Removal of some anionic and cationic detergents using an inorganic gel adsorbent

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The uptake of two cationic detergents, cetyltrimethylammonium bromide (CTAB), cetylpyridinium bromide (CPB) and two anionic detergents, sodium dodecylsulphate (SDS) and sodium dodecylbenzenesulphonate (ABS) has been observed on copper ferrocyanide which is prepared and characterised by well known methods. Sorption data have been correlated with both Langmuir and BET adsorption models. The presence of mono and divalent cations increase the uptake of ABS and SDS and the enhancement is much more in the presence of trivalent salt like AlCl₃. Thermodynamic parameters indicate the feasibility of the process while kinetic measurements provide the necessary mechanistic information. Desorption of anionic detergents from loaded copper ferrocyanide has also been achieved.

One of the most important series of compounds, from the viewpoint of environmental pollution, has been synthetic detergents. Most commonly employed detergents are the anionic type, and being non-biodegradable in nature, their removal has been a subject of interest for quite some time. Out of all the methods tried for the purpose, adsorption at solid/liquid interface is extremely important in view of its adaptability in wide range of applications. Adsorbents used, so far, are granular carbon, carbon black, sulphur, γ-Alumina, silica and activated carbon. Efforts made to use sand, flyash, digested sludge, soil etc did not meet with much success. Recent investigations in this regard, still deal with carbon, clay minerals etc.

Inorganic gels possessing high sorption or exchange capacity are much better materials for the uptake of surfactants from aqueous solutions. These are mechanically and chemically more stable, exhibit specific selectivity and thus can be used even in drastic physical conditions. Their stability, possibility of chemical regeneration and quantitative elution of adsorbate from these materials, are some of the added advantages of this class of compounds and make the process economically feasible.

Investigations presented in this paper include the uptake and kinetics of the two cationic detergents viz., cetyltrimethylammonium bromide (CTAB) and cetylpyridinium bromide (CPB) and two anionic detergents viz. sodium dodecylsulphate (SDS) and sodium dodecylbenzenesulphonate (ABS) on copper ferrocyanide gel, under different conditions of temperature, concentration, particle size of the adsorbent etc.

Materials and Methods
CTAB, CPB, SDS and ABS were obtained from BDH. All other reagents used were A.R. grade chemicals. All solutions, standards and dilutions were made using doubly distilled water. pH measurements were made with a pH-meter, model pH 821, E.C.I., India. Absorbences were recorded on Bausch and Lomb spectronic-20 and Unicam-500 spectrophotometers. The mean particle radius was evaluated using Agfa Diameter (Germany).

Preparation and characterization of the adsorbent material
Preparation and characterization of copper ferrocyanide were carried out as reported by Kourim et al. The product, brown in colour, was ground and sieved to different particle sizes. The mechanical and chemical stabilities of the gel are evident by the fact that no significant change in mean radius of the particles was observed when kept in water or in detergent solution under study.

The cation and anion exchange capacity of the
compound as determined by standard method are 2.60 meq/g and 0.21 meq/g respectively.

**Adsorption experiments**

Sorption studies were conducted in a routine manner by batch technique. Isotherms were run by taking different concentrations of surfactants (10^-4 to 10^-5 M in the case of cationic and 10^-5 to 10^-6 M for anionic detergents) at pH 6.2 and 4.0 respectively. Stoppered glass tubes containing detergent solution and a definite amount of gel (particles 170-200 B.S.S. mesh size) were stirred (10-15 min) and then kept for 12 h (in the case of cationic detergents) and 48 h (in the case of anionic detergents) at 30°C with intermittent shaking. The supernatant liquid was centrifuged and analysed for the detergent. The effect of NaCl, CaCl_2 and AlCl_3 (varying concentrations) on the uptake of anionic detergents has also been observed.

**Desorption measurements**

The desorption of anionic detergents was tried with OH^- and Cl^- ions and also with K_2SO_4 and a mixture of C_2H_5OH and H_2SO_4.

**Kinetic studies**

Kinetic measurements were made by batch technique (finite bath system). A number of test tubes (50 ml capacity) containing a known volume (20 ml in each case) and concentration of solutions of the anionic and cationic detergents were placed in thermostatic shaker. When the desired temperature was reached, a known amount of adsorbent (0.025 g) was added into each tube and the solutions were agitated by mechanical shaking. After pre-decided interval of time, the solution of the specified tube was separated from the sorbent material and the uptake of the detergent was obtained as a function of time.

