Kinetics of Xylene Coagulation in Water Emulsion Stabilized by Phthalylsulfathiazole

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Kinetics of coagulation of Phthallylsulfathiazole stabilized xylene in water emulsion in the presense of some cationic detergents is examined. Kinetic parameters such as rate constant of flocculation, coalescence and creaming have been evaluated. Studies were also made to determine zeta potential values and stability factor W_1 in the presence of same additives with the help of some equations. Temperature effect was also calculated by determining coalescence rate constant at different temperatures. With the help of these kinetic parameters particle loss mechanism or coagulation has been delineated. This approach explained the kinetics of coagulation i.e., which process is the rate determining one and also expose the comparative account of effect of the detergents used in the systems under investigation.

Alkylpyridinium or ammonium halides constitute a group of cationic detergents with well known surface properties. The kinetics of emulsion breaking or in general coagulation, comprises flocculation and coalscence. It has been reported (1) that cations and anions at low concentrations retard the coalescence and association of dispersed phase of emulsions.

Sharma and Srivastava (2,3) have determined emulsion stability from the rate of coagulation as well as by measuring the zeta potential with the variation of concentration of cationic detergents and electrolytes. Recently some expressions have been proposed by Reddy et al (4-6) for the calculation of Brownian and sedimentation collision frequencies and creaming. However, their application to our experimental data is not possible because it involves some adjustable parameters i.e., a_1 and a_1, particle radii. The turbidity technique (5,7) has been used to determine the stability of suspensions by assuming that turbidity is directly proportional to particle concentrations. Recently coalescence rate constants of detergents stabilized polar oil/water emulsion have also been evaluated (8).

The present paper deals with kinetics of coagulation of Phthallylsulfathiazole stabilized xylene in water emulsion in the presence of some cationic detergents. Rate of flocculation, rate of coalescence and rate of creaming have been determined. To estimate the stability of the present systems their zeta potentials have been measured and stability factors calculated. Temperature effect on the system was also studied.

Materials and Methods

The emulgent Phthallylsulfathiazole, an important drug, was a gift from May and Backer, Bombay (India). The cationic detergents Cetyl Pyridinium Bromide (CPB), Cetyl Pyridinium Chloride (CPC), Cetyl Trimethyl Ammonium Bromide (CTAB), Lauryl Pyridinium Chloride (LPC) used in the system were obtained from British Drug House Lts., Poole, England. The oil phase consisting of xylene was also of B.D.H. (A.R.) quality. Corning glass apparatus was used throughout the experimental work.

Emulsion

The emulsions were prepared by suspending 4.0% by volume of xylene in 0.01 M aqueous solution of the emulgent phthallylsulfathiazole (alkaline, pH 10.48) and 0.01 M KCl. The mixture, after being hand shaken for 15 minutes, was homogenized three times in a stainless steel homogenizer (Scheer Sci.Co., Chicago). The method is explained in the theoretical part. All chemicals were used without any further purification.

Theoretical

Rate of flocculation was determined by counting the number of particles haemocytometrically using an improved Neubauer model. Hand tally counter (Erma, Tokyo) was used to count the numbers of associated and unassociated globules under Olympus microscope. The average size of emulsion droplet was found to be 1.15 μm from the size frequency analysis of microphotograph (9). Particle size and its distribution have been calculated and presented in Figure 1 and Figure 2.

From Smoluchowski's (10) theory we have

$$\frac{1}{n} - \frac{1}{n_o} = 4\pi\,DRt \qquad\qquad [1]$$

Where n_o and n are number of singlets present initially and at time t, D is the diffusion coefficient and R = 2a, a being particle radius. $\emptyset$ is the phase volume ratio ($\emptyset$ = 0.04 in our system). If Vm is mean drop volume of n drops after time t, we have –

$$Vm = \emptyset/n \qquad\qquad [2]$$

combining [1] and [2]

