Adsorption of Non-ionic Surfactants onto Sand and Its Importance in Naphthalene Removal

Santanu Paria*,† and Pak K. Yuet

Department of Process Engineering and Applied Science, Dalhousie University, P.O. Box 1000, Halifax, NS, Canada B3J 2X4

The kinetic and equilibrium adsorption studies of four NP (nonylphenyl ethoxylates) series non-ionic surfactants with different EO (ethylene oxide) groups on sand are presented here. The adsorption behavior of a NP series of surfactants is compared in batch and continuous column studies. The adsorption isotherms are found to be similar in nature in all cases, and the maximum amount adsorbed per gram of sand decreases with an increasing number of EO groups. The comparison of maximum amounts adsorbed in the batch and column shows that the amount adsorbed is the same for both cases. When two surfactants were mixed with a calculated average EO number, the mixed solution showed the same equilibrium amount adsorbed to that of the actual EO number, although transportation through the column showed different behavior. The organic removal efficiency of the surfactants from a sand column depends on the adsorption density on the sand surface and the lowering of the surface tension at the air−water interface. The order of naphthalene removal efficiency of different NP surfactants from a sand column are NP-40 < NP-15 < NP-9. The main objective of this study is to improve the knowledge of surfactant adsorption and its importance in organic removal from the sand surface for the application of soil and groundwater remediation.

1. Introduction

The improper disposal, accidental spills, and leaks of petroleum hydrocarbons and organic solvents have resulted in long-term persistent sources of contamination of soil and groundwater, which has become a serious environmental concern because of its impact on health. Various techniques, including soil vapor extraction, bioremediation, solidification/stabilization, and soil washing, have been used to remediate contaminated sites. Among the in situ techniques, surfactant-enhanced remediation (SER) has been recognized as one of the promising technologies.[1−6] In SER, surfactants play an important role in micellar solubilization and the removal of trapped organics by lowering the oil/water interfacial tension.[3,7,8] Non-ionic surfactants are often used because of their lower critical micelle concentration (CMC) as compared to ionic surfactants, their higher degree of surface-tension reduction, and their relatively constant properties in the presence of salt, which result in better performance and lower concentration requirements. In particular, the non-ionic ethoxylate surfactants have been suggested for the removal of organic contaminants from soil because of their high solubilization capacity and biodegradability.

In addition to these factors, in selecting surfactants for use in SER processes, consideration must also be given to the environmental impact and retention of surfactants.[5] Surfactants retained in the soil matrix after the SER processes themselves act as environmental contaminants. Since surfactant retention is closely related to adsorption on soil particles, insight into the adsorption behavior of non-ionic surfactants is therefore critical in facilitating the application of SER technologies.

The adsorption mechanisms of non-ionic surfactants depend on the nature of the sorbent and the surfactant molecules.[9,10] A number of researchers has investigated the adsorption of non-ionic surfactants on soil,[11−14] sand,[2,15−19] and silica gel[9,20−22] using batch and/or column experiments. Non-ionic surfactants are physically adsorbed rather than chemisorbed, and small changes in the concentration, temperature, and molecular structure of the surfactant can have a considerable effect on their adsorption behavior due to adsorbate−adsorbate and adsorbate−solvent interactions, which may cause surfactant aggregation in bulk solution and lead to changes in orientation and packing of surfactants at the surface.[23] When the adsorption is controlled by bonding between the hydrophobic group of the surfactant and hydrophobic surfaces, adsorption increases with increasing organic content of the soil.[13] Ethoxylate surfactants may also be adsorbed onto charged surfaces by hydrogen bonding between the EO groups and the surfaces. In this situation, the extent of adsorption will depend on the solution pH[24] and electrolyte concentration.[25] Adeel and Luthy[16] observed a two-step breakthrough curve for sorption of TX-100 through a sand column. The two sorption regimes depend on the surfactant concentration and molecular conformation. In the first regime, below CMC, the surface coverage is sparse, and adsorption is rapid; in the second regime, above the CMC, the surfactant clusters, such as partial bi-layers, are formed, and sorption is relatively slow. They also observed that the maximum adsorbed surfactant mass in the column studies was less than that of batch studies due to a lesser accessible surface area in the packed column. Abdul and Gibson[18] found an S-shaped curve for the adsorption of alcohol ethoxylate surfactants on sand in the case of both batch and column experiments.

