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Studies on the Effect of Some Anionic Detergents on the Stability of Emulsions Stabilised by Partially Flocculated Sols

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A partially flocculated $Fe(OH)_3$ sol has been used as an emulsifying agent to stabilize toluene/water system. The electrophoretic mobilities of the emulsion thus obtained in the presence of different anionic detergents have been measured microelectrophoretically and from these values the zeta potentials have been calculated. At the charge reversal concentrations the adsorption and free energy constants were calculated. From the surface potential values the repulsion and attraction energies were evaluated which clearly showed that the flocculation occurrs in the secondary minima. The operating van der Waals constant A has been estimated by correlating the results of degree of aggregation obtained haemocytometrically with the theoretical values. It was found to be 1.05×10^{-12} erg. The values of interfacial tension have been reduced by the addition of these detergents which are directly connected with the chain length of the detergent and adsorption characteristics.

Adsorption and its relation with electrokinetic potential for various detergents has been studied by some workers.[1–6] Haydon[7] also studied the relationship between the electrokinetic potential and surface charge density for long chain alkyl sulphates. Levich and Kuzhetsov[8] observed the retardation effect of surface active agent on the movement of the drop in a liquid between the regions of high and low interfacial tensions. The coagulation kinetics of rutile in hydrocarbon solutions of Aerosol OT reported by McGown and Parfit[9] showed an excellent agreement with the DLVO theory over a wide range of zeta potential.

A study of literature reveals that detergents influence the stability of colloidal systems, as they get ionized and affect zeta potentials. In the case of emulsions stabilized by solid substances and specially by metal hydroxides, practically no quantitative measurement has been done on the stability in the presence of detergents. In the present work an attempt has been made to study quantitatively the stability of emulsions in the presence of anionic detergent especially in the light of DLVO[10–12] theory. Electrokinetic measurements have been used for the interaction between the droplets and haemocytometric device for flocculation studies.

Theoretical

According to Derjaguin and Kussakov,[13] the repulsion energy V_R between the two spherical particles for the system having $\kappa a \gg 1$ is given by

$$V_R = \frac{\varepsilon a \psi_0^2}{2} \ln(1 + \exp(-\kappa H)) \qquad (1)$$

where ψ_0 is the surface potential (approximately equal to zeta potential for the present system), H is the distance of separation of the droplets and κ is the Debye-Hückel parameter equal to the reciprocal thickness of the double layer

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$$\kappa = \frac{1}{d} = \left[\frac{4\pi e^2 \sum n_i z_i^2}{\varepsilon k T}\right]^{1/2} \tag{2}$$

where z is the valency of the ions of ith kind and n_i is the number of ions per m*l*.

The attraction energy V_A at intermediate distances where the force is partially retarded is given by Schenkel and Kitchener[14] as follows.

For $H > 150$ Å,

$$V_A = -\frac{Aa}{\pi}\left(\frac{2.45\lambda}{120H^2} - \frac{\lambda^2}{1045H^3} + \frac{\lambda^3}{5.62\times 10^4 H^4}\right) \tag{3}$$

For $H > 150$ Å

$$V_A = -\frac{Aa}{12H}\left(\frac{\lambda}{\lambda + 3.54\pi H}\right) \tag{4}$$

where λ, the wavelength of the intrinsic electronic oscillations of the atoms, is taken to be equal to 1000 Å.

The change in charge density caused by the addition of a small quantity of foreign ions which are adsorbed on emulsion particles will be given by the Stern equation[15,16]

$$\sigma_C = \frac{N_1 ze}{1 + \frac{55.6}{C}\exp\left(\frac{\Delta G}{kT}\right)} \tag{5}$$

where C is the molar concentration of the added detergent, N_1 the number of binding sites available per cm^2 and ΔG is the electrochemical free energy of adsorption per molecule. This can also be put in the form[17–19]

$$\Delta\sigma_C = \frac{K_1 C}{1 + K_2 C} \tag{6}$$

which is similar to Langmuir adsorption isotherm.[20] K_1 and K_2 are called adsorption constants.