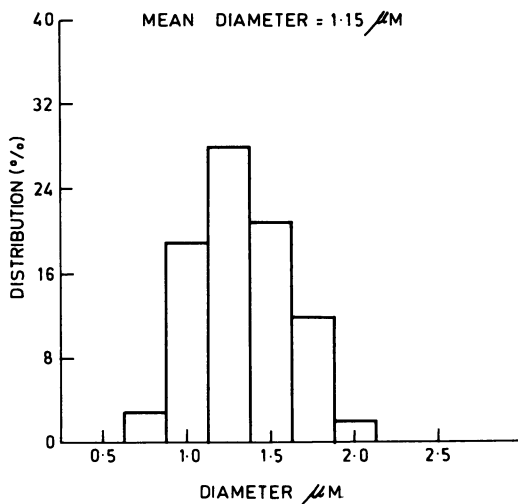$$Vm = \emptyset/n_o + 4\,DR\emptyset t \qquad\qquad [3]$$

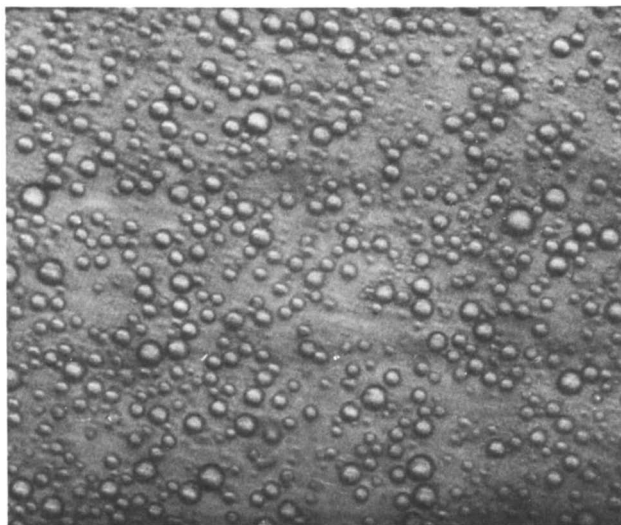Figure 1. Plot for particle size distribution of phthalyl-sulfathiazole-stabilized system.

Figure 2. Microphotograph of phthalylsulfathiazole-stabilized emulsion.

As the phase volume ratio remains the same during coalescence, we
may have

$$\emptyset = nVm = n_o Vm_o$$

Where Vm_o is mean drop volume of initial drops, hence,

$$Vm = Vm_o + 4\pi DR\emptyset t = K_f t \qquad\qquad [4]$$

Where K_f is Smoluchowski's flocculation rate constant.
    For determination of the stability factor W_1 eq. [4] may be
modified as

$$Vm = Vm_o + 4\pi DR\emptyset t \ e^{-W_1/kT}$$

Plot of Vm against time will be a straight line. The slope of this
curve = $4\pi DR\emptyset t \ e^{-W_1/kT}$. Using Einstein equation $D = kT/6\pi\eta a$, W_1
values were calculated (11).
    Coalescence occurring in the system was measured tubiditi-
metrically. Turbidity is found to decrease with time for dilute
emulsions. As droplets coalesce, there is a net decrease of oil
surface area and an increase of average globule diameter. This has
been shown (12) that the turbidity for a dilute emulsion as measured
in Klett-Summerson photoelectric colorimeter is directly proportional
to the surface area of the globules. Thus for Phthallylsulfathiazole
stabilized emulsion it is possible to relate the ratio of number of
droplets at any time t and that at time = 0 (N_t/N_o) to Klett
readings, provided that the size distribution of emulsion droplet
does not vary much. If R_t and R_o are the Klett readings at any time
t and t = 0 and r_t and r_o are average volume surface radii iat
respective times, then

$$R_t \propto 4\pi r_t^2 N_t \qquad\qquad [5]$$

$$R_o \propto 4\pi r_o^2 N_o \qquad\qquad [6]$$

if the total volume of oil is constant, then

$$4/3 \quad \pi r_t^3 N_t = 4/3 \ \pi r_o^3 N_o \qquad\qquad [7]$$

From equations [5] to [7]

