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Mechanism of Emulsification with Special Reference to Solid Stabilized Emulsions

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Mechanism of emulsification with special reference to ferric hydroxide as emulsifier has been studied. The sol of ferric hydroxide having maximum possible stability has been prepared. Its particle size as determined by electron microscope is of 63 Å radius. The stability of the sol in presence of different amounts of electrolytes of different valencies has been studied by measuring its zeta potentials in terms of interaction energy curves. By using these different stages of partially flocculated ferric hydroxide sol as emulsifier the emulsions of toluene in water were prepared and their relative stabilities assessed by adding various electrolytes. Then the stability of the emulsions formed has been studied by the measurement of zeta potentials micro-electrophoretically in the light of the D.V.O. theory. The size of the emulsion globules as determined microphotographically is 1.1μ radius. The pH and interfacial tension measurements have also been carried out. From interfacial tensions between the disperse phase and the dispersion medium at different amounts of electrolytes, the surface charge of the emulsions has been deduced which is found to be in good agreement with the electrophoretic results. Finally a correlation has been sought between the stability of the emulsions and the corresponding partially flocculated sols used in emulsification.

A few workers[1–4] have used insoluble inorganic precipitates such as calcium and barium carbonates, basic sulphates, oxychlorides, hydrous oxide and hydroxides of various metals as emulsifiers. Pickering[5] was first to use such substances as emulsifiers for oil in water type of emulsions and was able to conclude that the size of the oil globules depends on the size of the powder. An analogous behaviour was also observed by Bechhold, Dede and Reiner[6] who concluded that smaller the grains the better is the emulsion until an optimum is reached after which smaller grains have less effect. Briggs[7] found that oil in water type emulsions could not be stabilized with colloidal ferric hydroxide or arsenious sulphide but can be obtained by the addition of some weak flocculating agents. However, emulsification was not possible by the completely flocculated sol. A similar effect was also noticed by Van der Waarden[8] for emulsions of water in mineral oil which could only be stabilized by asphaltenes if the asphaltenes were near or above the point of incipient flocculation.

In the literature the theories of stabilization of the emulsions by the solid particles generally deal with the effect of wetting and with the contact angle. Therefore, in the present work it is proposed to explain the mechanism of emulsification and subsequent stabilization on the basis of energy considerations.

Materials and Preparations

The ferric chloride and ammonium carbonate for the preparation of sol were of Analar Grade obtained from B.D.H. For the preparation of emulsion the oil phase toluene was of B.D.H. Analar Grade, which was weighted by bromoform obtained from Rhome-Poulene, France and was distilled and the fraction of 148—149°C were collected. All the other chemicals used were of B.D.H. or E. Merck (Analar Grade) and used as such. The glass apparatus used was all pyrex and the water was twice distilled.

The ferric hydroxide sol was prepared by adding concentrated ammonium carbonate solution to a solution of ferric chloride with constant stirring until the precipitate just ceased to dissolve. The precipitated ferric hydroxide was then dissolved by adding just the sufficient quantity of concentrated ferric chloride solution. The sol was then dialysed in a parchment paper bag against running distilled water, until maximum stability obtained.

The concentration of the sol was 0.002 g/m*l* of ferric hydroxide. To this sol were then added different

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[1] T. R. Briggs and H. F. Schimdt, *J. Phys. Chem.*, **19**, 484 (1915).

[2] A. U. M. Schlaepfer, *J. Chem. Soc.*, **113**, 522 (1918); *Kolloid Z.*, **81**, 184 (1937).

[3] S. N. Srivastava and L. N. Mukherjee, *Kolloid Z.*, **147**, 146 (1956).

[4] F. R. Newman, *J. Phys. Chem.*, **18**, 34 (1914).

[5] S. U. Pickering, *J. Chem. Soc.*, **91**, 2001 (1907).

[6] H. Bechhold, L. Dede and L. Reiner, *Kolloid Z.*, **28**, 6 (1921).

[7] T. R. Briggs, *Ind. Eng. Chem.*, **13**, 1008 (1921).

[8] M. Van der Waarden, *Kolloid Z.*, **156**, 116 (1958).

amounts of electrolytes so as to bring about partial flocculation. Then 5 m*l* of toluene were dispersed per 100 m*l* of the partially flocculated sol, the dispersion medium. The emulsions were first well hand shaken and then homogenized well in a hand operated stainless steel homogenizer (C.W. Logenman Co., U.S.A.). The sampling was done under identical conditions.

Experimental and Theoretical

The Sol. The size of the sol particles was determined by taking the photographs (Fig. 1) by the electron microscope using 19400 x times magnification. The size of 400 particles was then measured with the help of a Cathetometer and a size frequency curve was plotted as shown in Fig. 2. The average radius was found to be 63 Å.

