BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1787—1795 (1969)

Effect of Some Cationic Detergents on Macromolecularly Stabilised Emulsions with Special Reference to Sodium Alginate and Gum Arabic as Emulsifiers

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(Received August 21, 1968)

The effect of some cationic detergents *viz.* cetyl pyridinium bromide, lauryl pyridinium chloride and phenyl trimethyl ammonium chloride has been studied on stabilised by sodium alginate and gum arabic emulsions. Zeta potentials were measured at different concentrations of cationic detergents microelectrophoretically. The particle size was determined microphotographically. With the help of zeta potential and particle size the interaction energies were calculated by summing up attraction and repulsion energies in the light of D.V.O. theory. For attraction energy the van der Waals constant was computed theoretically from the optical data and was obtained to be 6.7×10^{-14} erg. The interaction energies thus obtained gave very high energy barriers which completely obviated the occurrence of flocculation in primary minima, causing flocculation to occur in secondary minima. The theoretical degrees of aggregation were calculated and plotted at different values of A. The flocculation occurring in the system was observed haemocytometrically by counting the number of singlets and doublets and the degrees of aggregation were calculated. With the help of observed degrees of aggregation the operating value of van der Waals constant has been estimated by interpolating them into the theoretical curves, which is an indirect approach to ascertain the value of van der Waals constant. The values of A obtained are 3.0×10^{-13} and 2.6×10^{-13} erg for sodium alginate and gum arabic systems respectively. The binding parameters, number of binding sites available and free energy of adsorption have also been calculated.

Cationic detergents are the substances, generally, of high formula weight and are very specific in their surface active effects. These substances ionize in water giving positively charged long chain groups as well as anion. This positively charged part behaves as a typical polyvalent cation and hence is more efficient in flocculating negatively charged sols and emulsions. Cationic detergents produce hydrophobic surfaces, thus they have got much importance in industry. The hydrophobic groups bearing cationic polar heads are adsorbed on the surface of either negatively charged oil globules of an emulsion or solid sol particles.

A number of references on detergents are available in the literature of colloid science. Neogy and Ghosh[1] have made an exhaustive investigation of xylene-in-water emulsions stabilised by cationic detergents *viz.* cetyl dimethyl benzyl ammonium chloride, cetyl pyridinium bromide and cetyl trimethyl ammonium bromide. Recently Haydon and Phillips[2] have published some papers dealing, in general, with cationic and anionic detergents. They dealt with Gibbs equation and the surface equation of state for soluble ionized monolayers in absence of added electrolyte at the oil-water interface. They[3] studied the influence of trace of electrolytes on interfacial tension at the oil/water interface for dodecyl trimethyl ammonium bromide and sodium dodecyl sulphate systems. Haydon and Taylor[4] investigated the influence of ionic size on double layer potentials at the oil-water interface. They tested the systems for adsorbed long chain alkyl sulphates in water and of sodium dodecyl sulphate and dodecyl trimethyl ammonium bromide. Biswas and Haydon[5] studied the effect of tetradecyl trimethyl ammonium bromide on the stability of petroleum ether drops at flat surface in 0.1% bovine serum albumin solution and also compared the stability of petroleum ether drops stabilized by 0.1% bovine

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[1] R. K. Neogy and B. N. Ghosh, *J. Indian Chem. Soc.*, **29**, 573 (1952); **30**, 113 (1953).

[2] D. A. Haydon and J. N. Phillips, *Trans. Faraday Soc.*, **54**, 698 (1958).

[3] D. A. Haydon and J. N. Phillips, *Nature*, **178**, 813 (1956).

[4] D. A. Haydon and F. H. Taylor, III Intern. Congress of Surface Activity Cologne, Vol. 2 (1960).

[5] B. Biswas and D. A. Haydon, *Kolloid-Z.*, **185**, 32 (1962).

serum albumin in presence of tetradecyl trimethyl ammonium bromide, with the shear moduli of elasticity of the adsorbed films. Lyklema[6] recieved the factors governing the stability of thin detergent films.

From the survey of the above literature it is concluded that a number of studies have been made covering different aspects of cationic detergents but still there is lack of quantitative data in the light of D.V.O. theory. Therefore, under the present investigation an attempt has been made to study the effect of some cationic detergents *viz.* phenyl trimethyl ammonium chloride (Ammonyx-200), lauryl pyridinium chloride and cetyl pyridinium bromide on emulsion stability in the light of D.V.O. theory and to evaluate van der Waals constant with the help of flocculation data. These studies were made in detail with sodium alginate system only and partially with gum arabic emulsion also.

Experimental

Sodium alginate and gum arabic samples were obtained from B.D.H. A pure sample (99.5%) of phenyl trimethyl ammonium chloride was obtained with the courtesy of Onyx Corporation, U.S.A. A pure sample of lauryl pyridinium chloride (LPC) was supplied by Industrial Products, Bombay, which was further crystallised with acetone. An I.C.I. sample of cetyl pyridinium bromide was used which was recrystallised with acetone.

