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Effect of Cationic Detergents on the Lecithin Stabilized O/W Emulsion

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An oil-in-water system (Nujol being the oil phase) stabilized by the phospholipid, lecithin, has been chosen in this study. The system being negatively charged initially, cationic detergents like lauryl pyridinium chloride (LPC), Cetyl pyridinium bromide (CPB), Phenyl trimethyl ammonium chloride (Ammonyx-200) and Cetyl dimethyl benzyl ammonium chloride (CDBAC) have been employed in order to study their influence on the flocculation and coalescence rates and the degree of aggregation haemocytometrically. Zeta potentials (ξ) have been determined at the corresponding concentrations of the detergents by microcataphoresis and with these values the potential energies and then ultimately the operating van der Waals constant of the system has been determined. From the log C-ξ values it is evident that except Ammonyx-200 which is not an effective cationic detergent, all the others have reversed the charge of the system and their efficiencies are in the order CDBAC>CPB>LPC. The different binding parameters, number of binding sites available for adsorption and free energy of the surface have also been calculated.

The practical utility of detergents in technological field as well as in experimental studies is well known because of their surface activity. Of late much attention is being paid to probe into the more and more complicated structural aspects of these detergents and their molecular orientation on the surfaces and allied aspects. The relative efficiencies of these detergents depend on their carbon chain length and the corresponding adsorbabilities of these complex ions on the surfaces. Cationic surface-active agents are characterised by the fact that the hydrophobic grouping is found in the cation.

In the present studies some of the cationic detergents have been tried in the studies of oil-in-water emulsions stabilised by lecithin, an important phospholipid, which acts as an emulsifying agent in aqueous medium alone and promotes O/W emulsions in the same way as do proteins. Although many earlier workers[1–7] have tried to use different types of detergents in various O/W-W/O systems, the non-availability of adequate quantitative data with particular reference to the modern theory of colloid stability developed independently by Derjaguin, Verwey and Overbeek (DVO theory),[8–11] prompted us to take up these investigations with the phospholipid as an emulsifying agent in O/W system where Nujol has been chosen as the oil phase. In a previous communication,[12] the effect of inorganic cations has been tried with the same system and this is an extension with complex cationic detergents.

Zeta potentials have been determined at the corresponding concentrations of the detergents where degree of aggregation has been studied haemocytometrically, by microcataphoresis. With these values, the potential energies and then the operating van der Waals constant have been obtained. The binding parameters, number of binding sites available and the free energy of adsorption were also calculated with the electrokinetic data.

Experimental

Materials. The emulsifying agent, lecithin was of BDH quality and the oil phase which consisted of a mixture of Nujol and chlorobenzene were of Ward, Blenkinsop and Co. Ltd., and Polshic Odezymiki Chemiezue, Gliwico (Poland) respectively. Nujol was purified with NaOH.[13]

The detergents lauryl pyridinium chloride (LPC) and cetyl dimethyl benzyl ammonium chloride (CDBAC) were obtained from Industrial Chemical Products, Bombay and further purified with acetone and alcohol respectively. Cetyl pyridinium bromide (CPB) given by I.C.I. (India) was also purified with acetone. Ammonyx-200 (Phenyl trimethyl ammonium chloride) was from Onyx Corporation (U.S.A.) and not further purified. Pyrex galssware and double distilled water were used throughout the studies.

Experimental Methods. The emulsion was prepared by taking 1% of oil (a mixture of 5 parts of Nujol and 6.25 parts of chlorobenzene) containing 1% of emulsifying agent *i. e.*, lecithin with aqueous KCl (0.01 M). The mixture was shaken for a few minutes and homogenised with the hand operated stainless steel homogenizer. (Fisher Scientific Co., U.S.A.). In all the estimations emulsion was prepared under identical conditions.