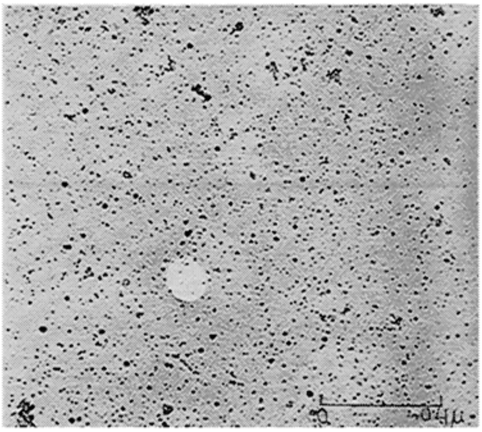

Fig. 1. Electron micrograph of $Fe(OH)_3$ sol × 77600.

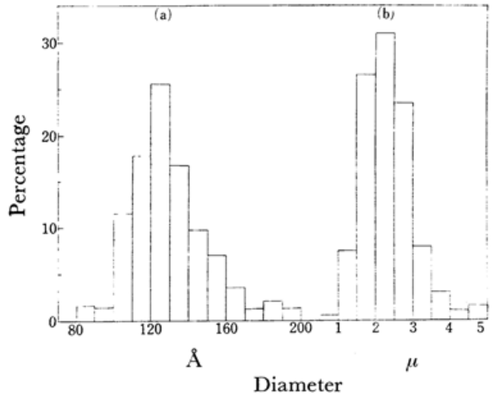

Fig. 2. Size-distribution curves.
Percentage of particles *vs.* diameter
(a) For $Fe(OH)_3$ sol (b) For Emulsion

The electrophoretic mobility of sol particles was measured by a modified form of the Burton tube method. The equiconducting solution of lithium chloride in the outer electrode vessel was used to prepare a sharp boundary, a constant current was supplied to the electrodes and the voltage across the two ends of the U tube was read off by the potentiovacuum tube voltmeter. The movement of the sol boundary per second under the applied potential gradient was measured by the Cathetometer and the electrokinetic potential ζ was calculated by the Hückel[9] equation. The correction for relaxation and the Henry effect were made using following equations given by Overbeek.[10]
For symmetrical electrolytes.

$$U=\frac{\varepsilon\zeta E}{6\pi\eta}\left[f_1(\kappa a)-Z^2\left(\frac{e\zeta}{kT}\right)^2 f_3(\kappa a)-\frac{\rho_+ + \rho_-}{2e}\,\frac{\varepsilon kT}{6\pi\eta e}\left(\frac{e\zeta}{kT}\right)^2 f_4(\kappa a)\right] \tag{1}$$

and for unsymmetrical electrolytes.

$$U=\frac{\varepsilon\zeta E}{6\pi\eta}\left[f_1(\kappa a)-(Z_+ - Z_-)\frac{e\zeta}{kT}f_2(\kappa a)-\frac{Z_+\rho_+ + Z_-\rho_-}{(Z_+ + Z_-)e}\,\frac{\varepsilon kT}{6\pi\eta e}\left(\frac{e\zeta}{kT}\right)^2 f_4(\kappa a)\right. \tag{2}$$

where U is the mobility per second per unit potential gradient, ε the dielectric constant (taken to be equal to the bulk phase *i. e.* for water at 25°C), η the viscosity of the medium, Z_+ and Z_- are the valencies, and ρ_+ and ρ_- the frictional constants of the cations and anions respectively, and f_1 is identical with the Henry function, f_2, f_3 and f_4 are the functions dependent on the values of κa which were noted from the tables.[11]

The interactions between the colloidal particles of lyophobic systems have been quantitatively treated by Derjaguin,[12] Verwey and Overbeek[13] (D.V.O. theory). On the basis of the free energy of the double layer and the London - Van der Waals' dispersion forces. According to their theory the net force on mutual approach of the particles is a resultant (V) of an attraction V_A and a repulsion V_R which increases differently as the distance apart decreases. The double layer repulsion V_R for the present system has been calculated from an approximate equation given by

$$V_R=\frac{\varepsilon a \Psi_0{}^2}{(U+2)}\,e^{-\tau U}\ \text{(for small values of } \tau\text{)} \tag{3}$$

where ψ_0 is the surface potential (assumed to be eual to the electrokinetic potential for the present system), $U=H_0/a$ and $\tau=\kappa a$ and a the particle

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[9] E. Hückel, *Z. Physik*, **25**, 204 (1924).

[10] J. Th. G. Overbeek, *Kolloid Beihefte*, **54**, 287 (1943).

[11] J. Th. G. Overbeek, "Advances in colloid sciences," Vol. III, Interscience, London (1950), p. 115.