The emulsion was prepared by dispersing 4% of petroleum ether in aqueous solution of sodium alginate or gum arabic containing 0.01% KCl initially. The counting of the drops for flocculation studies was carried out haemocytometrically as mentioned elsewhere.[7] The electrophoretic measurements were carried out in a rectangular Northrup and Kunitz flat type microcataphoretic cell mounted on the base of the Carl Zeiss Zena microscope. To minimise polarization Ag-AgCl electrodes were used, which were fitted in electrode chambers, filled with electrolyte solution of equiconducting to that of emulsion. A D.C. microammeter of Cambridge Industrial Co., Ltd., England, No. L 32132 was used for measuring the current. The microscope was focussed at stationary level which was obtained by studying the mobilities of particles at different depths which in trun gave a parabolic curve. The mobilities of the particles were measured in direct as well as reverse direction and the mean was taken. The accuracy of the apparatus was 1.0 mV.

From the mobility data, the zeta potentials were calculated by using the Overbeek[8] equation for symmetrical electrolytes, where the relaxation correction has been applied.

$$U=\frac{\epsilon\zeta E}{\sigma\pi\eta}\left[f_1(\kappa a)-Z^2\left(\frac{e\zeta}{kT}\right)^2 f_3(\kappa a)\right.$$
$$\left.-\frac{\rho_+ +\rho_-}{\sigma\pi\eta e}\left(\frac{e\zeta}{kT}\right)^2 f_4(\kappa a)\right]$$

where U, velocity of the particle, ρ_+ and ρ_- the friction constants, η the viscosity of the dispersion medium, k the Boltzmann constant, e the electronic charge. $f_1(\kappa a)$, $f_2(\kappa a)$, $f_3(\kappa a)$, $f_4(\kappa a)$, the Henry functions taken from elsewhere (Overbeek *loc. cit.*).

The interfacial tension measurements were carried out with Du Nouy tensiometer No. 70535 (Central Scientific Co., Chicago, U.S.A.) having an accuracy of 0.1 dyne.

Theory of the Particle Interaction

In the frame work of D.V.O. theory the interaction energy of the colloidal particles is given by $V=V_R+V_A$, where V_A, the attraction energy, V_R, the repuslvie energy and V, the sum of the repulsive and attraction energies. The repulsive energy calculations were carried out by using an approximate expression by Derjaguin and Kussakov.[9]

$$V_R=\frac{\varepsilon a\psi^{\circ 2}}{2}\ln\left(1+e^{-\kappa H}\right) \tag{1}$$

where ψ° the surface potential (assumed equal to the electro-kinetic potential for the present system having $(\kappa a \gg 1)$, ε is the dielectric constant in the double layer, a the particle radius, H the interparticle distance and κ the Debye-Hückel parameter.

The attraction energies were calculated, keeping in view the retardation correction, by equation due to Schenkel and Kitchener.[10]

$$\left.\begin{aligned} V_A &\approx \frac{-Aa}{\pi}\left(\frac{2.45\lambda}{120H^2}-\frac{\lambda^2}{1045H^3}+\frac{\lambda^3}{5.62\times10^4H^4}\right) \\ &\qquad\qquad\qquad\qquad\qquad \text{Valid for } H>150\text{Å} \\ V_A &\approx \frac{-Aa}{12H}\left(\frac{\lambda}{\lambda+3.54H\pi}\right) \qquad \text{Valid for } H<150\text{Å} \end{aligned}\right\} \tag{2}$$

where λ is the wavelength of the London frequency and is taken as 1000 Å, and A is the van der Waals constant.

Thus the interaction energy V can be evaluated. Therefore, knowing V, the number of particles in a shell ds around a central particle and consequently degree of aggregation or the total number of particles associated with a given central particle can be calculated[7] theoretically from the following equation.

$$D=\int 4\pi n_0 a^3 S^2 e^{-V/kT}\,ds \tag{3}$$

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6) J. Lyklema, *Rec. Trav. Chim.*, **81**, 890 (1962).

7) C. Prakash and S. N. Srivastava, This Bulletin, **40**, 1765 (1967).

8) J. Th. G. Overbeek, "Advances in Colloid Science," Vol. III, p. 115.

9) B. Derjaguin and M. Kussakov, *Acta. Phys. Chim., URSS*, **10**, 25 (1939).

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

where n_0 is the number of droplets per unit volume of the emulsion and $s=2+H/a$. The intergrand of the above expression is evaluated graphically and the integration limits are arbitrarily selected. The lower limit is readily chosen keeping in view that at sufficiently small values of s, V becomes strongly positive. Again as $s \to \infty$, $V \to 0$ and the integral tends to infinity. Therefore, the choice of the upper limit is not straightforward. In the present systems, however, V becomes strongly negative in a narrow range of s, and the value of the integral is, for any reasonable choice of the upper limit, approximately constant.

In case of the reversible or secondary minimum flocculation, as in the present system, a singlet-doublet equilibrium temporarily exists in the system and the extent of flocculation in the system can be determined from the formula.