Most of the research efforts in surfactant-enhanced remediation process have been focused on the adsorption of different surfactants on aquifer sediments and their efficiency of organic removal from the matrix. This work is the continuation of our previously published works.[26,27] The research presented in this paper is mainly focused on the experimental study of adsorption and desorption of a nonylphenol (NP) series of single and mixed non-ionic surfactants on sand with different hydrophililic chain lengths (EO) in both batch and column. The organic removal

* To whom correspondence should be addressed. Fax: 902 420 7639. E-mail: santanuparia@yahoo.com.

† Present Address: Department of Chemical Engineering, National Institute of Technology, Rourkela-769 008, Orissa, India.

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efficiency of the pure surfactants and the mixture of two non-ionic surfactants from a sand column is also studied.

2. Materials and Methods

A series of non-ionic surfactants was used as received, nonylphenyl ethoxylates (4-$C_9H_{19}C_6H_4(OCH_2CH_2)_nOH$ or NP-n (n = 9, 12, 40)) were obtained from Aldrich Chemicals and NP-15 (n = 15) from Nikko Chemicals. Ultrapure water of 18.2 MΩ resistivity (Barnstead International) was used for all experiments. The sand used for the studies was obtained from Bonar Inc., Canada; the density was determined experimentally to be 2.6 g/cm^3. The surface area of the sand was 0.3 m^2/g, determined by the methylene blue adsorption method.[28] The pH_{PZC} (point of zero charge) of sand is reported to be ~2, and the surface charge becomes more negative with an increasing pH up to ~11.[29] It was also reported that the surface charge was approximately −40 mV at pH 7.

2.1. Sand Sieving and Cleaning. The sand was sieved in a sieve shaker, and the 212−500 μm sized sand was taken for the experiments. The sand was cleaned prior to each experiment according to the procedure given in our earlier publication.[26]

2.2. Experimental Measurements. Surfactant concentrations were determined using a UV−vis spectrophotometer (Shimadzu, Model UV-1700) at 259 nm wavelength with quartz glass cells of 10 mm path length. The naphthalene concentration in the aqueous phase was determined using a UV−vis spectrophotometer at 275 nm wavelength, and when the surfactant was used, the same concentration surfactant solution was used in the blank. The surface tension was measured by the Wilhelmy plate method using a Kruss K100 tensiometer. CMC values (millimolar) of NP-9, NP-12, NP-15, NP-40, and NP-15$_{mix}$ are 0.05, 0.07, 0.09, 0.15, and 0.08, respectively. Details of the batch studies and the conditions were the same as our earlier publication.[26] The column experiments were conducted with a glass column with inner threaded PTFE caps shielded with O rings at both ends. The column was 30 cm in length and 1.5 cm in diameter. A constant flow rate (3.3 mL/min for all the experiments) was controlled using a peristaltic pump (Masterflex from Cole Parmer). The porosity, ϵ, of the sand bed was 0.42, calculated according to the following relation:

$$\epsilon = \frac{V - (m/\rho)}{V} \tag{1}$$

where V is the empty column volume, m is the mass of the sand used, and ρ is the sand density. Experimental details for the removal of naphthalene are given elsewhere.[27]

3. Results and Discussion

3.1. Batch Adsorption: Kinetic Studies. The adsorption kinetics of four different EO chain length surfactants were studied at the sand−water interface to obtain information about the equilibrium time and the rate of adsorption. The experimental data on adsorption kinetics of four NP surfactants are plotted in Figure 1. To analyze these data, the adsorption kinetics of the four different NP surfactants were normalized by their respective maximum amount of adsorbed values, and it is observed that there is no significant difference among the four surfactants (the plot is not shown). This observation suggests that the rates are almost similar for all four surfactants, that the rate of adsorption of NP surfactants on sand is very fast, and that about 55% of the maximum amount adsorbed is adsorbed in less than 1 min. Since the rate of adsorption is almost similar