Flocculation studies were carried out by taking a sample of the emulsion on a double Neubauer model haemocytometer and the counts were taken in 32 squares of the graticule fitted in the eye-picee (each square corresponds to a volume of 7.74×10^{-7} m*l*) with the help of a tally counter under an Olympus microscope (15×62 times magnification). A duplicate counting was always done and the average was taken, the reproducibility being about 5%. The size of the emulsion drops was determined to be 0.70μ dia. from the size frequency analysis of a microphotograph. The electrokinetic potentials were determined by microcataphoresis at a constant temperature of 30°C.

Calculations

The following theoretical aspects were considered before explaining the results of these investigations. In order to apply the D.V.O. theory to the present system, the interaction energy of a colloidal system is given by $V=V_R+V_A$ where V_R is the repulsive energy, V_A is the attraction energy and V is the sum of the two. These two types of energies were calculated with the following Eq.[14]

$$V_R = \frac{\epsilon a \psi_0^2}{2} \ln(1+e^{-\chi H}) \tag{1}$$

$$V_A = \frac{-Aa}{12H} \tag{2}$$

where ψ_0 is the surface potential (assumed equal to the electrokinetic potential for the present system having $\chi a \rangle\rangle 1$), ε the dielectric constant in the double layer (assumed equal to the bulk value 80 of that of water), a the particle radius, H the interparticle distance, χ the Debye-Hückel parameter, and A the van der Waals constant which is taken to be equal to 2.0×10^{-13} erg.

The theoretical degree of aggregation is evaluated as a function of A from the formula.[15]

$$D = 4\pi a^3 n_0 \int S^2 \exp\left(-\frac{V}{kT}\right) \mathrm{d}s \tag{3}$$

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1) M. Limburg, *Rec. Trav. Chim.*, **45**, 772, 875 (1926).

2) J. Powney and L. J. Wood, *Trans. Faraday Soc.*, (1941).**37**, 152

3) A. E. Alexander, "Colloid Science Course," Cambridge (1945), p. 25.

4) B. D. Powell and A. E. Alexander, *Can. J. Chem.*, **30**, 1044 (1962).

5) Van den Tempel, "Stability of oil-in-water emulsions," Rubber Stichting, Oostingel, 179, Delft (Holland) 1953.

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7) H. A. Abramson and R. H. Ottewill, R. H. *J. Colloid Sci.*, **17**, 883 (1962).

8) B. V. Derjaguin, *Trans. Faraday Soc.*, **26**, 203, 730 (1940).

9) B. V. Derjaguin, *J. Expt. Theort. Phys. U.S.S.R.*, **11**, 802 (1941).

10) B. V. Derjaguin and L. D. Landau, *Acta Physico. Chim.*, **14**, 633 (1941).

11) E. J. W. Verwey and J. Th. G. Overbeek, "Theory of Stability of Lyophobic Colloids" Elsevier, Amsterdam (1948).

12) T. G. Sastry and S. N. Srivastava, *Ind. J. Chem.* (under publication).

13) D. K. Chattoraj and H. B. Bull, *J. Phys. Chem.*, (1959).

14) B. V. Derjaguin and M. M. Kussakov, *Acta. Phys. Chim., U.R.S.S.*, **10**, 25, 153 (1939).

15) Ref. 11, p. 183.

TABLE 1

Detergent	Formula	Concentration at zero point charge
Ammonyx-200	$C_6H_5N(CH_3)_3Cl$	No reversal of charge even after the addition of $1.0\times10^{-1}\%$ (5.83×10^{-3} M)
LPC	$C_{12}H_{25}$–C_6H_5NCl	7.95×10^{-5} M
CPB	$C_{16}H_{33}$–C_6H_5NBr	6.31×10^{-5} M
CDBAC	$C_{16}H_{33}$–$N(CH_3)_2$–CH_2–C_6H_5Cl	1.0×10^{-6} M

where n_0 is the equilibrium number of unassociated particles and $S=2+H/a$. The integration of the above expression is evaluated graphically. The degrees of aggregation thus obtained are plotted against A values and from the graphs correct values of A are determined by interpolation of observed degree of aggregation determined haemocytometrically.