**Estimation of detergents**

Anionic detergents were estimated by the method of Lawrence using methylene blue dye and the method of Few and Ottaway was used for the estimation of cationic detergents.

**Results and Discussion**

In order to determine the equilibrium time and quantity of adsorbent for optimum adsorption, experiments were conducted by varying the time of contact, using different amounts of copper ferrocyanide at a fixed adsorbate concentration (5 x 10^-5 M for cationic and 5 x 10^-6 M for anionic detergents). Adsorbent concentration is varied from 10 to 50 mg per 20 ml of solution. These values of adsorbents were arrived at after a few trial runs. Results of these experiments are shown in the form of plots of percent detergent removal versus time of contact in the case of SDS [Fig. 1(A)]. Although similar plots were obtained for all the surfactants, only the data for SDS has been given. Many preliminary runs indicate the equilibration time as 48 h and 24 h for anionic and cationic surfactants respectively. The logarithmic plot of the data shows a linear variation [Fig. 1(B)] and the same may be mathematically represented as

\[ P_s = k_i t^m \]

or \[ \log P_s = m \log t + \log k_i \]

where \( P_s \) is the percent solute removal and \( t \) the time of mixing in hours. The slope \( m \) of the linear

Fig. 1—Plots showing the percentage removal of SDS with time at varying copper ferrocyanide concentrations ([SDS] = 5 x 10^-6 M, pH = 4.0, particle size = 170-200 mesh, temp. = 30 ± 0.2°C).
plot reflects the mechanism of adsorption while the constant $k$, is indicative of the rate factor. It is observed that the amount of adsorbent affects both rate as well as the mechanism of detergent uptake. It is seen from the plots that the value of $m$ decreases in each case with increase in the amounts of adsorbent, thus indicating a better adsorption mechanism at low adsorbent concentrations. Increasing values of the rate factor $k$, indicates an increase in the rate of removal at higher adsorbent concentration. Although percent detergent removal is more at high adsorbent concentrations, a large quantity of the same is comparatively less efficient if percent detergent removal per mg of adsorbent is considered. Moreover, very large quantities of adsorbent create handling problems and difficulties in the process of desorption. Also taking into account the lesser removal of adsorbate at low concentration, 20 mg of adsorbent for cationic detergents and 30 mg of adsorbent for anionic detergents per 20 ml have been used. For running the sorption isotherms, a moderate concentration of adsorbate, $10^{-4}$ to $10^{-5} M$ in the case of cationic and $10^{-5}$ to $10^{-6} M$ in the case of anionic detergents, has been chosen, keeping in view the surfactant levels likely to be present in various industrial processes. Various fractions of particle size have been tried and it was found that the uptake as well as desorption is most convenient and maximum on particles of 170-200 B.S.S. (0.082 mm) mesh size. Adsorption isotherms of CPB, CTAB, SDS and ABS on copper ferrocyanide at pH 6.2 and 4.0 are given in Figs 2(A) and 2(B). All the isotherms [Figs 2(A and B)] indicate a positive adsorption. These are regular and concave to the equilibrium concentration axis. The extent of adsorption increases with increase in detergent concentration, but the percent removal is high at low adsorbate concentration. Further, the nature of isotherms, in each case, reveal a rapid initial uptake of detergent, followed by a slow approach to saturation condition at high adsorbate concentration. Maximum uptake of detergents (both cationic and anionic) is much less than the cation or anion exchange capacity of the adsorbent material.

The effect of pH on the adsorption of CPB, CTAB, SDS and ABS shows that the uptake of CPB and CTAB increases with the increase in pH and that of SDS and ABS increases with acidity of the system. Variation of the uptake of CPB and SDS on copper ferrocyanide gel is given in Figs 3(A and B). Figure 3(A) shows that the adsorption of CPB increases with pH and the rise is quite sharp upto pH 5.0. Beyond this value a marginal increase is observed and thus the measurements of cationic detergents are made at pH 6.2. On the other hand the adsorption of SDS is almost constant upto pH 4.0 and beyond this value, a sharp decrease in the adsorption phenomenon is observed as shown in Fig. 3(B). Thus all measurements of anionic detergents are made at pH 4.0. Adsorption data correlate well with the Langmuir and BET models. It is observed [Figs 4(A, B) and 5(A, B)] that a good linear relationship for BET plots is only found at low concentration of adsorbate while the entire adsorption data is better represented by Langmuir model.