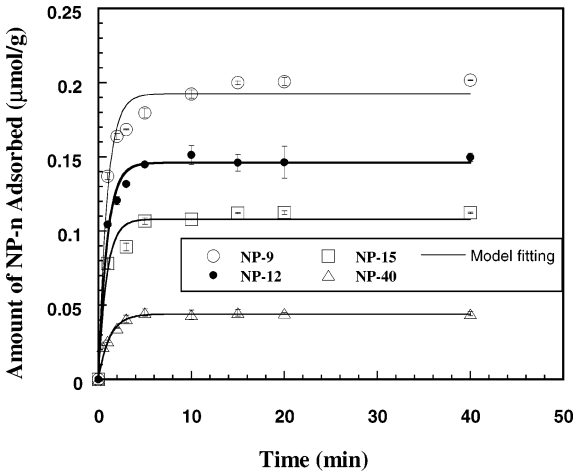

Figure 1. Comparisons of experimental data on the adsorption kinetics of different NP-n surfactants with the theory at 0.2 mM concentration and 25 °C.

for all the cases, the adsorption seems to be driven by the surfactant tail, which is identical for all the surfactants. The effect of the head group is reflected by the amount of surfactant adsorbed, where the larger the head group, the lesser the amount adsorbed due to the larger molecular area occupied on the sand surface.

To further quantify the adsorption rate constants, the rate of adsorption at time t is expressed as[30]

$$\frac{dx_t}{dt} = k_a(x_m - x_t)C_b - k_d x_t \tag{2}$$

where x_t is the amount of surfactant adsorbed at time t (mM/g), x_m is the maximum amount of surfactant adsorbed (mM/g), C_b is the bulk concentration of surfactant at time t (mM/L), k_a is the rate of adsorption (L mM^{-1} min^{-1}), and k_d is the rate of desorption (min^{-1}). C_b can be represented as

$$C_b = C_0 - \frac{mx_t}{v} = C_0 - zx_t \tag{3}$$

where m is the mass of adsorbent in grams, v is the volume of surfactant solution in liters, C_0 is the initial surfactant concentration in millimolar/liter, and z is m/v. Rearranging eq 2 yields

$$\frac{dx_t^{\,d}}{dt^d} = k_a^{\,d}[x_m^{\,d} - (bx_t^{\,d} + x_f^{\,d^2})] \tag{4}$$

where the dimensionless variables are defined as follows:

$$x_t^{\,d} = x_t z/C_0$$

$$x_m^{\,d} = x_m z/C_0$$

$$t^d = t/T$$

$$k_a^{\,d} = k_a T C_0$$

$$K = k_d/k_a C_0$$

$$b = -(x_m^{\,d} + K + 1)$$

where T is the characteristic time, which can be taken as the

Table 1. Values of Kinetic Parameters Obtained from the Model of Different Surfactants on the Sand−Water Interface

	parameters				
surfactants	k_a (L mM^{-1} min^{-1})	standard error	k_d (min^{-1})	$(x_m)_{expt}$ (μM/g)	$(x_m)_{model}$ (μM/g)
NP-9	5.344	0.717	0	0.202	0.193
NP-12	5.346	0.543	0	0.149	0.146
NP-15	5.676	1.064	0	0.112	0.108
NP-40	4.218	0.636	0	0.044	0.044

maximum time of measurement (40 min). Integrating eq 4 yields

$$x_t^{\,d} = -\sqrt{-q}\left[1 - \frac{\gamma_1}{\gamma_2}\exp[-(k_a^{\,d}\sqrt{-q})t^d]\right]^{-1} - \frac{\gamma_2}{2} \qquad (5)$$