[12] B. Derjaguin, *Trans. Faraday Soc.*, **36**, 203, 730 (1940); *J. Expt. Theor. Phys., USSR.*, **11**, 802 (1941); B. Derjaguin and L. B. Landau, *Acta Physico-Chim.*, **14**, 633 (1941).

[13] E. J. W. Verwey and J. Th. G. Overbeek, "Theory of Stability of Lyopyobic Colloids," N. Y. Elsevier, Amsterdam (1948).

radius, H the interparticle distance and κ is the Debye-Hückel parameter. The attraction energy is calculated from the following equation.[14]

$$V_A = -\frac{Aa}{12H} \tag{4}$$

Therefore, the total interaction energies of the lyophobic systems showing the nature of flocculation and the stability can be determined by the following equation.

$$V = \frac{\varepsilon a \Psi_0^2}{(U+2)} e^{-\tau U} - \frac{Aa}{12H} \tag{5}$$

The Emulsion. The size-frequency curve of emulsion was drawn by taking the photograph (Fig. 3) microphotographically with a Olympus Camera attached with a Olympus microscope. The radius of about 400 particles was measured by the Cathetometer and the average radius for all the emulsions was found to be 1.12μ (Fig. 2).

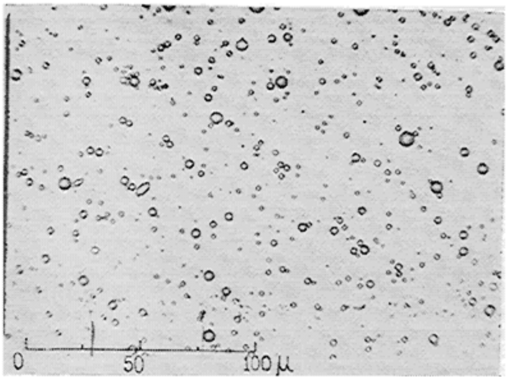

Fig. 3. Microphotograph of emulsion × 600.

The electrophoretic mobility of the emulsions was determined by microelectrophoresis apparatus. The micro-electrophoresis cell used in the apparatus was of Northrup and Kunitz type, fitted in a special design apparatus and was set in a air conditioned room. The diluted emulsion was filled in the cell and the electrode vessels were filled with equiconducting potassium chloride solution to avoid diffusion. A constant d. c. voltage was applied between the two electrodes (Ag-AgCl) and the current was measured by the microammeter. From the velocity of the particles measured under the applied voltage the mobility U was calculated by the relation.

$$U = \frac{dSA}{it} \tag{6}$$

where d is the distance travelled by the particle in a time t under the influence of current i, S the specific conductance of the emulsion and A is the area of the cell.

From a knowledge of the mobility electrokinetic potential ζ can be calculated by the following equation due to Helmholtz and Smoluchowski, which is applicable to the case for spherical particles and $\kappa a \gg 1$.

$$\zeta = \frac{4\pi\eta}{\varepsilon} U \tag{7}$$

The total interaction energy between the two diffuse double layers of the emulsion globules is the summation of repulsive and attractive energies, where the repulsion energy can be calculated by the approximate equation given by Derjaguin and Kussakov.[15]

$$V_R = \frac{\varepsilon a \Psi_0^2}{2} \ln(1 + e^{-\kappa H_0}) \tag{8}$$

and the attraction energy has been calculated from the following approximate equation.[16]

$$V_A = -\frac{Aa}{12H}\left\{\frac{\lambda}{\lambda + 3.54 H\pi}\right\} \quad \text{for } H < 150\,\text{Å} \tag{9a}$$

$$V_A = -\frac{Aa}{\pi}\left\{\frac{2.45}{120 H^2}\cdot\lambda - \frac{\lambda^2}{1045 H^3} + \frac{\lambda^3}{5.62\times 10^4 \cdot H^4}\right\} \quad \text{for } H > 150\,\text{Å} \tag{9b}$$

where λ is the wavelength of the London frequency (approximately equal to 10^{-5} cm) and A is the Van der Waals constant of the droplet.

Calculation of Surface Charge from Interfacial Tension. The Gibbs adsorption isotherm is

$$-\mathrm{d}\gamma = \Gamma_S \boldsymbol{RT} \mathrm{d} \ln C_S \tag{10}$$

This permits the determination of the surface excess Γ_S of the adsorbed ions from a knowledge of change in interfacial tension γ with the concentration of the adsorbed ions C_S. The surface charge of the particle is given by the following equation.

$$\sigma = eV\Gamma_S \tag{11}$$

If no excess of electrolytes is present, Γ_S will not correspond exactly with ρ/ve, because there is a deficiency of same charge ions in the diffuse part of the double layer, though this deficiency is only a few percent of ρ.