Calculation of Binding Parameters

Binding parameters were calculated from the treatment mentioned earlier[7] and the important equations are presented below

$$\sigma_s = \frac{N_1 e v}{1+\frac{55.6}{C}\exp\left(\frac{\Delta G}{kT}\right)} \tag{4}$$

where σ_s, the charge density of the Stern layer, e the electronic charge, v valency of the cation, c the molar concentration of the added electrolyte, N_1 the binding sites per cm^2 and $-\Delta G$ is the free energy of adsorption per molecule.

This can be put in the form

$$\sigma_s = \frac{k_1 c}{1+k_2 c}$$

$$\text{where} \quad \left.\begin{aligned} k_2 &= \frac{\exp\left(\frac{-\Delta G}{kT}\right)}{55.6} \\ k_1 &= N_1 k_2 e v \end{aligned}\right\} \tag{5}$$

These k_1 and k_2 are the adsorption constants which can be calculated from the following equations at the zero point of charge, which finally yields the following equations

$$\frac{1}{c} = \left(\frac{4\pi e v N_1 k_2}{\kappa \varepsilon \psi_\delta^\circ} - k_2\right) \tag{5}$$

$$\left(\frac{d\psi_\delta^\circ}{d \ln c}\right)_{\psi_\delta^\circ=0} = \left(\frac{\kappa\varepsilon\psi_\delta^\circ}{4\pi e v k_1} - 1\right)\psi_\delta^\circ \tag{7}$$

where v is the valency and $\left(\frac{d\psi_\delta}{d\ln c}\right)\psi^\circ_{\delta=0}$ is the slope of the log C-zeta potential curve (assuming $\psi_s^\circ = \zeta^\circ$), c is the concentration of the electrolyte at the zero point charge.

Computation of van der Waals Constant

Hamaker[11] suggested that van der Waals constant can be calculated from the following equation

$$A_{ii} = \pi^2 q_i^2 B_i \tag{8}$$

where q_i is the number of atoms of kind i contained in 1 ml of the matter. B_i is the London constant relative to the same substance, which is to be computed separately. But in the present system since the petroleum ether (p.e.), instead of being separated by a vacuum, is immersed in an aqueous medium, the net constant is given by following equation.[12]

$$A = (A^{1/2}_{\text{p.e.}-\text{p.e.}} - A^{1/2}_{\text{H}_2\text{O}-\text{H}_2\text{O}}) \tag{9}$$

The London constant, B can be calculated by four approximate formulae (a) The London equation[13]

$$B_{\text{L}} = \frac{3}{4}\alpha^2 h v_0 \tag{10}$$

Where v_0 is the characteristic London frequency corresponding to the rotation of peripheral electrons and α is the polarisability.

(b) The Slater-Kirkwood equation[14]

$$B_{\text{S-K}} = 11.25 \times 10^{-24} \cdot n^{1/2} \cdot \alpha^{3/2} \tag{11}$$

where n, number of valency electrons.

(c) The Slater-Kirkwood equation modified by Moelwyn-Hughes[15]

This new equation takes into account the effective number of dispersion electrons, S_1, thereby leading to

$$B_{\text{S-K-M}} = \frac{3}{4}\sqrt{S_1 n} \cdot h v_e \alpha^2$$

where v_e, the electronic vibration frequency is given by

$$v_e = \frac{2532}{\sqrt{\alpha}}$$

and S_1, is given by an empirical equation,

$$S_1 = 0.39n$$

$$B_{\text{S-K-M}} = 7.8 \times 10^{-24} \times n \cdot \alpha^{3/2} \tag{12}$$

(d) The Neugebaur, equation[16]

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[11] H. C. Hamaker, cited in "Theory of Stability of Lyophobic Colloids," Elsevier Publishing Co., Amsterdam (1948).

[12] H. C. Hamaker, *Physics*, **4**, 1058 (1937).

[13] F. London, *Z. Physik*, **63**, 245 (1930).

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

[15] Moelwyn-Hughes, "Physical Chemistry," Pergamon Press, London, pp. 383, 1957.

[16] Th. Neugebaur, *Z. Physik*, **167**, 785 (1937).

$$B_N = -1.62\times10^{-6}\cdot\alpha\chi \qquad (13)$$

where χ being the diamagnetic susceptibility.

As mentioned before, the calculation of van der Waals constant from Eqs. (10)—(13) requires the polarisability which has been calculated from the Clausius-Mosotti equation[17] modified by Moelwyn-Hughes (*loc. cit.*),

$$\alpha = \frac{3M}{4\pi Nd}\cdot\frac{\rho^2-1}{\rho^2+1}\cdot\frac{v_0{}^2-v^2}{v_0{}^2} \qquad (14)$$

where M, the molecular weight, N the Avogadro number and ρ is the index of refraction at the London wavelength. Since the refractive index is not directly available at the London wavelength, the quantity, $\frac{v_0{}^2-v^2}{v_0{}^2}$ is the extrapolation factor for ρ determined at the frequency. The latter quantity in its turn is also determined indirectly from the dispersion equation of Sellmeier[18] *viz.*