where $q = 4x_m^{\,d} - b^2$; $\gamma_1 = b + \sqrt{-q}$; and $\gamma_2 = b - \sqrt{-q}$. Equation 5 can be fitted to the experimental data to obtain b, q, and $k_d^{\,d}$. However, to obtain physically meaningful values, we put bounds on the parameters $x_m^{\,d}$, K, and $k_a^{\,d}$, namely, $x_m^{\,d} > 0$, $k_a^{\,d} > 0$, and $K \geq 0$ for the fitting. The last constraint allows for the possibility that there is no desorption. The experimental results are fitted with the model using SAS software. Different parameters obtained from the fitting of experimental data are given in Table 1. Table 1 shows that adsorption rate constant (k_a) values are very similar for NP-9, NP-12, and NP-15 but slightly different for NP-40. Slower rates of adsorption for NP-40 (lower value of k_a) may be due to the bulkiness of the long EO chain head group. It has also been found that the desorption rate constants are zero in all the cases, which may be reasonable because at the beginning, adsorption will predominate over desorption. The rate constant values were determined at 0.2 mM concentration. We also performed the adsorption at 0.4 mM concentration (data not shown), but we did not find any significant difference in adsorption kinetics between 0.2 and 0.4 mM concentration as both are above the CMC, so we report the results at 0.2 mM concentration. The experiments were accomplished above the CMC because for soil remediation, the presence of micellar clusters is important. There is a reported study on the effect of the surfactant concentration on adsorption kinetics.[31] The study shows that both above and below the CMC, the initial adsorption rate increases with increasing concentration. We believe the difference is because of the difference in the adsorption behavior. The fitting of experimental data with the theory is shown in Figure 1.

3.2. Batch Adsorption: Equilibrium Studies. Figure 2 shows the adsorption isotherm of four different NP surfactants. The nature of the isotherm is the same for all four surfactants, and the amount of surfactants adsorbed increased with the decreasing EO groups. To see the effect of the electrolyte on the adsorption isotherm of NP-9, an experiment was carried out in the presence of 100 mM NaCl, but no change in the equilibrium amount adsorbed or the shape was observed in this concentration (data not shown), which again further supports the hypothesis that the adsorption does not occurr by electrical interaction or hydrogen bonding between the surface and the head group but with the hydrophobic tail.[32]

The maximum amount adsorbed at the plateau is plotted in Figure 3. Figure 3 shows the amount of surfactant adsorbed with changing the number of EO groups and is not linear. The inset of Figure 3 shows the plot of the area occupied by one molecule of surfactants at the sand surface with different EO

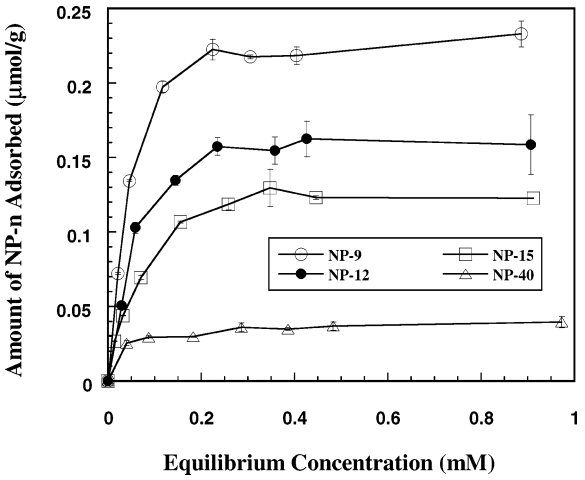

Figure 2. Adsorption isotherm of NP-*n* surfactants with different ethylene oxide groups on sand at 25 °C.