$$\log \ N_t/N_o = 3 \log R_t/R_o \qquad\qquad [8]$$

    For turbidity measurements, diluted emulsions were used to
avoid multiple scattering effects (13) which may produce non-
linearity between the photomicrographically determined surface area
and turbiditimetrically determined one.
    The electrophoretic mobilities were determined in a rectangular
closed cell of Northrup Kunitze type (14) in an air thermostat. The
usual precautions were taken.
    As the deserved droplets had large radii compared with the Debye
Huckel parameter (1/χ), the zeta potentials were calculated from the
following equation:

$$\xi = 4\pi\eta U/\varepsilon \ X \qquad\qquad\qquad [9]$$

Where η and ε are respectively the viscosity and the dielectric constant of the solution in the electrical double layer adjacent to the surface, U is the mobility and X is the applied field strength. In the present cases η and ε were taken as equal to their bulk values. The temperature for mobility measurements was at $25°\pm 0.1°C$.

RESULT AND DISCUSSION

Charge on Emulsion

Phthallylsulfathiazole stabilized xylene in water emulsion was found to be negatively charged. Since this compound is acidic in nature, the -COOH group ionises to furnish negatively charged carboxylate anions which impart the same charge on emulsion droplets at alkaline pH 10.48 by virtue of the adsorption of the emulgent.

R—remaining part of compound
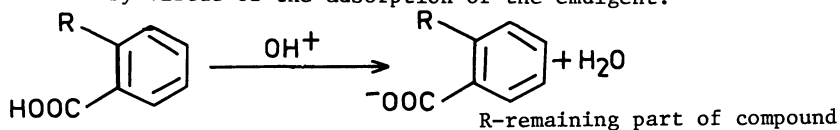
Effect of Cationic detergents on flocculation

Different concentrations of all the four detergents were used to study the flocculation occurring in the system. Unassociated and associated (monomers and dimers) globules were counted at various intervals of time. Individual oil globules (n_1 or monomers) against time in minutes were plotted. Here only one typical graph (Fig. 3) obtained from CTAB has been presented. Initially particle concentration was 2.39×10^9/ml. It is clear from Fig. 3 that the number of unassociated drops first decreases fastly and then it is slow. Later on it attains almost constancy which indicates reversibility of flocculation occurring in the system. Fig. 4 shows effect of different concentrations of different detergents. It is quite evident from this figure that the flocculation decreases as concentration increases. In the case of LPC the rate constants increase with increase in concentration. Rate constant K_f was of the order of 10^{-14}, 10^{-14}, 10^{-13}, and 10^{-13} for CPB, CPC, CTAB, and LPC, respectively, These low values of the rate constants are indicative of reversible nature of flocculation which in fact occurs in the secondary minimum.

Effect of Cationic detergents on Coalescence

There are three processes by which the number of oil drops in an emulsion is decreased. These are Brownian flocculation, sedimentation flocculation and creaming. But it should be noted that if the absorbed film strength is quite high, flocculation may not necessarily result in coalescence. It is also important to note that flocculation which may be due to any of above three reasons is reversible, but coalescence which follows flocculation is irreversible.

All the emulsions follow a first order kinetic equation of the form:

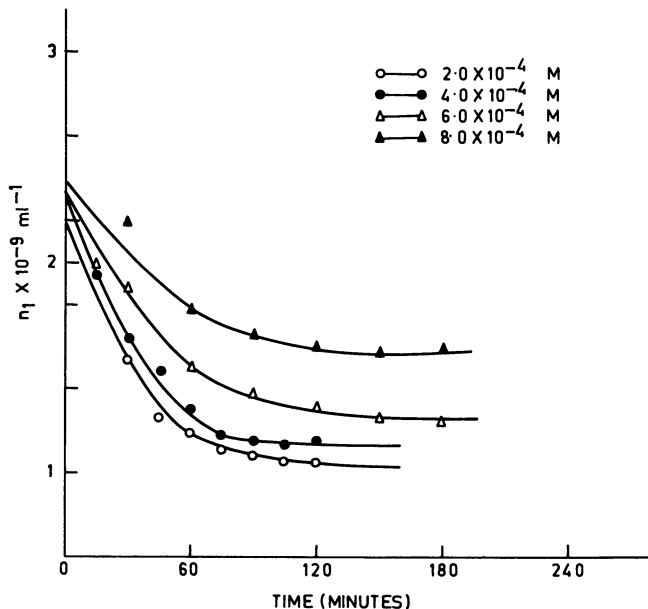$$N_t = N_o \ \exp \ (-K_c t) \qquad\qquad [10]$$