$$\rho^2-1 = \frac{C\lambda^2{}_1}{\lambda_1{}^2-\lambda_0{}^2}$$

where λ_1 and λ_0 are respectively the wavelengths of light and of the characteristic absorption bands and C is a constant. It is obvious that to solve such equation, refractive indices at least for two wavelengths are required. For this the refractive index of petroleum ether was measured spectrometrically at 4047 Å, 4358 Å, 5461 Å and 5770 Å and corresponding indices were found to be 1.419, 1.4155, 1.408 and 1.405 respectively. Feeding these values into the above equation λ_0 can be evaluated. The value of v_0 obtained from λ_0 is 2.50×10^{15} cm/sec. This leads to a value of the extrapolation factor to be 0.957 at 5770 Å. Thus the value of ρ for the calculation of α has been taken as 1.4056 at 5770 Å.

The molecular weight of petroleum ether has been taken as 100 which agrees with the observed value (98.5) of molecular weight determined cryoscopically. The observed value of density (d) is 0.72 at 25°C. The value of α found in this manner is 1.635×10^{-23} cm³/mol.

For calculating the London constant α, h and v_0 are available and with the proper choice of units the London constant is

$$B_{\mathrm{L}_{\mathrm{p.e.}}} = \frac{3}{4}(1.635\times10^{-23})^2\times6588\times10^{-27}\times2.5\times10^{15}$$

$$= 3.277\times10^{-57}\ \mathrm{erg\cdot cm^6}$$

$$B_{\mathrm{S-K}_{\mathrm{p.e.}}} = 11.25\times10^{-24}\times(8)^{1/2}\times(1.635\times10^{-23})^{3/2}$$

$$= 2.10\times10^{-57}\ \mathrm{erg\cdot cm^6}$$

where n, the number of electrons is 8, assuming that the petroleum ether molecule is composed of CH_4. Further

$$B_{\mathrm{S-K-M}_{\mathrm{p.e.}}} = 7.8\times10^{-24}\times8\times(1.635\times10^{-23})^{3/2}$$

$$= 4.12\times10^{-6}\times1.635\times10^{-23}$$

$$\times(-0.88\times10^{-6})\times\frac{100}{6\times10^{23}}$$

$$= 3.73\times10^{-57}\ \mathrm{erg\cdot cm^6}$$

where the value of the specific susceptibility is -0.88×10^{-6} cgs units.[19]

The corresponding values of these constant for water with $=1.43\times10^{-24}$ cm³/mol, $n=8$, $\chi=0.72\times10^{-6}$ cgs units as given by Verwey and Overbeek[20]

$$B_{\mathrm{L}}^{\mathrm{H_2O}} = 3.30\times10^{-59}$$

$$B_{\mathrm{S-K}}^{\mathrm{H_2O}} = 5.40\times10^{-59}$$

$$B_{\mathrm{S-K-M}}^{\mathrm{H_2O}} = 7.28\times10^{-59}$$

$$B_{\mathrm{N}}^{\mathrm{H_2O}} = 5.10\times10^{-59}$$

now by finding q (4.34×10^{21}), the number of molecules of petroleum ether contained per ml from the knowledge of its molecular weight and density with the help of Eq. (8), the van der Waals constant for petroleum ether and corresponding constants for water can be calculated and hence net attraction constant for petroleum ether drops can be estimated from Eq. (9). The results are summarised in Table 1, where in the last column a correction has been made for the reduction of London force due to its transmission through a medium whose dielectric constant is not equal to unity. This is done by dividing the constant A by 1.8, the square of the refractive index of water, 1.36. The mean of the first three readings was taken because fourth is very low.

The mean value of van der Waals constant thus obtained is 6.7×10^{-14} erg, which will be taken for calculation of interaction profiles.

Results and Discussion

(a) Particle Size. For particle size of the drops the microphotographs were taken with Olympus camera at 15×40 magnification. These were further enlarged four times. From the each photograph the size frequency curves were plotted by measuring the size of about 500 drops. The average size for sodium alginate is 1.0 μ and for gum arabic is 1.2 μ. The size frequency curve of

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[17] Ref. 15.

[18] W. Sellmeier, *Pogg. Ann.*, **143**, 272 (1871); "The Science and Petroleum," A. E. Dunsten *et al.*, Oxford University, London, **2**, 1141 (1938).

[19] International Critical Table, **6**, 362 (1929).