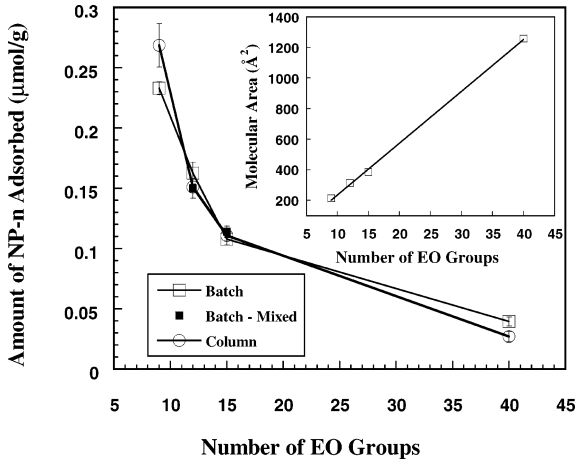

Figure 3. Comparisons of maximum amount adsorbed from batch adsorption of single and mixed surfactant systems and adsorption in column for single surfactants with varying EO number. Inset shows the plot of surface area occupied by each molecule of NP surfactants on sand with different EO numbers.

numbers. The area occupied per molecule in angstroms squared is calculated as

$$a = \frac{S \times 10^{26}}{\Gamma N} \qquad (6)$$

where a is the area occupied per surfactant molecule in angstroms squared, $S = 0.3$ m^2/g is the surface area of sand, Γ is the amount of surfactant adsorbed at the plateau in micromoles per gram, and N is Avogadro's number. The figure shows that the area covered by a molecule on the solid surface linearly increases with increasing EO groups. Furthermore, to understand the mechanism of adsorption, we have mixed a calculated amount of two surfactants NP-9 and NP-40 to obtain a calculated average EO number of the mixed surfactant system. We have mixed NP-9/NP-40 = 9:1 and a 4:1 mole ratio to obtain calculated average NP-12$_{mix}$ and NP-15$_{mix}$. Interestingly, we obtained very close values of the maximum amount adsorbed at the plateau to that of the original NP-12 and NP-15, which are shown in Figure 3. Since the area occupied per molecule of surfactant on the sand surface linearly increases with the EO chain length, the mixture of two surfactants with calculated amounts also shows a similar average molecular area after adsorption to that of a single surfactant of the same average EO number.

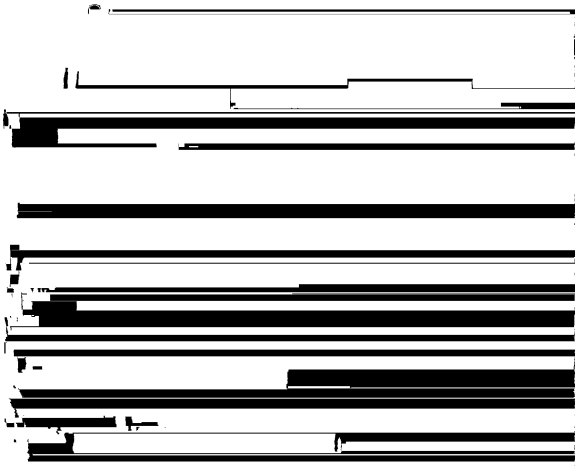

Figure 4. Plot of concentration vs surface tension of NP-9, NP-15, NP-40, and NP-15_{mix} at 25 °C.

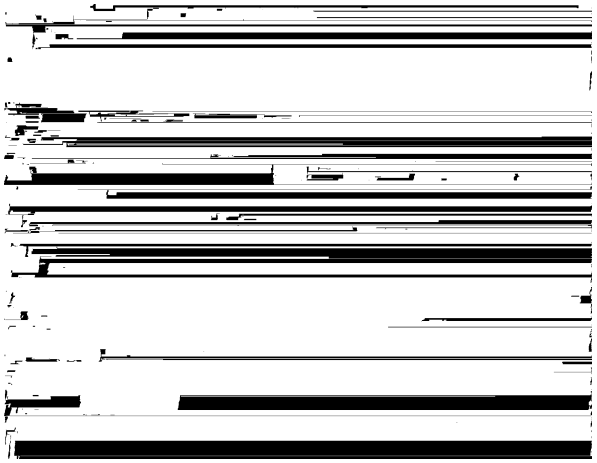

Figure 5. Surfactant adsorption breakthrough curve for NP-9 at three different concentrations at 25 °C. Inset shows same plot at lower time scale.