The relation between log C, ψ_δ (here $\psi'_\delta = \xi$) and N_1 at the isoelectric points where $\kappa a \gg 1$ is given by the equations

$$\frac{1}{C} = K_2\left\{\left[\frac{4\pi e N_1 Z}{\xi' \varepsilon \kappa}\right] - 1\right\} \tag{7}$$

where C is the concentration of detergents at ($\xi = 0$) zero point of charge and ξ' is the initial zeta potential taken instead of ψ_δ, and assuming that only a single adsorbed layer was formed upto $\xi = 0$.

$$\left(\frac{d\xi}{d \log C}\right)_{\xi=0} = 2.303\xi'\left(\frac{\xi'\varepsilon\kappa}{4\pi e z N_1} - 1\right) \tag{8}$$

The chemical free energy of adsorption ΔG has been calculated by the equation[21]

$$-\Delta G = kT(\ln K_2 + \ln 55.6) \tag{9}$$

The degree of aggregation, *viz*., the total number of particles associated with a given central particle can be determined with knowledge of the depth of the secondary minima by solving the following equation where the integration has been carried out graphically.

$$D = 4\pi a^3 n_0 \int s^2 \exp(-V/kT)\,ds \tag{10}$$

Experimental

A positively charged ferric hydroxide sol was prepared, dialyzed and partially flocculated by the addition of 0.15 mmol of potassium oxalate. To this sol toluene (5%, weight) was dispersed by shaking by hand and the emulsion was then well homogenized using a stainless steel homogenizer (C. W. Logemann Co. U.S.A.). After half an hour the creamed layer was removed and same emulsion was prepared under the same conditions.

In order to study the effect on stability the following detergents have been used: dibutyl ester of sodium sulphosuccinic acid, dioctyl ester of sodium sulphosuccinic acid, sodium salt of secondary alkyl sulphate containing 17 carbon atoms and sodium lauryl sulphate. All the detergents were obtained from BDH and used as they are. For the sake of convenience they have been represented by the BSS, OSS, SAS and SLS. The other chemicals and reagents used were of Analar grade.

Electrokinetic measurements were carried out by micro electrophoresis apparatus using a Northrup-Kunitz rectangular type cell in which the direct movement of the emulsion droplets was observed with a microscope for a definite distance under a suitable electric voltage which was measured by the VTVM across the two ends of the cell. An equiconducting solution of KCl was used in electrode vessels and the zeta potentials were calculated by means of the relation

$$z = \frac{4\pi n u}{\varepsilon} \tag{11}$$

the relaxation correction being neglected because of the large sized particle (radius 1.12 μ) (Fig. 1 and Fig. 2).

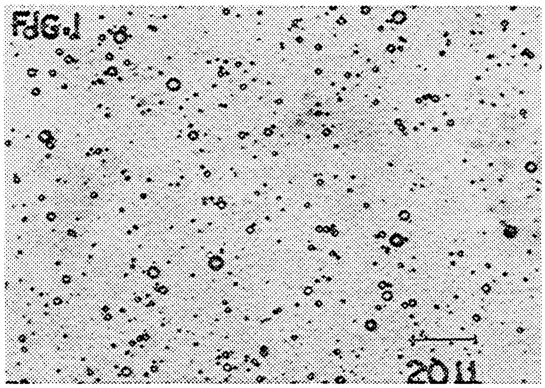

Fig. 1. Microphotograph, 600 times magnified.