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

Table 1

Equation used	$A_{p.e.-p.e.}$ in vacuum $\times 10^{13}$ erg	$A_{H_2O-H_2O}$ $\times 10^{13}$ erg	A in H_2O $\times 10^{14}$ erg	A (corrected) $\times 10^{14}$ erg
S-K	1.34	5.95	16.5	9.16
S-K-M	2.64	7.70	13.2	7.33
N	2.39	5.61	6.2	3.44
L	2.10	3.66	2.2	1.22
				Mean of the first three values=6.7

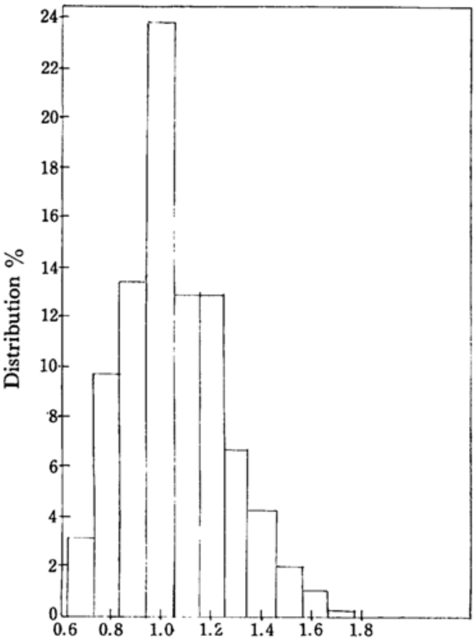

Fig. 1. Particle size distribution of sodium alginate emulsion.
mean diameter$=1.0\ \mu$

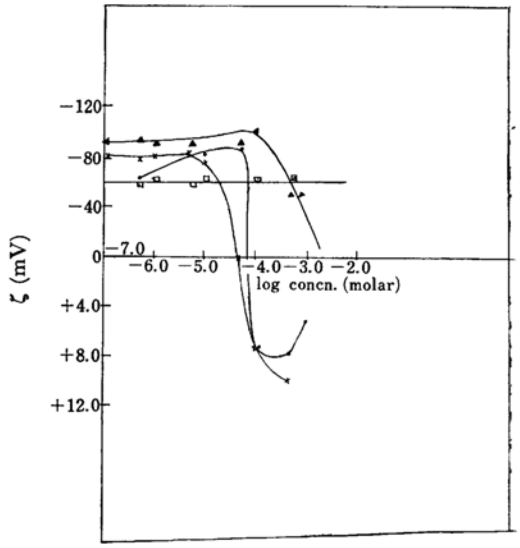

Fig. 2. Zeta potentials as a function of log concentration (molar) of cationic detergents.
Sodium alginate
(•) Lauryl Pyridinium chloride
(×) Cetyl Pyridinium bromide
(▲) Phenyl trimethyl ammonium chloride
Gum arabic
(⊡) Lauryl Pyridinium chloride

sodium alginate is shown in Fig. 1.

(b) Effect of Cationic Detergents on Zeta Potential. The zeta potentials of stabilised emulsions by sodium alginate and gum arabic were measured in the presence of cetyl pyridinium bromide (CPB, $C_{16}H_{33}C_6H_5NBr$), lauryl pyridinium chloride (LPC, $C_{12}H_{25}C_6H_5NCl$) and phenyl trimethyl ammonium chloride (Ammonyx-200, $C_6H_5N(CH_3)_3Cl$). In Fig. 2 the plots of zeta potential against log molar concentration are given for sodium alginate and gum arabic systems.

The curves obtained, in general, are of inverted S-shape. It can be seen that only LPC and CPB could reverse the charge of sodium alginate system. The effect of LPC on gum arabic emulsion was studied only. An appreciable change in zeta potential could not be observed even upto 1 mM of it. The relevant data are presented in Table 3. Ammonyx-200 could not reverse the charge even upto 10^{-2}M, exhibiting thereby its weak efficacy. With increasing concentration of LPC and CPB, the zeta potential decreases continuously but at higher concentrations the charge of the system is reversed. After reversal of charge the absolute value of the zeta potential again increases with increasing concentration and the system again acquires stability, though the emulsion globules are now positively charged. During this the critical micelle concentrations of the surfactants are also reached. These variations in stability can be explained as follows. It is likely that during the addition and mixing concentrated solution of detergent to the system conditions could occur in which the micellar solution of the detergent became submicellar. The breaking down of micelles to submicelles is a very fast reaction.[21] The time required during mixing the detergent to the system is of the same order as required for breaking down of the micelles, mutual coagulation would occur between the micelles and the stabilised emulsion drops resulting in an artificial decrease in stability.

Ammonyx-200 seems to have a very weak cationic efficacy. The ζ-potential increased with increasing concentration of the detergent and then a continuous decrease is obtained. This behaviour has got close analogy with 1 : 1 electrolytes.

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21) R. H. Ottwill and M. C. Rastogi, *Trans. Faraday Soc.*, **56**, 866 (1960).

(c) Determination of Flocculation Concentration and Calculation of Some Binding Constants. The flocculating concentrations obtained at the zero point of charge are presented in respective Table 2. From the flocculating concentrations it is obvious that the capacity for reversing the charge is CPB, LPC, Ammonyx-200 because the carbon chain lengths are in decreasing order and hence their CMC values are expected to be in increasing order. Therefore, the concentrations required for flocculation should be in increasing order as the carbon chain decreases.

The low flocculating concentrations are in accordance with the idea that coagulation under these conditions is due to the adsorption of the cationic surface active agent on the negatively charged drops. At low detergent concentrations adsorption appears to occur by interaction of the positively charged head group of the molecules. Thus increasing chain length decreases the available area for adsorption and hence decreases the flocculation concentration. Therefore, CPB with larger chain length is more effective than LPC. Bromide and chloride ions have little influence on the process.[21] The same interpretation can be given for Ammonyx-200 also.