The fraction of the counter ions present in the Stern layer can be represented by the following equation by the application of the Langmuir-Stern equation.[17]

$$\frac{\sigma_1}{eV} = \frac{N_1}{1 + \frac{N}{n} e^{(ve\psi_0/kT)}} \tag{12}$$

where N_1 is the number of available positions in 1 cm^2 of the Stern layer (here assumed to be equal to 1×10^{15}), N is the number of positions available

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

[15] B. Derjaguin and M. Kussakov, *Acta Phys. Chim.*, **10**, 25, 155 (1939).

[16] J. N. Schenkel and J. A. Kitchener, *Trans. Faraday Soc.*, **56**, 161 (1960).

[17] H. R. Kruyt, "Colloid Science," Vol. I, N. Y. Elsevier, Amsterdam (1952), pp. 130, 133.

to the counter ions in 1 cm^3 of the homogeneous solution (which is to be equal to $6.02\times10^{23}/18$), n is the number of counter ions of valency V in 1 cm^3 of the homogeneous solution, e is the elementary charge and ψ_0 is the potential in the Stern layer with respect to a point in the aqueous phase far from the interface.

The diffuse part of the double layer has a charge σ_2 which is related to the potential at the boundary between the Stern and the Gouy Layers ψ_0 by the equation

$$\sigma_2=\left(\sqrt{\frac{\varepsilon kT}{\pi}\sum nv^2}\right)\sinh\left(\frac{ve\psi_0}{2kT}\right) \tag{13}$$

From the condition of electrical neutrality the total charge σ is

$$\sigma=\sigma_1+\sigma_2 \tag{14}$$

Thus the surface potential ψ_0 can be calculated as a function of n and σ with the help of the above equations.

The interfacial tensions between the disperse phase and the dispersion medium containing various amounts of sol and electrolytes were measured by the drop weight method. The apparatus used was as designed by Cook and Kitchener,[18] in which the drops of disperse phase were made at the edge of the capillary tube by the displacement of the mercury. A number of drops was allowed to fall into the dispersion medium, the average volume being noted from the reading of microburette. The interfacial tension was calculated by the formula

$$\gamma=\frac{v(d_2-d_1)}{rg}f \tag{15}$$

where d_1 and d_2 are the densities of the disperse phase and the dispersion medium respectively, which were determined by the pycknometer taking water as standard, r the radius of the edge of the capillary, v the volume of the one drop of oil and f is the factor depending upon the value of v/r^3 being taken from the standard tables.[19]

Results

(a) Influence of Electrolytes on Zeta Potentials of the Sol. The ferric hydroxide sol was prepared in the excess of ferric chloride and was positively charged on account of excess of ferric ions, adsorbed to the surface of the ferric hydroxide sol particles. The flocculation was, therefore, brought about by different valent anions. The electrokinetic mobilities at different concentrations of electrolytes were measured and zeta potentials calculated by Eqs. (1) and (2). The observed value of the zeta potential of the initial sol is 154.5 mV at 25°C.

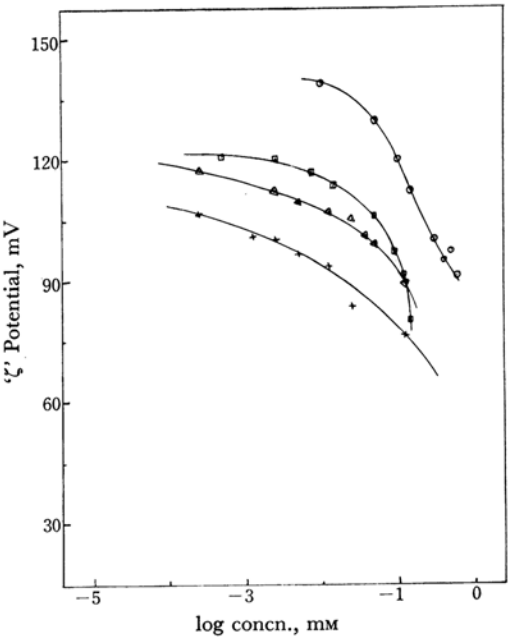

Fig. 4. Curves showing the variation in zeta potentials at various concentrations of electrolytes.
⊙ Pot. oxalate, ⊡ Pot. citrate, △ Pot. ferricyanide
× Pot. ferrocyanide

The curves for the zeta potentials of ferric hydroxide sol particles as a function of log molar concentration of different electrolytes, *viz* KBr, $K_2(C_2O_4)$, $K_3Fe(CN)_6$, $K_3(C_6H_5O_7)$ and $K_4Fe(CN)_6$ are represented in (Fig. 4). In general, the zeta potential decreases as the concentration of electrolytes increases. In case of potassium bromide and potassium oxalate the fall of zeta potential is