The extent of reversible flocculation can be calculated from the formula.

$$D=\frac{\text{Number of doublets}}{\text{Number of doublets + Number of singlets}} \tag{4}$$

where D is the number of particles associated with a specific particle *i. e.* the degree of aggregation. Here the singlet means one oil globule which is unassociated and doublet means the combination of two singlets *i. e.*, just flocculated but no coalesced.

From the mobility data, the potentials were calculated by using the Overbeek equation[16] for symmetrical electrolytes, where the relaxation correction has been applied as the particle was small.

$$U=\frac{\varepsilon\zeta E}{6\pi\eta}\left[f_1(\chi a)-\mathcal{Z}^2\left(\frac{e\zeta}{kT}\right)^2 f_3(\chi a)\right.$$
$$\left.-\frac{\rho_+ +\rho_-}{6\pi\eta e}\left(\frac{e\zeta}{kT}\right)^2 f_4(\chi a)\right] \tag{5}$$

where U, velocity of the particle (average of 10 readings was taken), ρ_+ and ρ_- the friction constants, η the viscosity of the dispersion medium, k the Boltzmann constant, e the electronic charge, $f_1(\chi a)\cdots f_4(\chi a)$ the functions taken from Table 2 (Overbeek *loc. cit.*).

The charge density of an emulsion droplet by adding small quantities of cationic detergents which are likely to adsorb is given by Stern equation.[17]

$$\sigma_s=\frac{\mathcal{N}_1 e z}{1+\dfrac{55.6}{c}\exp\left(\dfrac{\varDelta G}{kT}\right)} \tag{6}$$

where c is the molar concentration of the added detergent, $\mathcal{N}_1$ the binding sites per cm^2 and $\varDelta G$ is the free energy of adsorption per molecule. The same equation can be written in the form (*cf.* Wilkins *et al.*[18] and Ottewill *et al.*[6])

$$\sigma_s=\frac{K_{1c}c}{1+K_2c} \tag{7}$$

where $K_2=\dfrac{e^{-\varDelta G/kT}}{55.6}$ and $K_1=\mathcal{N}_1K_2ez$.

K_1 and K_2 are the adsorption constants which have been calculated from the treatment given by Srivastava[19] at zero point of charge which finally yields the following equations.

$$\frac{1}{c}=\frac{4\pi ze\mathcal{N}_1k_2}{\chi\varepsilon\psi_0\delta}-k_2 \tag{8}$$

$$\left(\frac{d\psi\delta}{d\ln C}\right)_{\psi_0\delta=0}=\left(\frac{\chi\varepsilon\psi\delta}{4\pi ez\mathcal{N}_1}-1\right)_{\psi_0\delta} \tag{9}$$

where z is the valency and $\left(\dfrac{d\psi\delta}{d\ln C}\right)_{\psi_0\delta=0}$ is the slope of the loc C-zeta potential curve (assuming $\psi_0{}^\delta=\zeta$), C the concentration of the detergents at the zero point of charge.

Results and Discussion

(a) Effect of Detergents on Flocculation. The flocculation of the emulsion droplets has been studied by adding different concentrations of the four detergents and counting the number of singlets

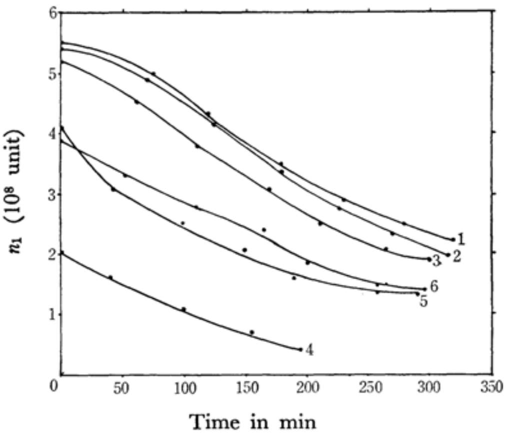

Fig. 1. Plots of time and number of monomers/m*l* (*n*: 10^8 unit) (which are not flocculated) at different concentrations of CPB.
(1) 1.0×10^{-6} M (2) 5.0×10^{-6} M (3) 1.0×10^{-5} M (4) 1.0×10^{-4} M (charge reversal range) (5) 5.0×10^{-4} M (6) 1.0×10^{-3} M

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16) J. T. G. Overbeek, "Advances in Colloid Science," Vol. III (1950), p. 114.