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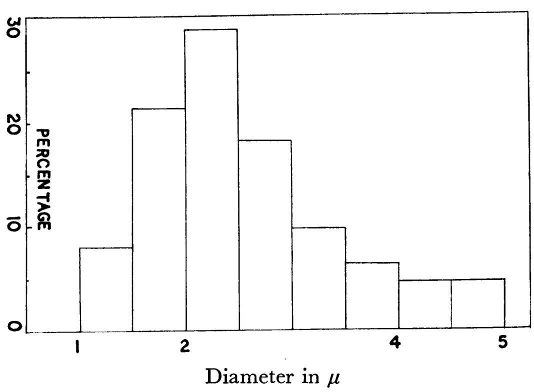

Fig. 2. Size-distribution curve of the emulsion globules, radius 1.12 μ.

Results and Discussion

Effect of Anionic Surface Active Agents on Zeta Potential. The zeta potentials of the emulsions in the presence of different concentrations of surface active agents have been plotted against log molar concentrations in Fig. 3. In general, as the concentration of these detergents is increased in a low range the zeta potential decreases very slowly until a certain concentration is reached after which it gradually decreases to a certain fixed value of nearly 50 mV, with increasing gradient. Further increase in concentration gave visible flocculation where the measurements were not feasible because of agglomeration of a large number of solid particles on oil globules on account of small zeta value. On a further increase of concentration, reversal of charge took place and the zeta became increasingly negative.

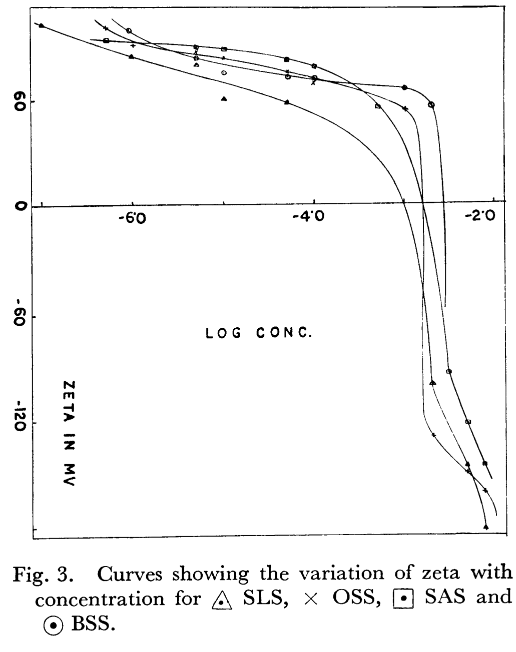

Fig. 3. Curves showing the variation of zeta with concentration for △ SLS, × OSS, ⊡ SAS and ⊙ BSS.

Increase in zeta value in this range of concentration is very sharp. With a small change in concentration an appreciable increase in zeta took place which increases upto critical micelle concentration. Over this CMC there should be no further change theoretically. However, a decrease was observed only in one case with SLS. The decrease in zeta after CMC can be explained as follows. It is likely that during the mixing of concentrated solution of detergent to the system, conditions could occur in which the miceller solution of the detergent becomes submiceller. The breakdown of micelles to submicelles is a very fast reaction.[22] The time required during mixing of the detergent in to the system is of the same order as required for breaking down of the micelles, and mutual coagulation would have occurred between the micelles and the stabilized emulsion droplets resulting in an artificial decrease of stability.

The flocculating concentration at which zeta potential becomes zero was obtained from zeta-log C curves. From them the efficiency of reversing the charge or the extent of adsorption is in the order SLS>OSS>SAS>BSS, and their CMC are to be expected in the increasing order. Thus a higher concentration of SAS is required to reverse the charge than SLS. The charge reversal was not obtained with BSS though relatively high concentration of the order of 2.0×10^{-3} mol/l has been reached. This is presumably on account of a comparatively smaller chain length of the detergent. This order of their efficiencies is also confirmed by their structural formulae; SLS possesses a long chain of 12 carbon atoms, OSS and SAS possess of only eight carbon atoms while BSS has only 4 carbon atoms in its chain. Thus their efficiencies increase as carbon chain increases. The distinction between SAS and OSS is on the basis that OSS possesses a bigger head group than SAS.