The binding constant k_1, k_2, number of binding sites available N_1, and free energy of adsorption $-\Delta G$ were calculated with the help of flocculating concentration and the slope of the log concentration-zeta potential curve. The calculated values are presented in the Table 2.

From the values of the number of binding sites, in case of these detergents, it is evident that LPC and CPB are having fewer number than Ammonyx-200 which clearly shows that number of sites available would depend upon its capacity for charge reversal. Thus Ammonyx-200 could not reverse the charge in spite of adding upto 1×10^{-3}M concentration while in the case of others of the order of 10^{-5}M is quite sufficient. The low value of the free energy is in conformity with the value that Ammonyx-200 is a weak cationic detergent. The greater number of cations is required to reverse the charge if cations have got low free energy of adsorption.

(d) Interfacial Tension Measurements in Presence of Cationic Detergents. Since interfacial tension has some bearing on the stability of emulsion, it was thought of interest to make some interfacial tension measurements also in the presence of cationic detergents on sodium alginate system. The interfacial tension studies were carried out in the presence of 0.01% KCl and 0.01% sodium alginate in aqueous phase. The cationic detergents used were LPC and CPB. The interfacial tension in dynes/cm is plotted against log molar concentration in Fig. 3.

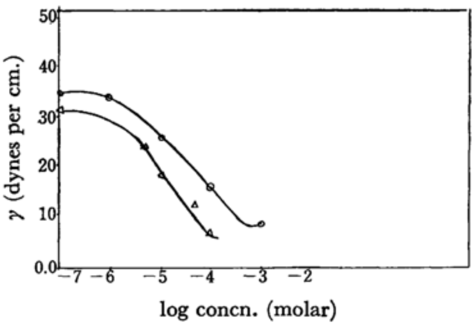

Fig. 3. Interfacial tension of sodium alginate emulsions as a function of cationic detergents.
(⊙) Lauryl pyridinium chloride
(△) Cetyl pyridinium bromide

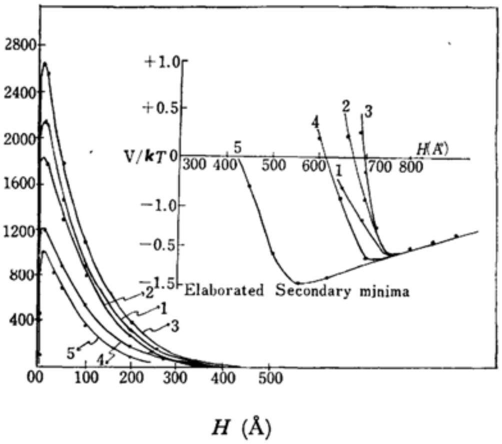

Fig. 4. Plot of interaction energy *versus* interparticle distance for sodium alginate emulsions flocculated by lauryl pyridinium chloride.

(1) 1×10^{-7}M	(4) 1×10^{-4}M
(2) 1×10^{-6}M	(5) 1×10^{-3}M
(3) 1×10^{-5}M	

TABLE 2

Detergent	Flocculating concentration	k_1	k_2	N_1 groups/cm^2	$-\Delta G$ kcal/mol
Sodium alginate system					
LPC	8.1×10^{-5}M	2.84×10^7	3.70×10^4	1.60×10^{12}	7.92
CPB	5.0×10^{-5}M	2.26×10^6	1.24×10^4	3.80×10^{11}	8.58
Gum arabic system					
LPC	Charge reversal is not obtained up to the concentration of 5.0×10^{-4}M.				

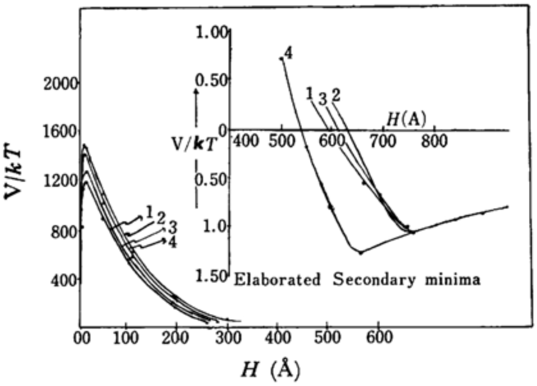

Fig. 5. Plot of interaction energy *versus* interparticle distance for gum arabic emulsions flocculated by lauryl pyridinium chloride.
(1) 5×10^{-7}M (3) 1×10^{-4}M
(2) 1×10^{-5}M (4) 5×10^{-4}M