BET as well as Langmuir parameters are given in Tables 1 and 2. $Q_0$ values as calculated from BET expression for anionic and cationic detergents are much less as compared to those calculated from Langmuir plots. Since BET plots have only been shown at low concentration of adsorbate, the same would not give a correct value of the amount of detergent necessary to form a

![Fig. 2—Adsorption isotherms of (A) cationic, (B) anionic detergents on copper ferrocyanide (temp. = 30 ± 0.2°C, particle size = 170-200 mesh).](image-url)
monolayer on the adsorbent surface. Probably due to limited validity of adsorption data for BET model and different nature of sorption sites involved in the process of anionic and cationic adsorption, the BET parameter, A, shows great variation and does not reflect any consistency with the adsorption behaviour of the detergents. As mentioned earlier the $Q^0$ values as calculated from Langmuir model are higher for SDS and CPB as compared to ABS and CTAB. The values of the Langmuir parameter $b$ which reflect the steepness of the approach to saturation are higher
for SDS and CPB as compared to ABS and CTAB, thereby indicating greater tendency towards adsorption. The values of the constant A which reflect the energy of interaction with the surface are higher for SDS as compared to ABS and Q° values calculated from BET expression are higher for ABS as compared to SDS while it was not possible to make the BET plots for CTAB.

Uptake of SDS and ABS has also been studied in the presence of different concentrations of NaCl, CaCl₂ and AlCl₃ in solution at fixed absorbate and adsorbent concentrations. Mono as well as divalent cations increase the adsorption of SDS and ABS in the pH range 4-7 as shown in Figs 6(A and B). Trivalent salt like AlCl₃ causes much increase in adsorption in this pH range. A 25 to 40 per cent increase in adsorption with mono or divalent cations and 50 per cent increase in the presence of Al³⁺ ions, is observed at the same pH. At higher salt concentration, adsorption of these two compounds decreases.

The increased removal of SDS and ABS in the presence of ionic salts in solution, probably, cannot be accounted for by any single mechanism. Several probabilities seem consistent in terms of interpretation of these results such as:

(i) Possible lowering of cmc of detergents in the presence of salts. Micelles are known to have a higher degree of surface activity.
(ii) Formation of smaller micelles below the normal cmc.
(iii) Adsorption of ABS or SDS as Al-OH-ABS/SDS complex in acid solution.

A quantitative understanding of the sorption dynamics and other mechanistic aspects help in proper optimization and modelling of the process. Kinetic data, as obtained by the Finite Bath method has been treated by Eqs 2 and 3 which are va-

![Fig. 5 - B.E.T. plots of (A) cationic, (B) anionic detergents on copper ferrocyanide (temp. = 30 ± 0.2°C; particle size = 170-200 mesh).](image)

![Fig. 6 - Plots showing the effect of salt solutions on the uptake of anionic (A) SDS, (B) ABS surfactants using copper ferrocyanide (temp. = 30 ± 0.2°C, particle size = 170-200 mesh).](image)
lid for finite as well as infinite bath techniques, under the present experimental conditions employed. This is in accordance to the observations of Reichenberg and have also been used in earlier studies.

\[ F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -\frac{D_1 \pi^2 n^2 t}{r_0^2} \right) \]  

(2)

or \[ F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n} \exp (-n^2 Bt) \]  

(3)

where \( F \) is the fractional attainment of equilibrium at time \( t \) and is obtained by the expression

\[ F = \frac{Q_t}{Q_0} \]  

(4)

where \( Q_t \) is amount taken up at time \( t \) and \( Q_0 \) is the maximum equilibrium uptake and

\[ B = \frac{\pi^2 D_1}{r_0^2} = \text{time constant} \]  

(5)

where

- \( D_1 \) = effective diffusion coefficient of ions in the adsorbent phase,
- \( r_0 \) = radius of the adsorbent particle assumed to be spherical, and
- \( n = 1, 2, 3 \ldots \) are the integers defining the infinite series solution obtained for a fourier type of analysis.

For every observed value of \( F \), corresponding \( Bt \) values as derived from Eq. (3), have been obtained from Reichenberg’s Table. The linearity test of \( Bt \) versus \( t \) plots are employed to distinguish between the film and particle diffusion controlled rates of exchange.