Charge Density and Binding Parameters. The number of binding sites available per cm^2,

Table 1. Binding parameters and number of binding sites for different detergents

Detergent	K_1 Coulomb l/cm^2 mol.	K_2 l/mol	$\frac{K_1}{K_2}\times10^7$ Coulomb/cm^2	Binding sites N_1 group/cm^2
SLS	1.55×10^{-3}	2.1×10^{3}	7.37	4.6×10^{12}
OSS	4.26×10^{-5}	6.6×10^{2}	0.65	0.4×10^{12}
SAS	0.72×10^{-5}	1.0×10^{3}	6.84	4.3×10^{12}
BSS	9.23×10^{-5}	4.5×10^{2}	2.05	1.3×10^{12}

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22) R. H. Ottewill and M. C. Rastogi, *Trans. Faraday Soc.*, **56**, 866, 880 (1960).

TABLE 2. FREE ENERGY AND SURFACE CHARGE OF STERN LAYER FOR DIFFERENT DETERGENTS

Detergent	σ_s Coulomb/mol	$-\Delta G$ kcal/mol	Area/mol Sq. Å
SLS	1.5×10^3	2.95	2174
OSS	1.0×10^2	2.66	25000
SAS	1.3×10^3	2.78	2326
BSS	3.2×10^2	2.32	9793

TABLE 3. ZETA POTENTIALS, MAXIMUM ENERGY AND DEPTH OF SECONDARY MINIMA FOR DIFFERENT DETERGENTS

Concentration mol/l	κa	Zeta potential in mV	Maximum energy in kT	Distance at V=0.Å	Depth of sec. minima
SLS					
2.0×10^{-8}	141.2	106.3	6834	665	−2.08
1.0×10^{-7}	141.2	101.9	6203	650	−2.08
5.0×10^{-7}	141.2	93.1	5029	635	−2.15
1.0×10^{-6}	141.3	86.2	4063	620	−2.18
5.0×10^{-6}	141.5	79.5	3416	610	−2.24
1.0×10^{-5}	141.7	60.5	1717	540	−2.49
5.0×10^{-5}	143.6	57.5	1481	520	−2.90
Reversal					
2.0×10^{-3}	217.4	−101.3	5416	360	−5.57
5.0×10^{-3}	297.2	−147.3	12719	290	−9.87
7.5×10^{-3}	350.1	−182.0	19901	240	−12.86
OSS					
5.0×10^{-7}	141.2	101.5	6146	655	−2.10
1.0×10^{-6}	141.3	91.9	4866	635	−2.05
5.0×10^{-6}	141.5	86.3	4191	620	−2.06
1.0×10^{-5}	141.7	82.5	3744	610	−2.14
5.0×10^{-5}	143.6	74.6	2904	590	−2.28
1.0×10^{-4}	146.0	68.4	2330	560	−2.53
1.0×10^{-3}	183.2	54.5	1131	340	−5.28
Reversal					
2.0×10^{-3}	217.4	−103.3	10139	410	−4.99
5.0×10^{-3}	297.2	−150.7	13400	290	−9.59
7.5×10^{-3}	250.1	−162.1	15189	230	−13.69
SAS					
5.0×10^{-8}	141.2	103.4	6415	660	−2.08
5.0×10^{-7}	141.2	94.2	5162	640	−2.08
5.0×10^{-6}	141.5	89.2	4533	625	−2.14
1.0×10^{-5}	141.7	88.5	4447	620	−2.15
5.0×10^{-5}	143.6	80.8	3541	590	−2.26
1.0×10^{-4}	163.6	55.8	1281	420	−3.96
Reversal					
3.0×10^{-3}	246.9	− 94.6	4386	290	−7.90
5.0×10^{-3}	297.2	−123.4	8309	270	−10.80
7.5×10^{-3}	350.1	−146.0	11939	222	−14.29
BSS					
5.0×10^{-8}	141.2	108.1	7100	665	−2.08
5.0×10^{-7}	141.2	99.2	5837	650	−2.15
5.0×10^{-6}	141.5	83.3	3835	610	−2.20
1.0×10^{-5}	141.7	74.8	2917	590	−2.28
1.0×10^{-4}	146.0	71.0	2563	565	−2.46
1.0×10^{-3}	183.2	65.9	1915	380	−4.80
2.0×10^{-3}	217.4	56.5	1124	270	−7.95