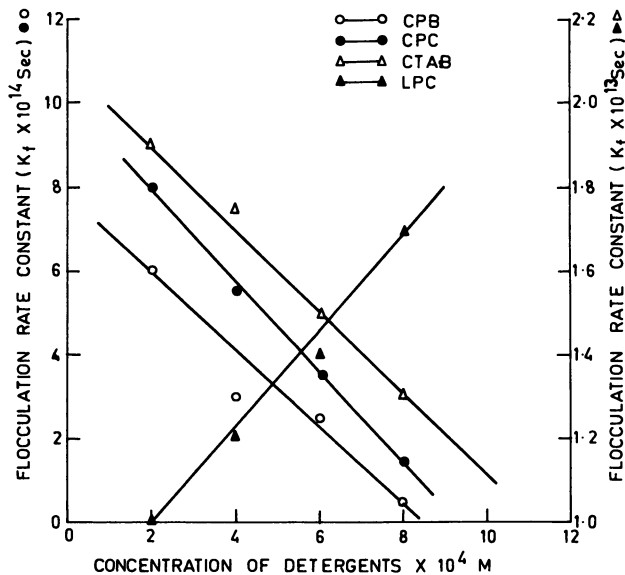Figure 3. Plots of monomer against time for the system flocculated by CTAB.

Figure 4. Plots of flocculation rate constant (K) against concentration of detergents.

Where K_c is the first order rate constant. On addition of increasing amounts of the cationic detergents the corresponding doalescence rate constants of the emulsion decrease rapidly except in the presence of LPC which increases the rate of coalescence. This is depicted in Fig. 5, which is a plot of rate constants vs. concentration of different detergents. This figure presents a clear picture of comparative study of effects of all detergents taken in our system. It is also interesting to note that the rate constants in the presence of surfactants are of the order of 10^{-5} S^{-1}, $10^{-5}S^{-1}$, $10^{-4}S^{-1}$ and $10^{-4}S^{-1}$ for CPB, CPC, CTAB and LPC respectively. This means the stability of the emulsion increases with the chain length. From Figs. 4 and 5, it is obvious that rate constants of coalescence and rate constants of flocculation follow the same trend, so it can be assumed that flocculation is resulting in coalescence.

It is evident from the date recorded in Table I that at higher temperature coalescence rate constant is higher, that is in order of $K_{c30°} < K_{c40°} < K_{c50°}$. The temperature effect for all detergents was found to be in the order LPC < CTAB < CPC < CPB. This implies that in the presence of CPB the coalescence rate constant of the emulsions increases enormously (e.g. four to six times for every 10°C rise of temperature) with the rise of temperature whereas in the presence of LPC the increase in the rate is not that pronounced.

From the coalescence rates of different temperatures it has also been possible to calculated some kinetic and thermodynamic parameters such as energy of activation (E_a), enthalpy change ($H°$), entrophy change ($S°$) and free energy change ($F°$) from the equation:

$$RT \ln K_c = -\Delta F° = -\Delta H° + T\Delta S° \qquad [11]$$

within the formalism of flocculation/coalescence rate theory assuming that the intermediate floc of the following overall process of coalescence may be taken to be identical with the transition state or activated complex of the Transition State Theory of Chemical Kinetics.