17) D. J. Z. Stern, *Electro Chem.*, **30**, 568 (1924).

18) Wilkins *et al.*, *J. Theorot. Biol.*, **2**, 173, 186 (1962).

19) S. N. Srivastava, *J. Ind. Chem. Soc.*, **41**, 203 (1964).

and doublets present at various intervals of time. The initial particle concentration of the emulsion was found to be 8.05×10^8 globules/m*l*. Graphs have been plotted between the number of particles (n_1: 10^8 unit) and time. Here only one of the typical graphs (graph 1) obtained from CPB has been given. From the graph it is evident that with increase in concentration of detergent the number of particles decrease gradually and almost attains constancy after some time which shows that reversible flocculation occurs in the system. At comparatively higher concentration the charge reversal takes place and the number of particles suddenly decreases implying thereby that coalescence is appreciable.

(b) Effect on Zeta Potential. Changes in zeta potentials by the addition of these above mentioned cationic detergents have been studied. In our present investigations the pH of the emulsion after the addition of detergents being almost neutral, lecithin is not exhibiting any positive charge as was found by Hanai *et al.*[20] in the acidic range. On the other hand, the slight positive charge of tetramethyl amino group appears to be internally neutralised when it is taken in Nujol and its predominant negative bearing phosphotydal group seems to be contributing to the overall negative charge of the emulsion. So these cationic detergents have been used in flocculation as well as in electrokinetic potential determinations. The corrected zeta values were plotted against the

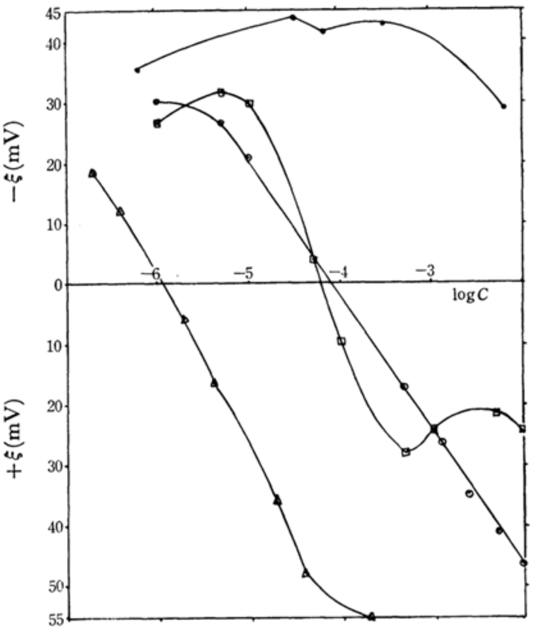

Fig. 2. Plots of log concentration (molar) *vs.* zeta potential (mV) ◎ LPC, ⊡ CPB, ● Ammonyx-200, △ CDBAC.