The experimental conditions were set up for particle diffusion as the sole rate determining step to study the thermodynamics of the sorption process. The energy of activation \( E_a \) has been determined by applying the Arrhenius type expression

\[ D_1 = D_0 \exp \left( \frac{-E_a}{RT} \right) \]  

(6)

The pre-exponential constant \( D_0 \) (analogous to Arrhenius frequency factor) gives the entropy of activation \( \Delta S^* \)

\[ D_0 = 2.72 d^2 \left[ \frac{kT}{h} \right] \exp \left( \frac{\Delta S^*}{R} \right) \]  

(7)

where \( d \) is average distance between the successive exchange sites and is taken as 5 Å (ref. 11).

The uptake of SDS, ABS, CAB and CTAB on copper ferrocyanide is particle diffusion controlled at and above \( 5.0 \times 10^{-5} \) M for SDS and ABS and \( 3 \times 10^{-5} \) M for CAB and CTAB as shown in Figs 7(A and B).

The increase in sorption rate of the four detergents with decreasing particle size of the adsorbent material [Figs 8(A and B)] and increase in temperature [Figs 9(i)A; 9(i)B and 9(ii)A; 9(ii)B] further support the particle diffusion mechanism.

![Fig. 7-Plots of F vs t and Bt vs t for (A) anionic surfactants, (B) cationic surfactants, using different solution concentrations at 30°C on copper ferrocyanide; \( r = 9.4 \times 10^{-3} \) cm.](image-url)
as the rate controlling process. An enhanced sorption rate at high temperature is probably due to an increase in the mobility of sorbing species. It is evident that the concentration of anionic detergents necessary for particle-diffusion mechanism are less in comparison to cationic adsorbates on the adsorbent copper ferrocyanide. This is attributed to a higher rate of sorption of cationic detergents on copper ferrocyanide as compared to anionic detergents.

The non linear behaviour of log (1-F) versus t plots drawn for some typical sorption systems [Figs 10(A and B)] is also an evidence in favour of particle diffusion mechanism as rate controlling step. The initial portions of McKay plots [Figs 10(A and B)] are convex to log (1-F) axis while the later portion lies on a straight line in each case. It is inferred that the sorption of CP+ and CTA+ cation and SD- and AB- anions, mainly involve two inter diffusion processes, a faster one

![Fig. 8-Plots of F vs t and Br vs t for (A) anionic surfactants (solution conc. = 6.5 x 10^{-6} M), (B) cationic surfactants (solution conc. = 7.5 x 10^{-5} M) using different particle sizes of copper ferrocyanide at 30°C: (1,2) r = 9.4 x 10^{-3} cm; (3,4) r = 5.13 x 10^{-3} cm.](image)

![Fig. 9(i)-Plots of F vs t and Br vs t for (A) SDS; 6.5 x 10^{-6} M, (B) ABS; 6.5 x 10^{-6} M at different temperatures using copper ferrocyanide (r = 9.4 x 10^{-3} cm).](image)

![Fig. 9(ii)-Plots of F vs t and Br vs t for (A) CPB; 7.5 x 10^{-5} M, (B) CTAB; 7.5 x 10^{-5} M at different temperatures using copper ferrocyanide (r = 9.4 x 10^{-3} cm).](image)
corresponding to the residual curve and a slower one corresponding to the latter portion of the plots lying on straight line, contributing to the overall rate of exchange. As the system tends towards equilibrium, the faster one becomes less significant and the slower one dominates. Srivastava et al.\textsuperscript{17} have reported similar results for the sorption of complex cations on chromium ferrocyanide gel. Rawat et al.\textsuperscript{18} have also observed similar behaviour for the exchange adsorption of metal ions on different substrates.

It may be argued that the effective diffusion coefficient, \( D_i \), in these systems, is mainly comprised of two components, which are due to the simultaneous diffusion of the ingoing detergent ions through the pores of different widths and different electric fields along the diffusion path. The diffusion within the pores of wider-widths and weaker retarding forces of electrostatic interaction (particularly at the surface of the sorbent) accounts for the faster one and the one within the pores of narrower mesh widths and stronger retarding forces, accounts for the slower component of \( D_i \). As the temperature increases the contribution of faster component of \( D_i \) increases. It is because of the increasing mobility of ingoing species at higher temperature, which to some extent overcomes the influence of retarding forces. The values of effective diffusion coefficient \( D_i \) are higher for CPB and SDS as compared to CTAB and ABS (Table 3). This is because of the geometry and bigger size of CTAB and ABS as compared to that of CPB and SDS, causing, thereby, more hindrance to its mobility within the pores of sorbent material. Further, the \( D_i \) values are less for anionic detergents in comparison to cationic detergents which may be due to a low anion-exchange value of copper ferrocyanide as compared to its cation-exchange capacity.