Different parameters reflected in Table II are within the expected range of values. The positive activation entropies denote that the entropy of the transition state floc is greater than the entropy of the separate globules. The stability preventing coalescence from the flocculated intermediate state may be due to the metastability of thin films against rupture which in their turn offer steric hindrance owing to the close packed ordered layers of the emulgent at oil/water interface. The intervening water films between the two droplets of the transition state floc may play the same sort of the role. In the wake of coalescence, rupture of the said films occur and the orderliness disappears and so the entropy increases.
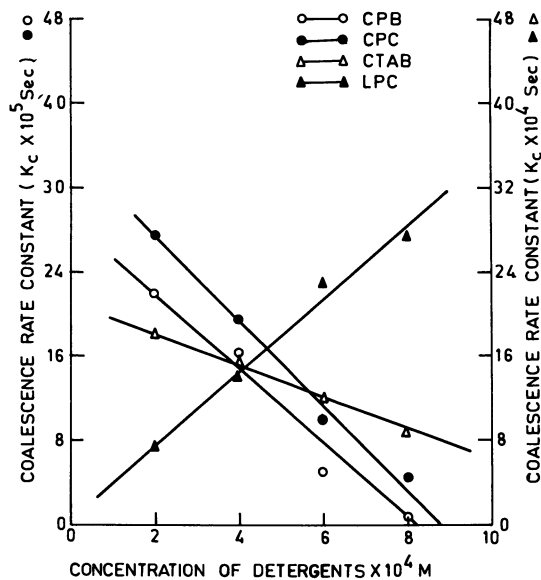
Figure 5.   Plot of coalescence rate constant (K_c) against
detergent concentration.

Table I.   Effect of Temperature on Coalescence Rate
Constant for the System

Detergent $(2.0 \times 10^{-4} M)$	$K_{c30°C}$ Sec.	$K_{c40°C}$ Sec.	$K_{c50°C}$ Sec.
CPB	2.2×10^{-4}	9.4×10^{-4}	1.3×10^{-3}
CPC	2.7×10^{-4}	4.7×10^{-4}	5.2×10^{-4}
CTAB	1.8×10^{-3}	2.4×10^{-3}	2.9×10^{-3}
LPC	7.5×10^{-4}	9.8×10^{-4}	1.1×10^{-3}

Effect on zeta potential

Figure 6 is a graphic representation of the zeta potential data as
a function of log molar concentration of different cationic surfac-
tants. At lower concentration, zeta potential is high while on
addition of additive it decreases slowly. This decrease is sharp at
higher concentrations. On continuous addition of surfactant, the
values first become zero and then reversal of charge takes place.
    It is very important to note the lower is the zeta potential,
the greater the flocculation. As it increases, charge also in-
creases. As charge increases, electrostatic repulsion (Coulombic
force) increases and hence flocculation decreases in the system
under investigation. The amount of detergent required to reverse the
charge is in the order LPC > CTAB > CPC > CPB (Table III).

Effect of Creaming

Brownian flocculation is dominating in the system as the particle
diameter is approximately equal to $1 \mu m$ (i.e. $1.15 \mu m$). Particles
under Brownian motion collide first and then coalesce to form
larger size particles. Simultaneously these coalesced particles are
creaming out due to the differences in the densities of the particles
and the continuous phase. In Figures 7 and 8 per cent creaming is
plotted against time in hours. In this experiment phase volume
ratio was changed from 0.04 to 0.4 to measure creaming data accu-
rately. It is obvious from these figures that the per cent creaming
is faster initially but later on it is very slow as the coalescence
becomes slow. It was noticed that per cent creaming rate follows
the same trend and order as in the case of both flocculation and
coalescence.