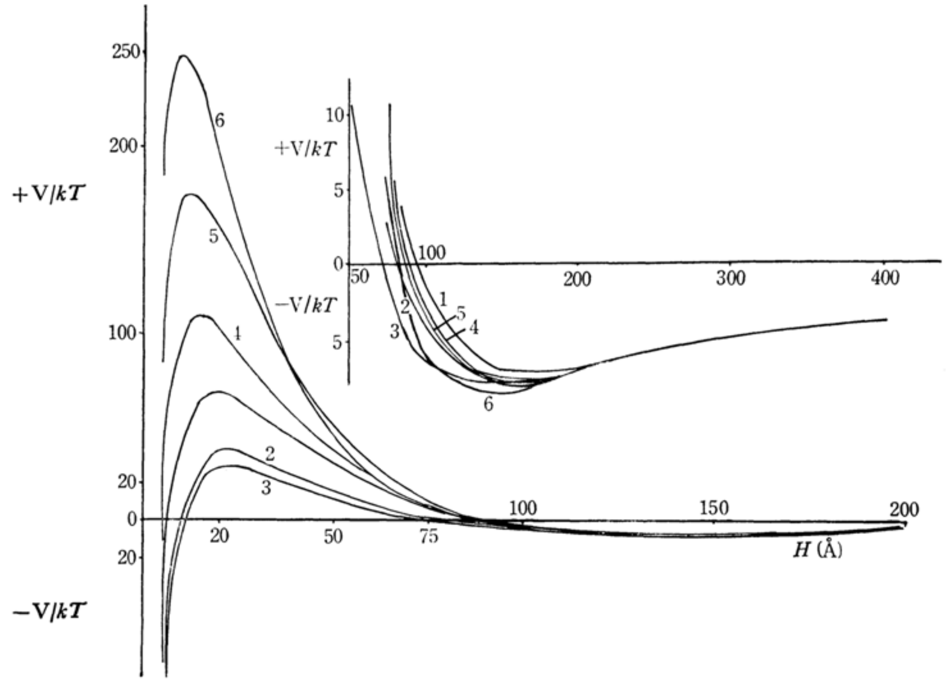

Fig. 3. Plots of distance and potential energy of interaction for LPC at different concentrations showing the heights of maxima and enlarged secondary minima separately. (1) 1.0×10^{-6} M (2) 5.0×10^{-6} M (3) 1.25×10^{-3} M (4) 2.5×10^{-3} M (5) 5.0×10^{-3} M (6) 1.0×10^{-2} M

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20) T. Hanai, *et al., J. Theorot. Biol.,* **9**, 378 (1965).

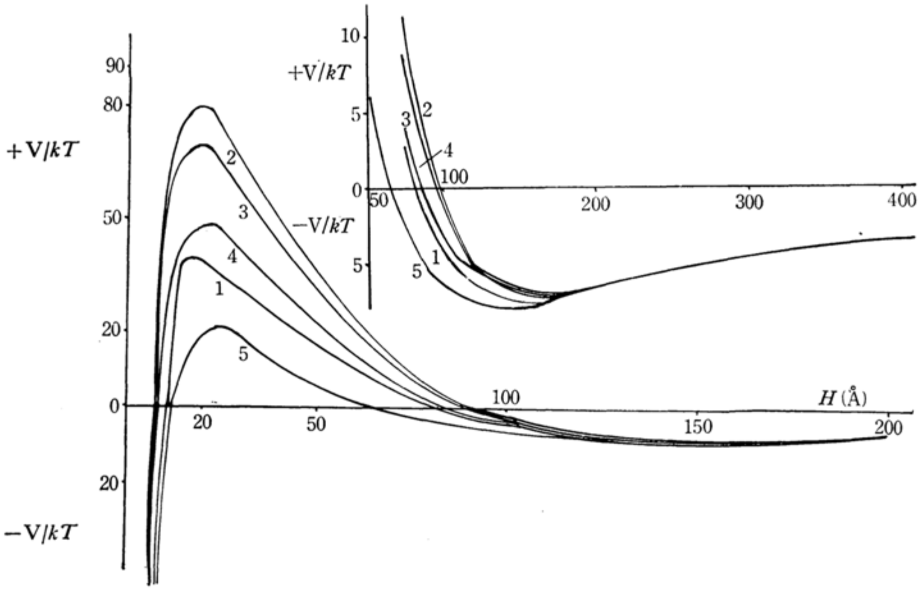

Fig. 4. Plots of distance and potential energy of interaction for CPB at different concentrations showing the heights of maxima and enlarged secondary minima separately. (1) 1.0×10^{-6} M (2) 5.0×10^{-6} M (3) 1.0×10^{-5} M (4) 5.0×10^{-4} M (5) 1.0×10^{-3} M