Further, to observe the bulk property of the mixed system, we have measured the surface tension of the mixed surfactant system. Figure 4 presents the surface tension versus concentration plot of NP-9, NP-15, NP-40, and NP-15_{mix}. The plot shows that with an increasing number of EO groups, the CMC values increase and the minimum surface tension values above the CMC also increase, but the minimum surface tension value of the mixed surfactant system is equal to that of NP-9, which is lower than NP-15. From an application point of view, the surface tension reduction is an indication of the detergent ability of a surfactant with the mechanisms of solubilization or roll-up of organics. Low surface tensions usually indicate lower CMCs and thus a higher potential for micellar solubilization and detergent ability.[33] On the other hand, lower surface tensions (which in turn, lower contaminant−aqueous solution interfacial tensions) might lead to larger contact angles of the organic phase on a solid substrate and thus to an improvement in roll-up for removing liquid contaminants. Thus, by summarizing the results on adsorption and surface tension of mixed surfactant systems, we can conclude that the mixed system (NP-15_{mix}) has a similar adsorption density on the solid surface than that of a single surfactant (NP-15) but will have a better solubilization efficiency and detergent ability. The solubilization efficiency of different single and mixed surfactant systems is discussed later in this paper.

3.3. Column Studies of Surfactant Adsorption and Desorption. 3.3.1. Effect of Concentration. Figure 5 represents the adsorption behavior of NP-9 through the column at three different concentrations: 0.1, 0.2, and 0.5 mM. The results are presented as the dimensionless concentration (ratio of outlet concentration (C_t) to inlet concentration (C_0)) versus time. The result presented in Figure 5 shows that the breakthrough curves are S-shaped. The time or pore volume required for starting the breakthrough and equilibrium are more when the surfactant concentration is lower. The reason for this observation is due to the fact that the surfactants are adsorbed from the mobile phase on the way through the column and that the surfactant concentration is depleted until the sand surface is saturated with surfactant. For saturating the column with the surfactant, the total surfactant passing through the column will be at least equal or more than that required for the saturation. When the concentration of the solution is less, more volume is required to pass through the column. Another explanation may be that diffusion plays an important role in the transport of the surfactant through the packed bed. Because the progress of the time surfactant concentration near the column outlet is less than the inlet concentration due to adsorption, as a result, initially there will be a concentration gradient inside the column. If the inlet concentration is more, the diffusive flux will be more as the concentration gradient increases; as a result, the outlet concentration will increase rapidly.

The total amount of surfactant adsorbed per gram of sand inside the column was also measured. A certain pore volume (500 mL) of the surfactant solution that is greater than the pore volume required to reach the equilibrium was passed through the column, and the change in concentration in the final solution was measured to calculate the amount adsorbed. The results of comparisons of surfactants with four different EO groups adsorbed in batch and column are presented in Figure 3. The results indicate that the values of the amount of surfactant adsorbed per gram of sand are very close in the batch and column. So, the maximum amount adsorbed does not depend on the batch or column type experiments. We have also checked the surfactant retained inside the sand column after flushing with pure water, which is an important factor in soil remediation application. In soil remediation, finally the surfactant retention is not desirable because of environmental concerns. For this experiment, 500 mL of a 0.2 mM NP-9 solution was passed through the column, and after the surfactant solution, 1100 mL of pure water was passed until the outlet concentration (checked in UV absorbance) was shown to be below the detection limit. We observed that the total amount of surfactant present in the outlet (1600 mL, 0.062 mM) was exactly same as the amount pumped through the column. So, as the non-ionic surfactants are mainly adsorbed physically and can be desorbed easily from the sand column by eluting with pure water, the cationic surfactants are not completely desorbed from the sand column.[26]

3.3.2. Effect of EO Groups. The results on the effect of variations of the EO groups on adsorption in the column are shown in Figure 6 a. The figure shows that with increasing the number of EO groups, the breakthrough starts very fast as well as the time required for the equilibrium also being less. The difference in breakthrough curves due to variations of the EO groups is mainly due to the difference in the amount of maximum surfactant adsorbed. NP-40 has a very low adsorption density on the sand surface that shows more outlet concentrations immediately after the solution coming out from the column, and the reverse occurs for NP-9.