N_1, binding parameters and charge density have been calculated with the help of the slope of zeta-log C curves and the concentration at which $\xi=0$, and are represented in Table 1. The area occupied by each anionic surface active agent when all the sites are covered is also calculated. The value of free energy of adsorption ΔG which determines the strength of binding of these surface active ions are shown in Table 2.

From the table we see that the values of K_2 are in the order SLS>OSS>SAS>BSS, which gives the order of adsorption. This can also be seen from zeta-log$C$ curves, where the slope of the curves are found to increase with increasing chain length of the surface active agents, and a shift of the zero point of charge to higher concentration for a smaller chain length is also observed.

The nature of adsorption of these anionic surface active ions can be explained on the basis of the binding parameters. At a smaller concentration the surface active ions go to the positively charged surface of oil globule, probably the surface occupied by potential determining ions. The surface sites are essentially the same for different surface active agents, because the values of N_1 obtained for each detergent are reasonably consistent. However, it is clear that the maximum number of sites is greater than the surface excess of ferric ions since the sign of zeta is reversed. Thus, it seems reasonable to assume that at a certain concentration nearly 5×10^{-4} mol/l, the surface active ion may be adsorbed directly on the surface at the sites other than those occupied by potential determining ions. Uncertainty may arise due to a slight differences in the values of N_1.

The adsorption can also be explained by the consideration that the oil phase is in reversible equilibrium with the ions in the solution. When surface active agents are added, one particle of it is adsorbed on one potential determining ion site, and an additional potential determining ion is adsorbed and this process will continue until the system becomes irreversible. In this process with the adsorption of detergent on potential determining ions, the adsorption directly on the oil surface also occurs.

Interaction Energy Curves and Secondary Minimum Flocculation. The interaction energies of the double layer around the particles at the different concentrations of the detergents SLS, OSS, SAS and BSS have been calculated with respective values of the zeta potentials, and are tabulated in Table 3. The corresponding curves for the interaction energy *vs.* the distance between the two particles are plotted, the only representative figure

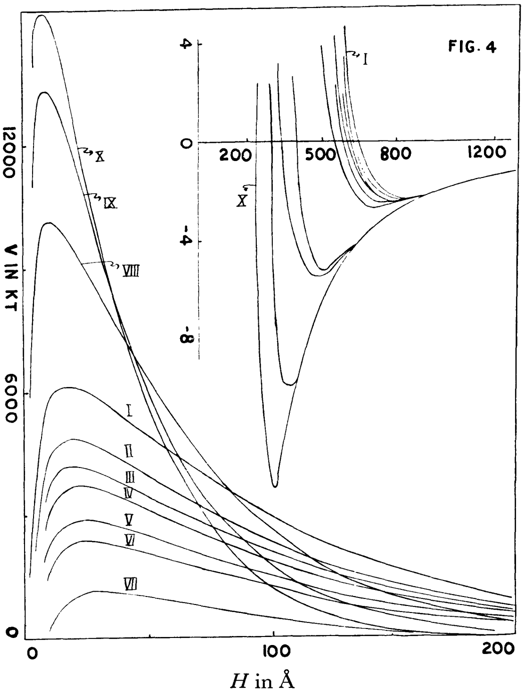

Fig. 4. Potential energy profiles and elaborated secondary minima for OSS at I, 5×10^{-7}, II 1×10^{-6}, III 5×10^{-6}, IV 1×10^{-5}, V 5×10^{-5}, VI 1×10^{-4}, VII 1×10^{-3}, VIII 2×10^{-3}, IX 5×10^{-3} and X 7.5×10^{-3} mol/*l*.

is shown in Fig. 4. The value of A *i. e.* van der Waals constant has been taken to be equal to 1.0×10^{-12} erg.