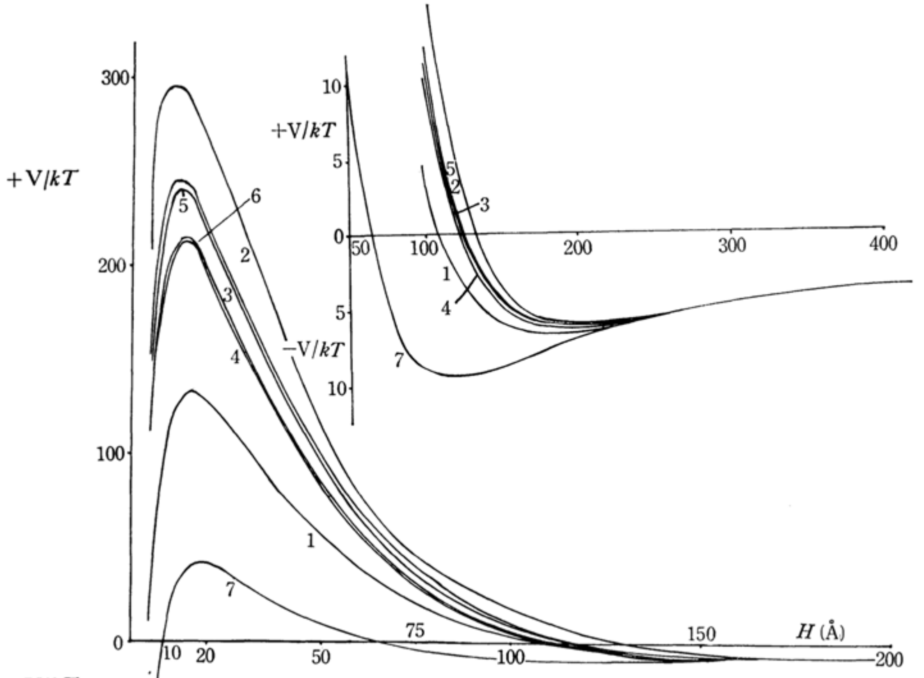

Fig. 5. Plots of distance and potential energy of interaction for Ammonyx-200 at different concentrations showing the heights of maxima and enlarged secondary minima separately. (1) 5.83×10^{-7} M (2) 5.83×10^{-6} M (3) 2.91×10^{-5} M (4) 5.83×10^{-5} M (5) 2.91×10^{-4} M (6) 5.93×10^{-4} M (7) 5.83×10^{-3} M

logarithmic concentrations of the detergents (graph 2). From the graph it is clear that except Ammonyx-200, all the other detergents (LPC, CPB and CDBAC) have reversed the charge of the emulsion globules. The relative efficiencies of these detergents are clearly indicated by the charge reversal concentrations as given in Table 1.