The dynamics of adsorption of mixed surfactants (NP-15_{mix}) through the column is also shown in Figure 6a. In the batch study, the mixed system showed the same equilibrium amount adsorbed to that of NP-15. In the column, although the

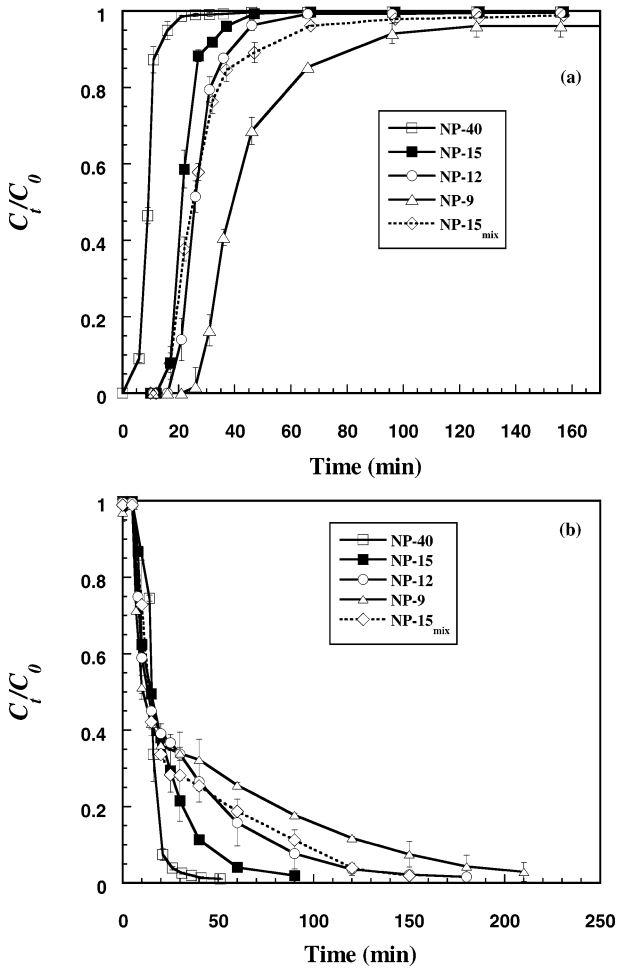

Figure 6. (a) Surfactant adsorption breakthrough curve for NP-9, NP-12, NP-15, NP-40, and NP-15_{mix} at 0.2 mM concentration and 25 °C. (b) Desorption of NP-9, NP-12, NP-15, NP-40, and NP-15_{mix} from the sand column in the presence of pure water.

beginnings of the breakthrough are very close to each other, the progress of time adsorption of the mixed system is slower for than that of NP-15 and faster than that of NP-9. This can be explained as follows. The beginning of the breakthrough mainly depends on two factors: (a) maximum amount of surfactant adsorbed and (b) initial gradient in concentration, which further depend initially on the inlet surfactant concentration. The maximum amount adsorbed and the total inlet concentration are the same for both NP-15_{mix} and NP-15, so the beginning of the breakthrough is very close. With the progression of time, the difference is due to the lower individual concentrations, as we have seen the effect of concentrations on the breakthrough curve in Figure 5.