Kinetics of Coagulation of the system under investigation

One may conclude from the figures and the data that the emulsions
are most stable in the presence of higher concentrations of CPB
while with LPC reverse is the case. So emulsion stability was
found to be in the order CPB > CPC > CTAB > LPC. Zeta potential
values also support this type of behavior as its values are lower for
LPC and higher for CPB. This comparative stability is also reflected
from the stability factors W_1 of the system recorded in Table IV.
Stability factor is greater for CPB and lower for LPC, e.g. for
8.0×10^{-4} M concentration of CPB and LPC, its values were found to
be 11.96 and 8.44 (in kT) respectively. This order clearly indicates
that the adsorption of these detergents on emulsion globules is in
accordance with their chain length. The curves in Figs. 4 and 5 also
shed light on the behavior of CPB and CPC which differ only in the
head group, the former being more efficient.
    To find whether flocculation or coalescence is the rate deter-
mining step in the system under investigation, the ratio of the half
lives of these two processes was determined. Half life of floccula-
tion is given by equation $1/K_f n_0$ whereas that of coalescence is
$1/1.47 K_c$ (assuming it is kinetically of first order). The relative
ratio is given by the ratio of the two half lives (i.e. $1.47 K_c/n_0 K_f$)
(11). Flocculation or coalescence is more rapid according as this
ratio is greater or less than unity. Since in the present case it

Table II.   Kinetic Thermodynamic Parameters of the
Coalescence Process

Detergent (2.0 x 10^{-4}M)	E_a (1)	$-F°$ (1)	$H°$ (1)	$S°$ (2)
CPB	4.6	−5.0	−27.3	73.9
CPC	6.2	−4.9	−10.4	18.1
CTAB	4.2	−3.8	−4.0	4.6
LPC	3.7	−4.3	−4.9	2.4

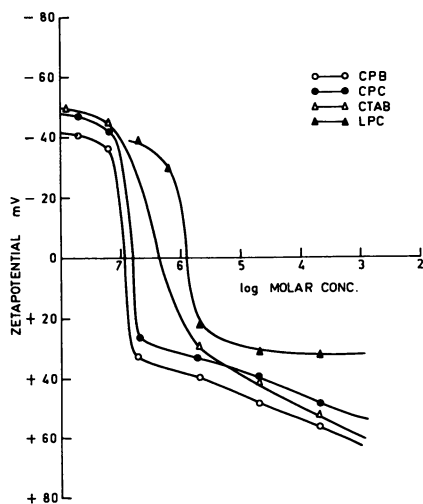(1) Kcal deg^{-1} mol^{-1} (2) Cal deg^{-1} mol^{-1}

Figure 6.   Plots of zeta potential as a function of log molar
concentration with different detergents.

Table III.   Values of Zeta Potential for the System Flocculated
By Different Cationic Detergents