From the equations of interaction energies it can be seen that the value of V depends mainly on the factors ψ_δ, κ and a which change with concentrations of the detergent. The κ a values remain almost the same nearly upto the concentration 1×10^{-4} mol/*l* in case of all the detergents, *i. e.* the ionic strength will not change much and hence practically no change in the value of interaction energies will be observed. Addition of the surfactants has an effect on ψ_δ or ξ. However, at higher concentrations both the factors κ a and ξ change and affect the value of V.

At smaller distances the values of interaction energies obtained are considerably high in all cases while at larger distances attraction prevails and secondary minima are obtained in which particles aggregate reversibly. The depth of secondary minima is nearly constant in the low range of concentrations and is equal to $2.5kT$ for all detergents. This is too shallow to trap the particles but at higher concentrations the depth increases upto 10—$15kT$ which is reasonable for the occurrence of flocculation. These high energy values and the occurrence of the secondary minima may be due to large particle radius ($a=1.1$ μ).

The relation between the interparticle distance H_m at which the minimum energy occurs and Debye-Hückel parameter κ can be represented by the equation

$$H_m^2 e^{-\kappa H_m} = 1.80\times10^{-9}\frac{v^2}{\kappa\nu^2}$$

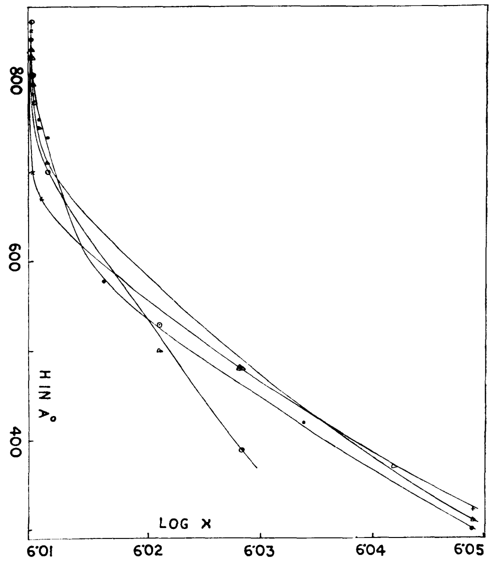

Fig. 5. Curves showing the depencence of κ Debye-Hückel parameter to H_m for × SLS, ⚠ OSS, ● SAS and ⊙ BSS.

The effect of κ upon H_m separation of particles when they are reversibly flocculated in secondary minima is shown in Fig. 5. The distance H_m decreases with the increase in concentration of the detergents. This H_m distance is also directly proportional to the valency of the added ions which are uni valent. Thus the value of H_m is nearly the same at low range of concentration and is just linear, but it varies with κ at higher concentrations. The depth of the secondary minima also depends

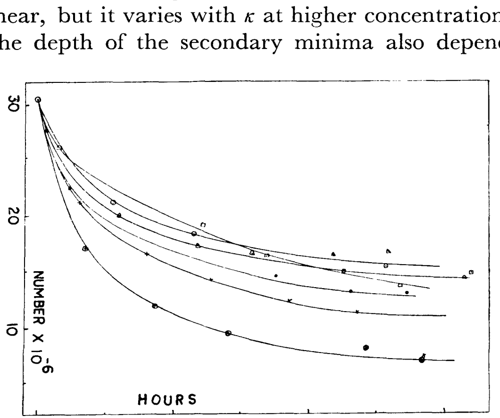

Fig. 6. Curves showing the change in number of monomers with time for SAS at ⊙ 5×10^{-8}, ⚠ 5×10^{-7}, ⊡ 5×10^{-6}, ● 5×10^{-5}, × 1×10^{-4} and ⊗ 5×10^{-4}M.