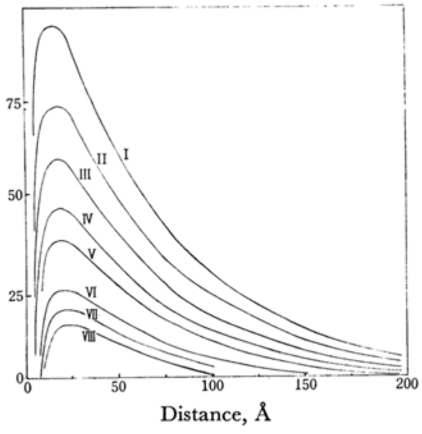

Fig. 5. Curves for potential energy of interaction in the presence of Pot. oxalate.
I Pure sol, II 0.01 mM, III 0.05 mM, IV 0.10 mM, V 0.15 mM, VI 0.40 mM, VII 0.50 mM, VIII 0.60 mM

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[18] J. R. Catch, A. H. Cook and J. A. Kitchener, *J. Chem. Soc.*, **1945**, 319.

[19] "International Critical Tables," Vol. IV, p. 435.

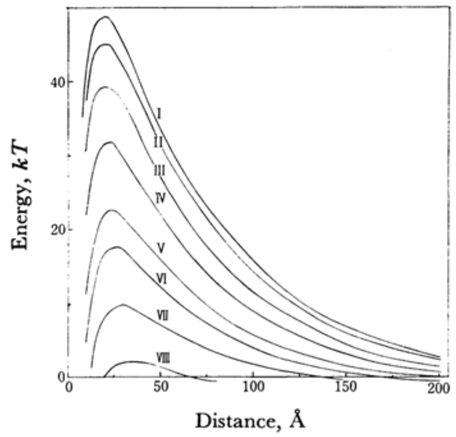

Fig. 6. Curves for potential energy of interaction in the presence of Pot. citrate.
I 5.0×10^{-4} mM, II 5.0×10^{-3} mM,
III 3.0×10^{-2} mM, IV 5.0×10^{-2} mM, V 0.1 mM,
VI 0.12 mM, VII 0.15 mM, VIII 0.4 mM

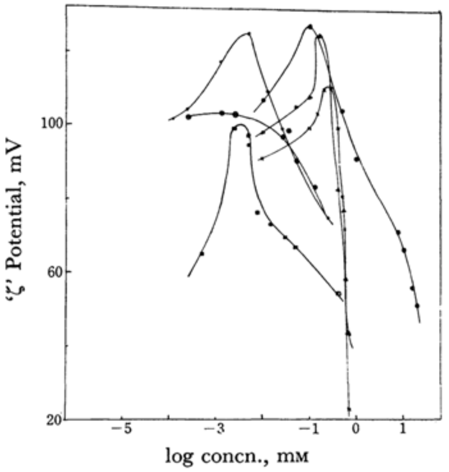

Fig. 7. Curves showing the values of zeta potentials for various concentrations of electrolytes.
⊙ KBr, △ $K_2(C_2O_4)$, × K_2SO_4, ⊡ $K_2(C_6H_5O_7)$, ⊗ $K_3Fe(CN)_6$, ● $K_4Fe(CN)_6$

almost linear throughout, but in case of ferricyanide, citrate and ferrocyanide it is comparatively slow at the initial stages and then becomes sharp.

(**b**) **Interaction Energy Curves.** For the complete assessment of the stability of the sol in presence of different amounts of electrolytes the potential energies of interaction for the sol particles were calculated. Only representative energy profiles are shown in Figs. 5 and 6.

The curve I of Fig. 5 shows that the net potential energy of interaction of the ferric hydroxide sol corresponding to zeta potential 154.5 mV has the maximum energy $V_m=94.3\,kT$ which is indicative of the complete stability of the sol. In these calculations the value of the Van der Waals constant A is taken to be equal to 3.13×10^{-12} erg, the calculated value by the physico optical data which is in the range suggested by Overbeek (*loc. cit.*) for solid particles suspended in water.

In general by the addition of electrolytes the maximum energy V_m and hence the sol stability decreases with the increase in concentration of the electrolytes (Table 1).

(**c**) **Studies of Zeta Potentials of the Emulsions.** The initial emulsion with pure ferric hydroxide sol without any electrolyte had zeta potential equal to 63.5 mV (*cf.* this with the value 154.5 mV of the emulsifying sol). The corresponding emulsions were prepared by the partially flocculated sol and the zeta potentials are plotted in Fig. 7 against the log molar concentration of the electrolytes used for partial flocculation.