The reversal of charge is due to the adsorption

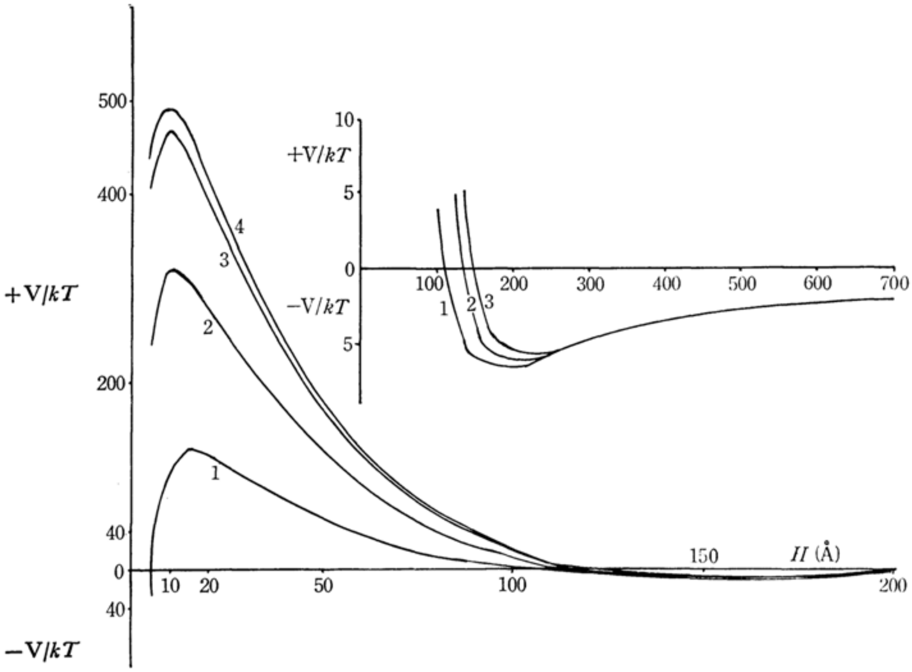

Fig. 6. Plots of distance and potential energy of interaction for CDBAC at different concentrations showing the heights of maxima and enlarged secondary minima separately (1) 1.92×10^{-5} M (2) 2.83×10^{-5} M (3) 1.92×10^{-4} M (4) 3.83×10^{-4} M.

of the cation onto the surface of the lecithin micelles. The flocculation results were also in conformity with the values of zeta potential variations. The efficacy of each detergent could easily be explained by the length of the carbon chain and critical micelle concentration (CMC). The CMC of LPC is determined as 1.66×10^{-2} whereas that of CPB is lower than this. The carbon chain lengths and so flocculating powers are in the increasing order of Ammonyx-200, LPC, CPB and CDBAC.

(c) Interaction Energy Curves and the Stability of Emulsion. In order to test the DVO theory in the present case and also to study the nature of flocculation, the interaction energies V/kT where V comprises of V_R+V_A have been calculated and are plotted as a function of the interparticle distance H (Å) and are presented in graphs 3—6. The high energies exhibited in different systems would naturally indicate the stability of the emulsion and the possibility of only reversible flocculation. When the surface of the emulsion droplet strongly adsorbs the ions of the opposite charge, the coated droplets act as a lyophobic colloid. So the flocculation can be either irreversible in the primary minima or reversible in the secondary minima. In the present investigations under question, the latter aspect seems to be more predominant as evidenced by the high energy above 25 kT and shallow minima of not more than 7 to 8 kT deep at an interparticle distance of 100—150 Å. The enlarged secondary minima portion have also been presented in the same graphs 3—6.

The details of the detergent concentrations and their corresponding zeta potentials, the energy maximum, depth of the secondary minima *etc.* are presented in Table 2.

These results are in conformity with our previous findings with inorganic cations.12) The only difference which is obvious is that the overall energy barriers have been reduced as compared to the previous ones, presumably, owing to the combined effect of 0.01 KCl + the highly effective cations of the detergents.

By counting the number of singlets and doublets by haemocytometry while doing flocculation studies, the degree of aggregation has been calculated. The theoretical value of the same has also been obtained.21) These two values did not agree because of the difference in van der Waals constant taken (2.0×10^{-13} erg). So a graph was plotted between different van der Waals constants and the theoretical values of $D\%$ (graph 7). From this graph the value of A corresponding to the observed value of D has been noted and found to be 2.6×10^{-13} erg which is almost same as obtained before with electrolytes. This further confirms the range of A obtained by earlier workers.19-22)

(d) Reversal of Charge and the Binding

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21) S. N. Srivastava, *Ind. J. Chem.*, **3**, 376 (1965).

