of $\exp(V/kT)/s^2$ *versus* s has been shown to calculate the stability ratio in the absence of electrolytes, where $W = 2.63 \times 10^{13}$, while the value of W calculated from approximate Eq. (4) is 7.4×10^{14}. In Figs. 11 and 12, the curves for log W against log C_e are given for varying concentration of the electrolytes which are of the similar shapes and the slope in the lower part of the slow coagulation range is also almost in the same range. It is found that the values of W obtained from the method of approximate equation are higher than those calculated from graphical integration. The values of the stability ratio in the zone of slow coagulation are comparable with those obtained by Ottewill and co-workers[28,29] on AgI and arachidic acid systems. The general shape of the log W *versus* zeta potential curves given in Fig. 13 is in keeping with the theory. It is obvious from the curves that higher the value of τ higher is the zeta potential at which flocculation can occur.

To calculate the coagulation concentration of various salts which are used to coagulate As_2S_3 sol the extrapolation of the linear portion of log W against log C_e curve was made to log C_e axis (*loc.*

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[28] R. H. Ottewill and A. Watanabe, *Koll. Zeit.*, **170**, 38 (1960); **173**, 122 (1960).

[29] R. H. Ottewill and D. J. Wilkins, *Trans. Faarday Soc.*, **170**, 132 (1960); **58**, 608 (1962); III Inter. Cong. Surf. Act. Cologne, **11**, 653 (1960).

TABLE 2. DATA OF STABILITY RATIO W FOR As_2S_3 SOL ($W=2.63\times10^{13}$)

Cation	Concentration mol/l	Zeta potential in mV	W from graphical integration	W from approximate Eq. (4)
Na^+	2.00×10^{-2}	112.0	1.38×10^{9}	9.84×10^{9}
	3.33×10^{-2}	106.0	1.61×10^{6}	4.45×10^{6}
	4.00×10^{-2}	98.4	3.22×10^{3}	1.36×10^{4}
	4.50×10^{-2}	94.5	1.63×10^{2}	5.64×10^{2}
	5.00×10^{-2}	91.5	3.04×10	1.00×10^{2}
	5.33×10^{-2}	87.4	3.80	1.13×10
	5.66×10^{-2}	81.3	0.46	1.01
Ba^{2+}	5.00×10^{-5}	95.4	3.50×10^{10}	7.20×10^{11}
	1.00×10^{-4}	94.5	—	—
	2.00×10^{-4}	90.3	5.65×10^{8}	3.18×10^{9}
	3.00×10^{-4}	87.3	1.80×10^{7}	2.23×10^{8}
	4.00×10^{-4}	82.3	6.96×10^{5}	6.59×10^{6}
	4.66×10^{-4}	79.2	9.60×10^{4}	8.31×10^{5}
	5.33×10^{-4}	76.2	1.56×10^{3}	1.30×10^{4}
	5.66×10^{-4}	70.0	8.80×10^{2}	6.28×10^{3}
	6.00×10^{-4}	65.8	1.61×10^{2}	9.15×10^{2}
UO_2^{2+}	5.00×10^{-5}	95.0	2.38×10^{10}	5.09×10^{11}
	1.00×10^{-4}	91.1	1.08×10^{9}	2.11×10^{10}
	2.00×10^{-4}	89.1	6.10×10^{7}	8.66×10^{8}
	3.33×10^{-4}	84.3	3.03×10^{6}	3.87×10^{7}
	4.00×10^{-4}	80.2	2.12×10^{5}	2.09×10^{6}
	5.00×10^{-4}	74.4	7.95×10^{3}	6.31×10^{4}
	5.50×10^{-4}	69.8	9.05×10^{2}	5.76×10^{3}
	5.70×10^{-4}	64.0	9.30×10	5.69×10^{2}
Al^{3+}	6.00×10^{-6}	88.7	8.50×10^{8}	1.98×10^{10}
	1.33×10^{-5}	86.3	1.33×10^{8}	2.85×10^{9}
	2.00×10^{-5}	81.5	6.25×10^{5}	1.14×10^{8}
	2.66×10^{-5}	75.1	1.57×10^{5}	2.52×10^{6}
	3.33×10^{-5}	71.0	1.92×10^{4}	2.65×10^{5}
	3.50×10^{-5}	69.2	7.65×10^{3}	1.00×10^{5}
	4.00×10^{-5}	65.0	1.18×10^{3}	1.32×10^{4}
	4.33×10^{-5}	62.8	1.92×10^{2}	1.93×10^{3}
Th^{4+}	1.00×10^{-6}	87.2	3.70×10^{8}	9.43×10^{9}
	8.33×10^{-6}	81.5	7.25×10^{6}	1.48×10^{7}
	1.33×10^{-5}	78.8	1.29×10^{6}	2.24×10^{7}
	2.00×10^{-5}	74.7	1.17×10^{5}	1.68×10^{6}
	3.33×10^{-5}	71.7	1.46×10^{4}	2.17×10^{5}
	4.00×10^{-5}	68.6	3.98×10^{3}	4.10×10^{4}
	4.50×10^{-5}	66.0	1.13×10^{3}	1.19×10^{4}
	5.00×10^{-5}	63.6	4.10×10^{2}	3.53×10^{3}
	5.20×10^{-5}	61.3	1.82×10^{2}	1.25×10^{3}