(**d**) **Interaction Energy Curves and the Flocculation in the Secondary Minima.** The potential energy V of the interacting emulsion droplets was calculated by Eqs. (8) and (9) and the energy curves were plotted, only a few typical curves being shown in Figs. 8 and 9 in case of potassium oxalate and potassium ferrocyanide.

From these curves it is seen that in all the emulsions globules possess a high potential energy barrier at intermediate distances, the extent of which depends upon the values of the zeta potential which invariably varies with the electrolyte concentrations. At small and larger separating distances between the particles there is net attraction which shows that at higher distances the particles are flocculated but still separated by a larger distance, called secondary minimum flocculation. The secondary minima have also been represented separately in a more elaborate form on the same graphs and are found to be 3 to 6 kT deep at 500—800Å distances (*cf.* Schenkel and Kitchener[16]). In these energy calculations the value of Van der

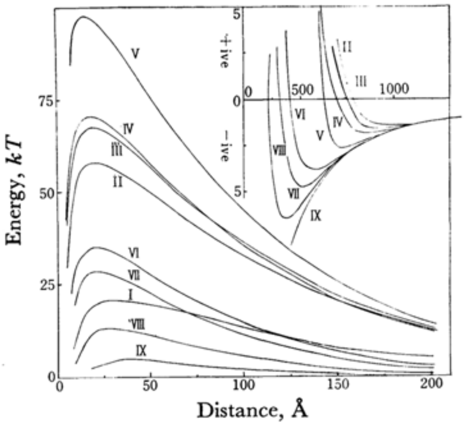

Fig. 8. Curves for potential energy of interaction in the presence of Pot. oxalate.
I Pure sol, II 0.01 mM, III 0.05 mM, IV 0.10 mM,
V 0.15 mM, VI 0.40 mM, VII 0.50 mM,
VIII 0.60 mM, IX 0.70 mM

TABLE 1.

Electrolyte concn. mM	Debye-Hückel parameter κ $\times 10^{-6}$	Potentials, mV		Max. energies V_m, kT		Depth of Sec. min. of emulsions, kT
		Sol	Emulsion	Sol	Emulsion	
Initial sol	1.043	154.5	63.5	94.3	2039	—
KBr						
0.01	1.049	149.5	106.3	85.7	7074	1.9
0.10	1.090	143.5	126.3	76.3	7718	1.45
0.25	1.160	137.3	109.1	67.0	7371	1.72
0.50	1.270	133.2	103.4	60.1	6397	2.19
1.00	1.470	121.4	90.6	43.9	4524	3.25
8.00	3.120	108.1	70.9	16.3	1645	24.58
10.00	3.440	98.1	65.9	7.9	1178	51.00
15.00	4.160	95.6	55.7	6.6	409	73.00
Pot. oxalate						
0.00	1.043	154.5	63.5	94.3	2039	—
0.01	1.060	140.4	97.5	72.9	5798	1.43
0.05	1.120	130.0	104.8	58.7	6765	1.57
0.10	1.190	119.7	107.2	45.7	7043	1.80
0.15	1.255	112.3	123.9	37.1	9621	2.65
0.40	1.540	95.2	82.3	18.6	3522	3.86
0.50	1.646	97.8	76.4	20.0	2844	4.76
0.60	1.740	91.4	58.1	14.2	1306	6.40
0.70	1.830	—	43.4	—	487	8.52
Pot. citrate						
0.00	1.043	154.5	63.5	94.3	2039	—
5.0×10^{-4}	1.044	120.7	64.9	48.8	2196	1.70
2.5×10^{-3}	1.051	120.5	98.7	48.5	5979	1.40
5.0×10^{-3}	1.059	117.6	97.0	45.1	5730	1.43
7.5×10^{-3}	1.066	116.9	76.0	43.3	3202	1.65
1.5×10^{-2}	1.088	113.7	72.9	40.5	2880	1.76
3.0×10^{-2}	1.132	112.9	69.3	39.2	2520	2.00
5.0×10^{-2}	1.180	106.1	66.9	31.6	2264	2.25
0.40	1.910	71.0	54.4	2.0	909	8.32
Pot. ferricyanide						
0.00	1.043	154.5	63.5	94.3	2039	—
2.5×10^{-4}	1.044	117.4	101.9	45.1	6431	1.40
1.25×10^{-3}	1.047	116.6	103.0	44.2	6588	1.36
2.5×10^{-3}	1.051	111.9	102.4	39.0	6492	1.38
5.0×10^{-3}	1.059	109.7	94.5	36.6	5390	1.45
2.5×10^{-2}	1.118	105.4	96.6	31.6	5642	1.64
5.0×10^{-2}	1.189	99.5	89.8	25.4	4667	1.96
0.125	1.380	89.1	82.8	15.2	3698	2.90
Pot. ferrocyanide						
0.00	1.043	154.5	63.5	94.3	2039	—
1.25×10^{-4}	1.044	99.8	101.6	27.0	6390	1.40
2.5×10^{-4}	1.045	106.8	104.1	33.8	6757	1.35
1.25×10^{-3}	1.050	101.3	116.9	28.3	8759	1.31
2.5×10^{-3}	1.056	100.6	—	27.6	—	—
5.0×10^{-3}	1.070	97.1	124.7	24.3	10057	1.30
1.25×10^{-2}	1.106	93.8	108.8	21.1	7387	1.49
2.5×10^{-2}	1.165	84.0	98.6	13.7	5839	1.78
0.125	1.560	76.4	—	6.5	—	—
0.250	1.946	—	74.5	—	2502	7.34