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

Table 2

Detergent concentration M	Zeta potential in mV	Height of maximum in kT	Interparticle distance at which $V=0$	Depth of secondary minimum
Ammonyx-200				
5.83×10^{-7}	-35.7	134	100—150Å	6.4
5.83×10^{-6}	-47.0	295	100—150Å	6.1
2.91×10^{-5}	-44.1	244	100—150Å	6.2
5.83×10^{-5}	-42.1	213	100—150Å	6.3
2.91×10^{-4}	-44.0	241	100—150Å	6.2
5.83×10^{-4}	-42.4	215	100—150Å	6.2
5.83×10^{-3}	-29.1	41	100—150Å	9.0
LPC				
$1.0\ \times10^{-6}$	-30.2	69	75—100Å	7.0
$5.0\ \times10^{-6}$	-26.5	38	75—100Å	7.5
7.95×10^{-5}	Charge reversal			
1.25×10^{-3}	$+25.9$	29	75—100Å	7.8
$2.5\ \times10^{-3}$	$+34.9$	109	75—100Å	7.6
$5.0\ \times10^{-3}$	$+41.1$	173	75—100Å	8.0
$1.0\ \times10^{-2}$	$+46.7$	248	75—100Å	8.4
CPB				
$1.0\ \times10^{-6}$	-26.7	38	75—100Å	7.5
$5.0\ \times10^{-6}$	-31.5	81	75—100Å	6.8
$1.0\ \times10^{-5}$	-30.5	71	75—100Å	7.0
6.31×10^{-5}	Charge reversal			
$5.0\ \times10^{-4}$	$+28.3$	49	75—100Å	6.7
CDBAC				
$1.0\ \times10^{-6}$	Charge reversal			
1.92×10^{-5}	$+35.7$	128	100—150Å	6.5
3.83×10^{-5}	$+48.3$	319	100—150Å	6.0
1.92×10^{-4}	$+55.6$	467	100—150Å	5.7
3.83×10^{-4}	$+56.9$	493	100—150Å	5.6

Table 3

Detergent	K_1	K_2	N_1 groups/cm^2	$-\Delta G$ kcals/mol	Concentration at zero point charge
LPC	1.27×10^{8}	4.50×10^{4}	5.86×10^{12}	6.04	7.95×10^{-5} M
CPB	6.74×10^{7}	3.31×10^{4}	4.24×10^{12}	5.30	6.31×10^{-5} M
CDBAC	4.84×10^{9}	2.24×10^{6}	4.50×10^{12}	5.33	$1.0\ \times10^{-6}$ M

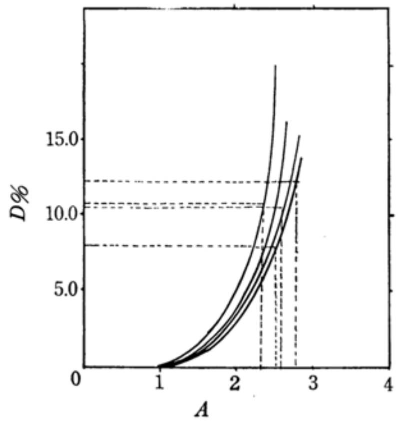

Fig. 7. Plots of Van der Waals constant ($A\times10^{-13}$ erg) and degree of aggregation ($D\%$) at (1) 1.92×10^{-4}M CDBAC, (2) 3.83×10^{-5}M CDBAC (3) 5.0×10^{-6} M CPB (4) 5.83×10^{-6} M Ammonyx-200.

Constants. With the help of the treatment given[17] regarding the calculation of the different binding parameters, number of binding sites available for adsorption and free energy of the surface have been calculated and presented in the Table 3.

From these obtained values it is evident that all these detergents have less number of available sites for adsorption than Ammonyx-200 reported earlier[23] which gives some indication for their capacity to charge reversal. Out of these three presented in the table LPC seems to be weaker than the other as confirmed from the electrokinetic and flocculation measurements. The free energy values are not significantly different from one another.

Finally it may be concluded from the above findings that Ammonyx-200 is not an effective cationic detergent whereas the others are capable of strong adsorption on the lecithin coated oil drops in aqueous KCl so as to cause the charge reversal and their relative efficiencies are in the

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[23] C. Praksh and S. N. Srivastava, Unpublished data.

order CDBAC>CPB>LPC.

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