The log \( D_i \) versus \( 1/T \) plots for the sorption of CPB, CTAB, SDS and ABS on copper ferrocyanide are linear in nature. This permits the use of Arrhenius equation for the determination of \( D_0 \) and \( E_a \) from the intercepts and slopes of the linear plots. \( D_0 \) values are further used to calculate the entropy of activation for the sorption of CPB, CTAB, SDS and ABS. The values of \( D_0 \), \( E_a \) and \( \Delta S^* \) for all the four systems investigated are listed in Table 4.

The values of activation energy (\( E_a \)) are higher for CTAB and ABS as compared to CPB and SDS. This is due to the bigger size of CTAB and ABS, which causes more steric hindrance to their mobility through the pores of the sorbent material and thus need more energy to undergo diffusion. The entropy of activation values are negative for all the systems and this indicates the lack of orientational effect upon the water environment

<table>
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<th>Detergents</th>
<th>30°</th>
<th>35°</th>
<th>40°</th>
<th>45°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPB</td>
<td>( 1.99 \times 10^{-9} )</td>
<td>( 2.49 \times 10^{-9} )</td>
<td>( 3.26 \times 10^{-9} )</td>
<td>( 3.77 \times 10^{-9} )</td>
</tr>
<tr>
<td>CTAB</td>
<td>( 1.57 \times 10^{-9} )</td>
<td>( 1.91 \times 10^{-9} )</td>
<td>( 2.82 \times 10^{-9} )</td>
<td>( 3.48 \times 10^{-9} )</td>
</tr>
<tr>
<td>SDS</td>
<td>( 2.45 \times 10^{-10} )</td>
<td>( 2.83 \times 10^{-10} )</td>
<td>( 3.79 \times 10^{-10} )</td>
<td>( 4.55 \times 10^{-10} )</td>
</tr>
<tr>
<td>ABS</td>
<td>( 1.43 \times 10^{-10} )</td>
<td>( 2.06 \times 10^{-10} )</td>
<td>( 2.65 \times 10^{-10} )</td>
<td>( 3.33 \times 10^{-10} )</td>
</tr>
</tbody>
</table>

Fig. 10—McKay plots for the sorption of (A) CTAB, (B) SDS on copper ferrocyanide.
Table 4—$D_0$ and thermodynamic parameters for the sorption of detergents

<table>
<thead>
<tr>
<th>Parameters</th>
<th>CPB</th>
<th>CTAB</th>
<th>SDS</th>
<th>ABS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_0$ (cm$^2$ s$^{-1}$)</td>
<td>$3.18 \times 10^{-4}$</td>
<td>$1.60 \times 10^{-2}$</td>
<td>$1.07 \times 10^{-4}$</td>
<td>$3.02 \times 10^{-3}$</td>
</tr>
<tr>
<td>$E_a$ (kcal mol$^{-1}$)</td>
<td>7.17</td>
<td>9.69</td>
<td>7.81</td>
<td>10.10</td>
</tr>
<tr>
<td>$\Delta S^*$ (Cal deg$^{-1}$ mol$^{-1}$)</td>
<td>-9.54</td>
<td>-1.75</td>
<td>-11.70</td>
<td>-5.07</td>
</tr>
</tbody>
</table>

of cations and anions and their faster diffusion through the sorbents. It may also be inferred that the uptake of detergent ions do not cause any structural changes in the sorbent material.

Recovery of the adsorbed material as well as the regeneration of the adsorbent is quite an important aspect for an efficient scavenging process. As such desorption of adsorbate from anionic detergent loaded copper ferrocyanide was tried with a number of eluting agents. Data of these experiments have been shown in the form of plots of percent desorption of anionic detergents versus concentration of eluting reagent added (Fig 11). It is observed that $\text{SO}_4^{2-}$ ions are more effective as compared to $\text{Cl}^-$ ions. An almost complete desorption of both SDS and ABS from copper ferrocyanide detergent complex, could be achieved with the help of two desorbing reagents $\text{K}_2\text{SO}_4$ and a mixture of $1 \text{ M } \text{H}_2\text{SO}_4$ and alcohol (1:1, v/v) (only the plots with $\text{K}_2\text{SO}_4$ are shown in figure). Both these eluting agents are equally effective and the adsorbent copper ferrocyanide can be regenerated for further use.

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References