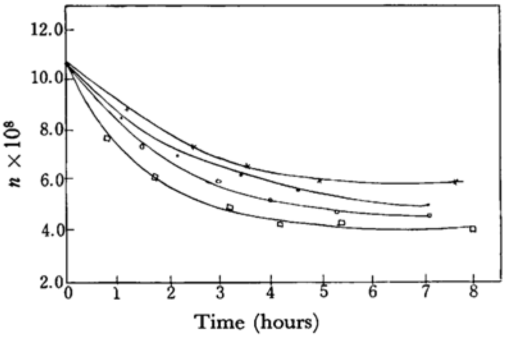

Fig. 6. Plot of number of individual drops against time for sodium alginate emulsions flocculated by lauryl pyridinium chloride.
(•) Zero, (□) 1×10^{-6}M, (○) 1×10^{-5}M,
(×) 1×10^{-3}M

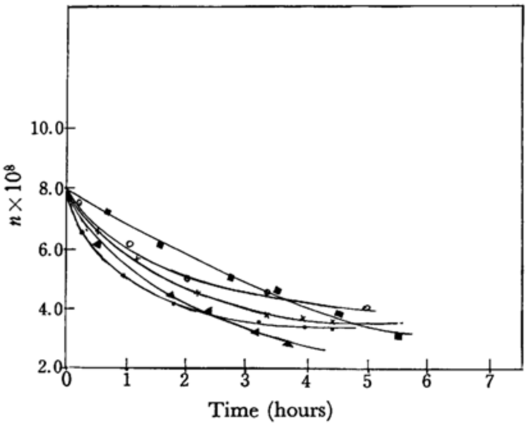

Fig. 7. Plot of number of individual drops against time for gum arabic emulsions flocculated by lauryl pyridinium chloride.
(•) Zero, (■) 1×10^{-7}M, (▲) 1×10^{-6}M,
(×) 1×10^{-5}M, (⊙) 5×10^{-5}M

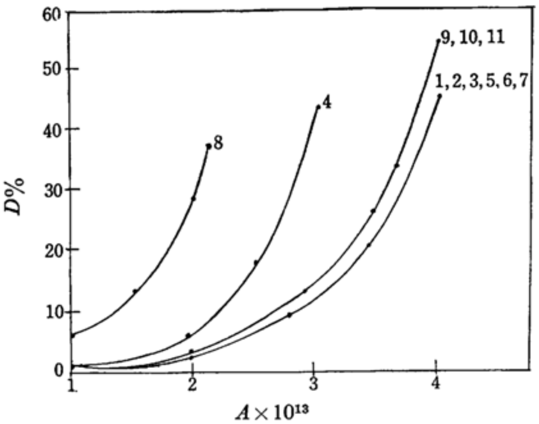

Fig. 8. Degrees of flocculation as a function of van der Waals constant for sodium alginate system.
1, 2, 3 for 10^{-7}M, 10^{-6}M, 10^{-5}M Lauryl pyridinium chloride.
4 for 10^{-3}M Lauryl pyridinium chloride.
5, 6, 7 for 10^{-7}M, 10^{-6}M, 10^{-5}M of cetyl pyridinium bromide
8 for 10^{-4}M of cetyl pyridinium bromide
9, 10, 11 for 10^{-7}M, 10^{-6}M, 10^{-5}M of Ammonyx-200

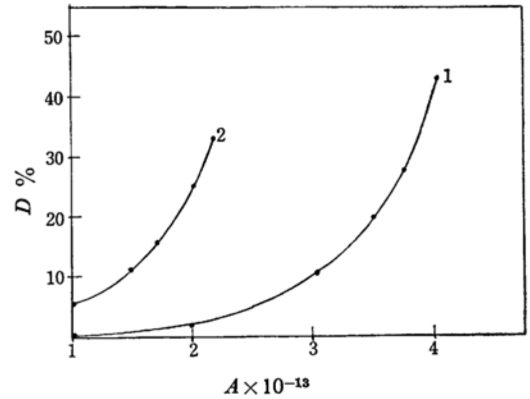

Fig. 9. Degrees of flocculation as a function of van der Waals constant for gum arabic emulsions.
1 for 10^{-5}M Lauryl pyridinium chloride
2 for 5×10^{-5}M Lauryl pyridinium chloride

From the figure it is obvious that the interfacial tension, at lower concentrations, does not change much but at higher concentrations the fall is rapid.

(e) Interaction Energy Curves, the Degrees of Aggregation and the van der Waals Constant of the Emulsion Droplets. The interaction energies between two drops at different concentrations of Ammonyx-200, LPC and CPB have been calculated with the help of corresponding zeta potentials. These energies, for $La(NO_3)_3$, are plotted against distance in Figs. 4 and 5 choosing as representative curves for sodium alginate and gum arabic systems. The relevant data for all the curves are presented in Table 3. From the table it is obvious that the energy barrier in each