TABLE 3. COAGULATION DATA FOR As_2S_3 SOL

Electrolyte	Coagulation concentration, mol/l		$-\mathrm{d}\log W/\mathrm{d}\log C_e$	
	For W from Eq. (4)	For W from graphical integration	For W from Eq. (4)	For W from graphical integration
NaCl	5.8×10^{-2}	5.7×10^{-2}	15.1	21.9
$BaCl_2$	7.0×10^{-4}	7.0×10^{-4}	42.6	32.4
$UO_2(NO_3)_2$	6.6×10^{-4}	6.4×10^{-4}	38.8	35.5
$AlCl_3$	6.3×10^{-5}	5.7×10^{-5}	19.8	18.00
$Th(NO_3)_4$	8.5×10^{-5}	7.5×10^{-5}	11.5	14.1

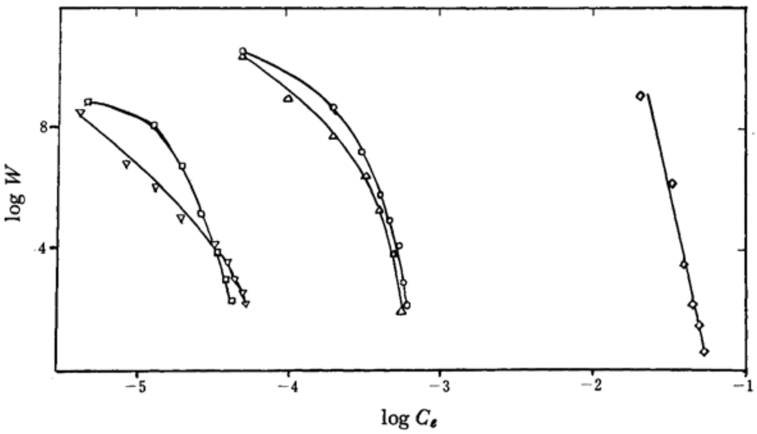

Fig. 11. log W *versus* log C_e curves (W from graphical integration).
◇ NaCl; ○ $BaCl_2$; △ $UO_2(NO_3)_2$; □ $AlCl_3$ ▽ $Th(NO_3)_4$

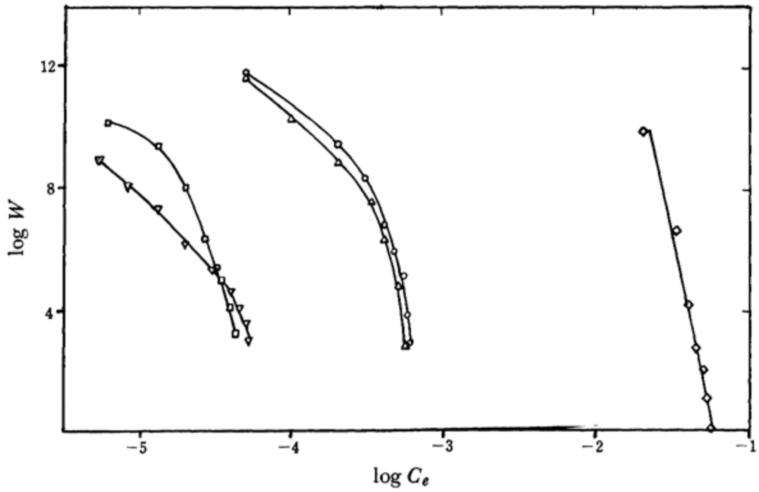

Fig. 12. log W *versus* log C_e curves (W from approximate equation).
◇ NaCl; ○ $BaCl_2$; △ $UO_2(NO_3)_2$; □ $AlCl_3$; ▽ $Th(NO_3)_4$

cit.) where log $W=0$ assuming the validity of the equation[30,31]

$$\log W = K_1 - K_2 \log C_e$$

The values obtained in this manner are given in Table 3. Comparison of the coagulation data given in Table 3 shows that the coagulating concentration is slightly higher in the case when the results were calculated by approximate Eq. (4) than for the results calculated by graphical integration. To confirm the flocculating concentrations so obtained, the turbidity work was carried out.[32]

From the view point of the Schulze-Hardy rule the flocculating concentrations of mono, bi, tri and tetra valent ions would be expected to be

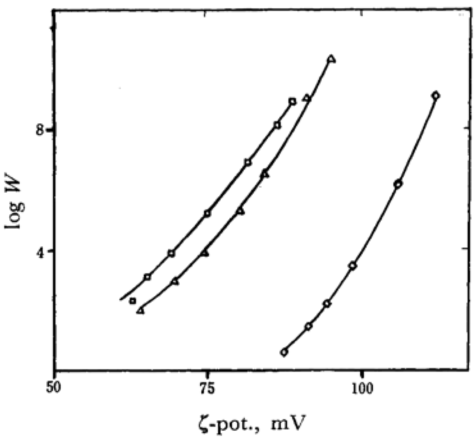

Fig. 13. log W against zeta potential (W from graphical integration).
◇ NaCl; △ $UO_2(NO_3)_2$; □ $AlCl_3$

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in the ratio of 100 : 1.6 : 0.13 : 0.024 taking the monovalent ion as 100. Experimentally the ratio for Na^+, UO_2^{2+}, Ba^{2+}, Al^{3+} and Th^{4+} was found to be 100 : 1.12 : 1.23 : 0.100 : 0.311 taking Na^+ ions as 100. Thus a marked deviation from the Schulze-Hardy rule occurs particularly with thorium. It appears that the thorium ion present in the pH ranges about 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-workers[37] 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.

It may be concluded that the D. L. V. O. theory seems to apply reasonably well to the present system for small spherical colloidal particles and high zeta potentials as it gives a satisfactory interpretation of the interactions between As_2S_3 sol particles.

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