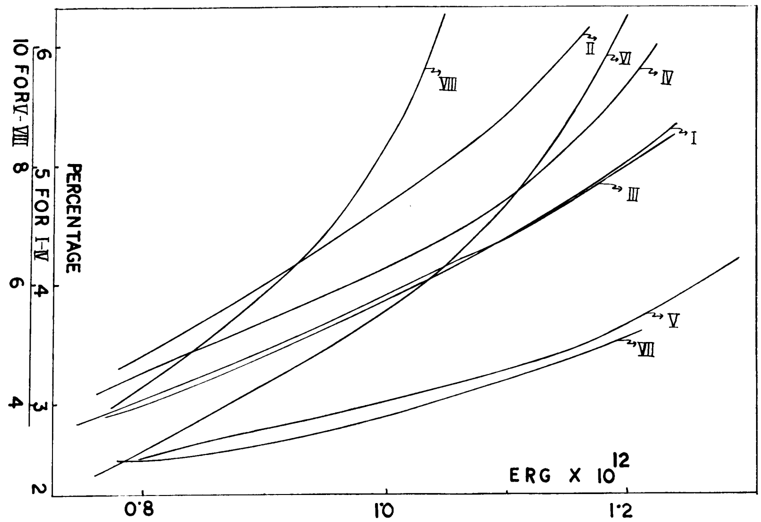

Fig. 7. Curves showing the variation in degree of aggregation D with van der Waals constant A at, I 1×10^{-7}, II 5×10^{-5}, mol of SLS, III 5×10^{-7}, IV 5×10^{-6} mol of OSS, V 1×10^{-4}, VI 5×10^{-4} mol of SAS, VII 5×10^{-7} and VIII 1×10^{-3} mol of BSS.

on the value of the van der Waals constant A.

Concerning flocculation, the singlets and doublets as obtained haemocytometrically were plotted with respect to time at different concentrations of detergents, the representative plot being shown in Fig. 6. They are levelled off after certain time because of attainment of a temporary equilibrium between singlets and doublets. This confirms the occurrence of secondary minimum flocculation in the emulsion of large particles.

Determination of the van der Waals Attraction Constant. In order to determine the van der Waals constant, the value of degree of aggregation D is required which has been calculated by Eq. (10) with the help of depth of secondary minima at different values of the van der Waals constant. These values of D are plotted for the different values of A as shown in Fig. 7. The observed value of D has been determined haemocytometrically with the help of the equation

$$D = \frac{\text{number of singlets}}{\text{number of singlets} + \text{number of doublets}} \tag{12}$$

The value of A corresponding to these values has been deduced from the graphs and given in Table 4. The mean value of A was found to be 1.0×10^{-12} erg which is reasonable for oil droplets coated by solid particles and agrees with the theoretical value calculated by physico optical data.[23]

Table 4. Values of the van der Waals constant in different detergents

Detergent	Concentration mol/l	Degree of aggregation D in %	van der Waals constant $A\times10^{12}$ in erg.
SLS	1.0×10^{-7}	3.5	0.91
	5.0×10^{-7}	3.2	0.83
	1.0×10^{-6}	4.2	1.02
	5.0×10^{-5}	6.1	1.16
OSS	5.0×10^{-7}	4.2	1.06
	5.0×10^{-6}	3.8	0.96
	5.0×10^{-5}	5.5	1.18
	1.0×10^{-4}	5.6	1.18
SAS	5.0×10^{-8}	3.3	0.86
	5.0×10^{-6}	5.0	1.16
	1.0×10^{-4}	6.4	1.28
	5.0×10^{-4}	7.7	1.14
BSS	5.0×10^{-7}	3.5	9.93
	5.0×10^{-6}	4.0	0.98
	5.0×10^{-5}	5.3	1.16
	1.0×10^{-3}	8.9	1.01