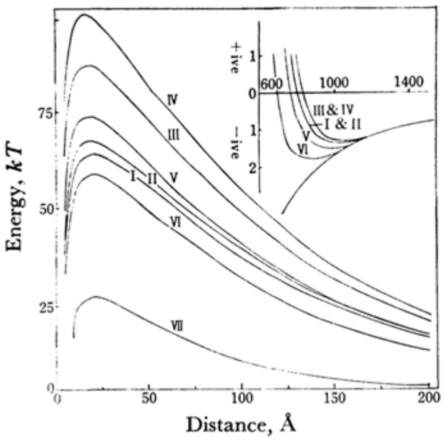

Fig. 9. Curves for potential energy of interaction in the presence of Pot. ferorcyanide.
I 1.25×10^{-4} mM, II 2.5×10^{-4} mM,
III 1.25×10^{-3} mM, IV 5.0×10^{-3} mM,
V 1.25×10^{-2} mM, VI 2.5×10^{-2} mM, VII 0.25 mM

Waals constant for the disperse globules in the dispersion medium is taken to be 1×10^{-12} erg which was obtained by physico optical data for toluene globules coated by ferric hydroxide sol and disperse in water. In case of all the electrolytes the potential energy first increases with the addition of electrolytes and after a certain maximum value it begins to decrease and the system becomes unstable.

The results obtained for ferric hydroxide sol and the corresponding emulsions for the various electrolytes are summarised in Table 1.

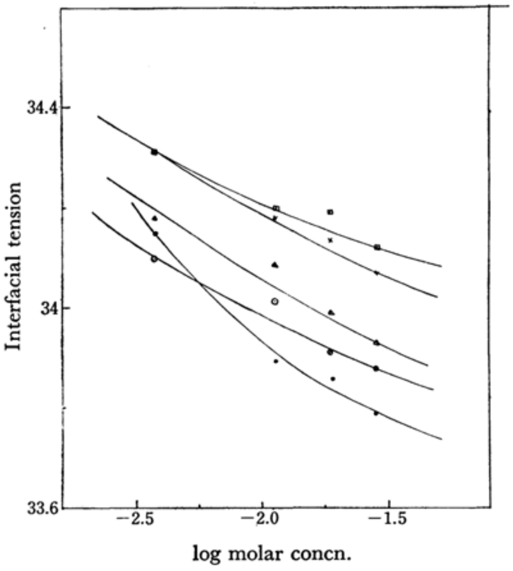

Fig. 10. Curves showing the change in interfacial tension with the concentration of $Fe(OH)_3$ sol in presence of Pot. bromide.
⊙ 0.10 mM, ⊡ 0.25 mM, × 1.0 mM, △ 8.0 mM, ● 15 mM

(e) **Surface Charge by the Interfacial Tension.** The change in interfacial tension with the concentration of ferric hydroxide sol in presence of different amounts of electrolytes has been also measured and a few representative curves have been shown in (Fig. 10). From these curves the surface excess of the sol particles at the particular concentration of the sol has been calculated which ultimately gives the total charge on the oil globules for that definite concentration of the sol.

The distribution of the charge between the Stern layer and diffuse double layer of the emulsion globule for the particular concentration of the sol at the same concentration of the electrolyte in the dispersion medium has been calculated from Eqs. (12), (13) and (14). A few typical curves showing the distribution of charge for the different values of $e\Psi_0/kT$ are given in (Fig. 11). From these curves the value of $e\Psi_0/kT$ has been calculated

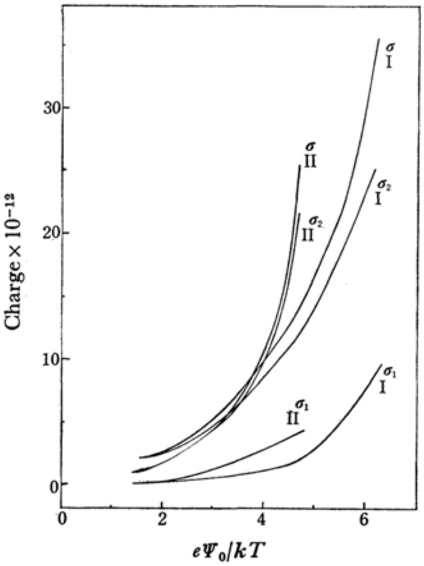

Fig. 11. Curves for the distribution of charge as a function of $e\Psi_0/kT$ in presence of I 1 mM of KBr, II 0.01 mM of Pot. oxalate.