| Concentration of Detergents		Zeta Potential (in mV)
CPB	2.0×10^{-8} M	40
	6.0×10^{-8} M	37
Charge Reversal	2.0×10^{-7} M	+35
	2.0×10^{-6} M	+39
	2.0×10^{-5} M	+48
	2.0×10^{-4} M	+56
CPC	2.0×10^{-8} M	48
	6.0×10^{-8} M	42
Charge Reversal	2.0×10^{-7} M	+31
	2.0×10^{-6} M	+33
	2.0×10^{-5} M	+39
	2.0×10^{-4} M	+48
CTAB	2.0×10^{-8} M	49
	6.0×10^{-8} M	36
Charge Reversal	2.0×10^{-7} M	+32
	2.0×10^{-6} M	+40
	2.0×10^{-5} M	+47
	2.0×10^{-4} M	+51
LPC	2.0×10^{-7} M	40
	2.0×10^{-6} M	30
Charge Reversal	2.0×10^{-5} M	+22
	6.0×10^{-5} M	+24
	2.0×10^{-4} M	+32
	6.0×10^{-4} M	+32
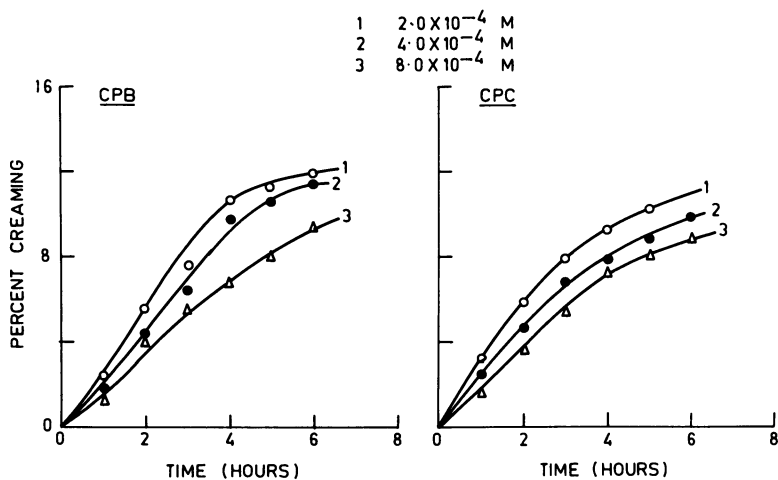
Figure 7.   Creaming % vs. time plots for phthalylsulfathiazole
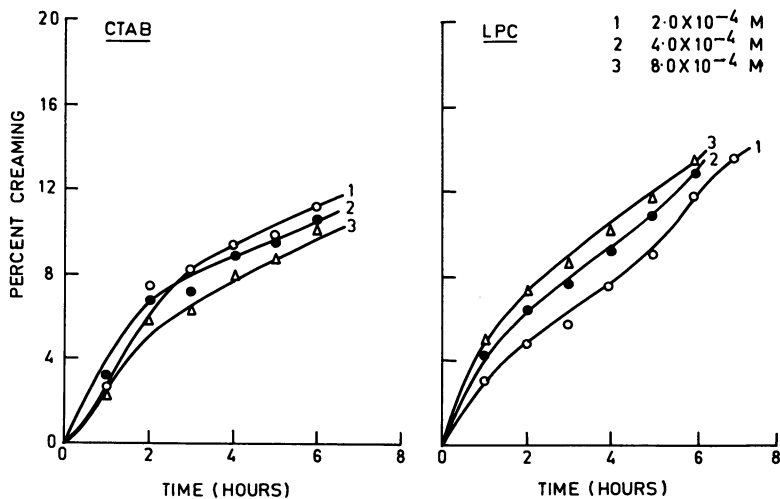system.

Figure 8.   Creaming % vs. time plots for phthalylsulfathiazole
system.

Table IV.   Kinetic Parameters for the System Stabilized
By Phthallylsulfathiazole

Conc. of Detergent x10^{-4} M	Coalescence Rate Constant (K_c)	Floccu-lation Rate Constant (K_f)	Creaming Rate Constant (Per Cent/ Hour)	Stability Factor (kT)
CPB	K_c x 10^5 Sec^{-1}	K_f x 10^{14} Cm^3 x Sec^{-1}		
2.0	22.1	6.0	2.2	9.5
4.0	16.5	3.1	1.7	10.2
6.0	5.0	2.5		10.3
8.0	1.2	0.5	1.4	12.0
CPC				
2.0	27.5	8.0	2.4	9.2
4.0	19.5	5.5	1.3	9.6
6.0	9.0	3.5	–	10.0
8.0	4.5	1.5	1.6	10.9
CTAB	K_c x 10^4 Sec^{-1}	K_f x 10^{13} CM^3 x Sec^{-1}		
2.0	18.2	1.9	3.7	8.3
4.0	15.5	1.7	3.4	8.4
6.0	12.0	1.5	–	8.6
8.0	8.5	1.3	2.9	8.7
LPC				
2.0	7.5	1.0	0.9	9.0
4.0	14.0	1.2	3.1	8.8
6.0	23.0	1.4	–	8.6
8.0	27.5	1.7	3.8	8.4

is greater than unity so coalescence is slower and hence it deter-
mines the rate of coagulation of these systems.

Conclusion

The emulgent, phthallylsulfathiazole provides highly stable type of
emulsions. Even in the presence of cationic surfactants, these
emulsions were found to be reasonable stable. Effect of detergents
on the stability was in the order CPB < CPC < CTAB < LPC, which is
compatible with their chain length. The rate determining step of
coagulation kinetics of the system under investigation is the coale-
scence as this is slower than flocculation.

Acknowledgments

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