Effect of Anionic Detergents on Interfacial Tension. The interfacial tension between oil phase and continuous phase were measured by an Agla micrometer syringe. The volume of a drop falling in oil phase was noted and the interfacial tension was calculated by the density difference of the two phases by equation

$$\gamma = \frac{(d_2-d_1)v}{gr}f \tag{13}$$

The interfacial tensions in presence of different

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[23] S. P. Jain and S. N. Srivastava, *Kolloid-Z. Z. Polym.*, **235**, 1230 (1969).

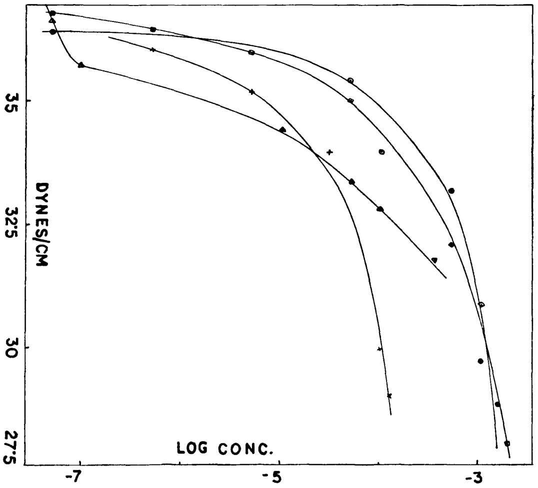

Fig. 8. Curves showing the change in interfacial tension with log molar concentration for △SLS, × OSS, ⊙ SAS and ⊡ BSS.

amounts of anionic detergents have been measured and the curves between interfacial tension and log molar concentration are given in Fig. 8. The change in interfacial tension and the volume of each drop are reported for all the detergents in Table 5. The value of interfacial tension decreases which implies a positive adsorption as suggested by Gibbs adsorption equation. These anionic surface active ions are adsorbed at the surface of positively charged oil particles and cause instability with increase in concentration of the detergents. The decrease in interfacial tension is greater in the cases of SLS and OSS than in cases of SAS and BSS which indicates that the effect depends on the chain lengths of the detergents. This is also in accordance with electrokinetic results.

Table 5. Effect of anionic surface active agents on interfacial tension

Detergent	Concentration mol/l	Volume of one drop in ml	Interfacial tension in dynes/cm
SLS	5.0×10^{-8}	0.2472	36.37
	1.0×10^{-7}	0.2430	35.75
	1.0×10^{-5}	0.2336	34.43
	5.0×10^{-5}	0.2258	33.39
	1.0×10^{-4}	0.2218	32.82
	3.5×10^{-4}	0.2145	31.78
OSS	5.0×10^{-7}	0.2452	36.08
	5.0×10^{-6}	0.2392	35.21
	3.0×10^{-5}	0.2304	33.98
	8.0×10^{-5}	0.2115	31.34
	1.0×10^{-4}	0.2014	29.85
	2.5×10^{-4}	0.1973	29.39
SAS	5.0×10^{-8}	0.2478	36.45
	5.0×10^{-5}	0.2414	35.50
	1.0×10^{-4}	0.2308	34.05
	5.0×10^{-4}	0.2146	33.22
	1.0×10^{-3}	0.1996	29.70
	1.5×10^{-3}	0.1932	28.82
BSS	5.0×10^{-8}	0.2503	36.84
	5.0×10^{-7}	0.2482	36.51
	5.0×10^{-6}	0.2450	36.04
	5.0×10^{-5}	0.2380	25.04
	5.0×10^{-4}	0.2166	32.10
	1.0×10^{-3}	0.2080	30.89
	2.0×10^{-3}	0.1876	28.06