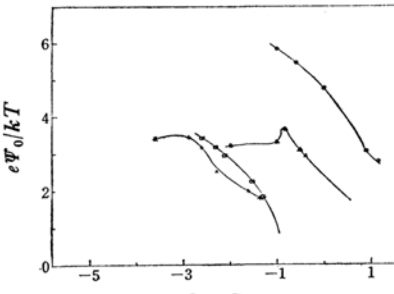

Fig. 12. Curves for the $e\Psi_0/kT$ as a function of log concentration.
⊙ KBr, △ Pot. oxalate, ⊡ Pot. citrate, × Pot. ferricyanide

corresponding to the experimentally obtained value of the total surface charge σ. The graphs in Fig. 12 have been plotted between the log molar concentrations and the value of $e\Psi_0/kT$ obtained from the interfacial tension data and the results are also given in Table 2. The results, in general, agree with those obtained electrophoretically.

Table 2.

Electrolyte	Concn. mmol	$\sigma/e\times10^{-13}$	$e\Psi_0/kT$	Ψ_0 mV
Pot. bromide	8.0	1.77	3.05	78.5
Pot. oxalate	0.4	3.01	2.94	81.0
Pot. citrate	7.5×10^{-3}	2.51	2.95	79.0
Pot. ferricyanide	1.25×10^{-3}	2.60	3.46	95.0

(f) Effect of pH on the Stability of the Emulsion. This is depicted in Fig. 13 where it is found that pH of the emulsion continuously increases with the addition of the electrolyte. But zeta potentials first increase with pH, reach a maximum and then decrease regularly. The increase in pH may be due to desorption of OH^- ions from the flocculated particles which are obtained by the addition of respective anions.

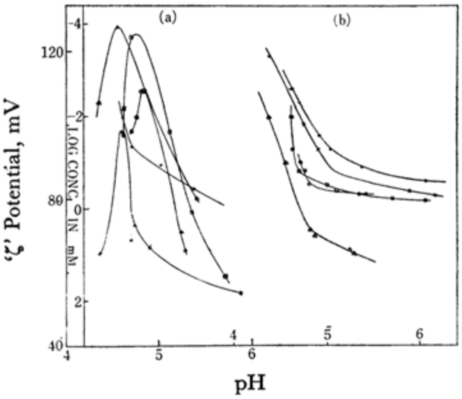

Fig. 13. (a) Curves showing the changes in zeta potential as a function of pH in presence of various electrolytes.

△ Pot. bromide, ⊡ Pot. oxalate, × Pot. citrate, ⊙ Pot. ferricyanide

(b) Curves showing the changes in pH as a function of log concentration in the presence of various electrolytes during emulsification.

△ Pot. bromide, ⊡ Pot. oxalate, × Pot. citrate, ⊙ Pot. ferricyanide

Similar curves were obtained when pH is adjusted after emulsification.[20]

Discussion

The zeta potential of the emulsion prepared by the most stable ferric hydroxide sol (having zeta= 154.5 mV and energy barrier 94.3 kT) was 63.5 mV but by the addition of small amounts of different electrolytes the zeta potential of the emulsion first increases with the increase of electrolyte and after a certain maximum value it decreases by the further addition of electrolyte thereby indicating instability. It can be seen from Fig. 7 that the decrease is much more sharp in case of mono and bivalent anions than with tri and tetra valent.

However, when the sol is partially flocculated by the additon of electrolytes and the zeta potential is lowered to about 110±10 mV and the corresponding energy barrier is reduced to nearly 40±5 kT, more stable emulsions are obtained, which have zeta potentials in the range 115±10 mV and the energy barrier above 7500 kT.

It is obvious that for the efficient stabilisation of an emulsion by solid particles some prevalent attraction between the sol particles is necessary. The emulsification is governed by the flocculation of the sol particles in the continuous liquid phase and the stabilizing power of solid particles as a function of their degree of flocculation thus first increases, then reaches a maximum and at still higher degrees of flocculation again decreases. Thus by the pure sol a stable emulsion cannot result on account of high potential energy barrier whereas in the case of flocculated sol by the addition of electrolytes stable emulsions can be formed when the potential energy barrier between the stabilising particles is reduced.

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20) S. P. Jain and S. N. Srivastava, Under communication.