TABLE 3

Detergent concentration molar	Zeta potential mV	Height of maxima kT	Interparticle distance at $V=0$ (graphically) Å
For sodium alginate emulsion			
Cetyl pyridinium bromide			
1×10^{-7}	-81.0	2481.5	670
1×10^{-6}	-80.3	2401.5	670
1×10^{-5}	-75.8	2146.5	620
1×10^{-4}	$+75.0$	2134.5	625
Lauryl pyridiniym chloride			
1×10^{-7}	-57.0	1163.5	570
1×10^{-6}	-69.3	1788.0	650
1×10^{-5}	-82.7	2585.0	670
1×10^{-4}	$+76.0$	2134.5	620
Ammonyx-200			
1×10^{-7}	-90.0	2469.0	670
1×10^{-6}	-92.0	3236.0	720
1×10^{-5}	-60.0	1296.5	630
1×10^{-3}	-57.9	2361.5	625
For gum arabic emulsion			
Lauryl pyridinium chloride			
1×10^{-5}	-64.0	1444.5	650
1×10^{-4}	-61.1	1241.5	580
1×10^{-4}	-63.0	1391.5	610

TABLE 4

Concentration of the detergent	$D\%$ observed	Value of A corresponding to $D\%$ observed $A\times10^{13}$ erg	Mean value
Sodium alignate emulsion			
Ammonyx-200			
1×10^{-7}M	18.7	3.16	
1×10^{-6}M	18.0	3.30	
1×10^{-5}M	16.4	3.07	
CPB			
1×10^{-7}M	13.1	3.05	3.03×10^{-13} erg
1×10^{-6}M	16.0	3.20	3.0×10^{-13} erg
1×10^{-5}M	13.5	3.10	
1×10^{-4}M	12.4	3.05	
LPC			
1×10^{-7}M	13.0	3.05	
1×10^{-6}M	14.1	3.10	
1×10^{-5}M	10.9	2.95	
1×10^{-3}M	12.1	2.30	
Gum arabic emulsion			
LPC			
1×10^{-5}M	15.9	3.30	2.6×10^{-13} erg
5×10^{-5}M	17.9	1.80	

case is very high, which obviated the possibility of occurrence of flocculation in the primary minima. The observed flocculation occuring in the system is only possible in secondary minimum. All the curves are levelled off after certain time indicating the flocculation in secondary minima. To indicate the nature of flocculation occurring in the systems, the monomers and dimers were counted at different intervals. The number of monomers are plotted against time and two representative set of curves for both the systems are shown in Figs. 6 and 7. Therefore, these secondary minima, which are of main importance, are depicted separately. These secondary minima are a few kT deep. These depths though sufficient for the occurrence of secondary minima flocculation are rather insufficient to explain the observed degrees of aggregation. This apparent discrepancy may be due to not choosing the correct (operating value) of A. Therefore, an indirect method of estimating A has been adopted. To estimate van der Waals constant of the system, the theoretical degrees of aggregation were calculated at dirrerent values of A at different concentration of the detergents. These observed degrees of aggregation were interpolated in the theoretical curves, as shown in Figs. 8 and 9, and

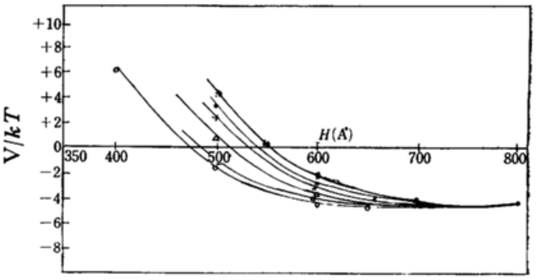

Fig. 10. Plot of secondary minima with observed value of van der Waals constant for sodium alginate.
(●) 1×10^{-7}M Cetyl pyridinium bromide
(×) 1×10^{-5}M Cetyl pyridinium bromide
(○) 1×10^{-7}M Lauryl pyridinium chloride
(△) 1×10^{-6}M Lauryl pyridinium chloride
(※) 1×10^{-7}M Ammonyx-200
(□) 1×10^{-5}M Ammonyx-200

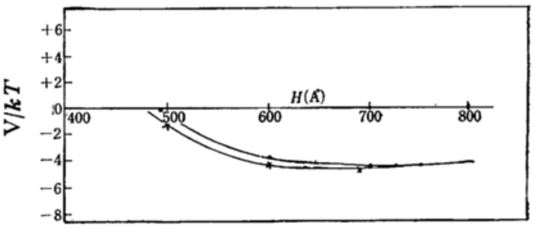

Fig. 11. Plot of secondary minima with observed value of van der Waals constant for gum arabic.
(•) 1×10^{-5}M Lauryl pyridinium chloride
(×) 1×10^{-4}M Lauryl pyridinium chloride

the corresponding values of A obtained are tabulated in Table 4.

The theoretical and experimental degrees of aggregation were calculated similarly as mentioned before. The van der Waals constants for sodium alginate and gum arabic systems are 3.0×10^{-13} erg and 2.6×10^{-13} erg respectively. The van der Waals constant of petroleum ether differs from the theoretical value (6.7×10^{-14} erg) of A, probably because of the difference between adsorption of an emulsifier and that of detergent.22) The secondary minima are plotted with the revised value of A, which are sufficiently deep to warrant reversible flocculation (Figs. 10 and 11).

The authors wish to express the thanks to Professor B. N. Ghosh, Calcutta University for kindly allowing one of them to carry out microelectrophoresis and also to the authorities of C.S.I.R., New Delhi for kindly granting a fellowship to one of them (C.P.).

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