Desorption characteristics of surfactants with different EO groups and the mixed surfactant are presented in Figure 6b. For the desorption study, after the system has reached equilibrium in the presence of surfactant, pumping of surfactant solution was stopped, and pure water was used, and subsequently, the change in outlet concentration was measured with time. It was found, as expected, that after pumping one pore volume of water, the concentration was dropped suddenly, and approximately up to 20 min, all the surfactants showed similar behavior. Finally, as the number of EO groups increased, the desorption was very fast since a smaller number of molecules was adsorbed and they are more hydrophilic in nature. In the case of the NP-15_{mix} system, after 30 min, the outlet surfactant concentration was higher than that of NP-15 and was very close

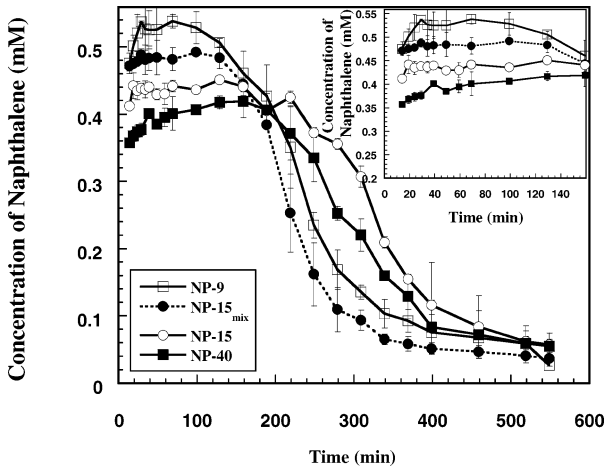

Figure 7. Naphthalene removal efficiency from a sand column using NP-9, NP-15, NP-40, and NP-15_{mix} at 2 mM concentration and 25 °C. Inset shows same plot at lower time scale.

to that of NP-9. The difference is possibly due to the fact that mostly NP-9 molecules are present after 30 min and that NP-40 eluted first, and after 20 min, the desorption rate of NP-9 was slower than the rate of NP-15 as shown in the desorption nature of the single NP surfactants.

3.4. Removal of Naphthalene from the Sand Column. In this section, we discuss the removal efficiency of naphthalene from the sand column by flushing different NP surfactants. The naphthalene removal efficiency of surfactants from a sand column is considered in terms of the maximum concentration of naphthalene showing in the outlet aqueous phase when the surfactant was passed through the column. Separate batch solubility experiments show that the solubility of naphthalene is very close for all NP surfactants.[27] So, the experiment of naphthalene removal efficiency was carried out at the same surfactant concentrations. The removal of organics by solubilization is a very complex process, especially when another solid phase (sand) is present. Even the mechanism may be different when the solute is solid or liquid. Figure 7 shows the plot of the outlet naphthalene concentration with the progression of time from a sand column in the presence of different single and mixed NP surfactants (NP-9, NP-15, NP-40, and NP-15_{mix}) at 2 mM concentration. Figure 7 shows that initially (plateau section of the curves) the increasing order of naphthalene removal efficiency among the NP series surfactants is NP-40 < NP-15 < NP-9, although the difference between NP-15 and NP-40 is very close. The order is similar to that of the molecular density of NP surfactants adsorbed on the sand surface (see inset of Figure 3). NP-9 shows higher maximum solubilization than the other two. The solubilization value of NP-9 at the maximum is very close to that of batch experiments (maximum limit of the *Y*-axis represents the maximum value of solubilization in batch experiments), but the maximum values for NP-15 and NP-40 are less than that of NP-9. The higher removal efficiency of NP-9 may be due to the higher adsorption density on the sand surface. As more surfactant molecules are adsorbed on the solid surface, more naphthalene can be detached or removed from the sand surface and will be easily available for solubilization. Another reason may be the lowering of the surface tension. Lowering the surface tension is important for a good wetting agent.[34] Low surface tension values can help to penetrate the surfactant solution in the small pore of the packed bed, as well as between the small restricted pores between the organic and the sand surface, which, in turn, can make better wetting and more organic molecules available for solubilization. Figure 7

also presents the solubilization efficiency of NP-15_{mix}; the mixed system shows a higher removal efficiency than NP-15 and is closed to that of NP-9. This can be explained in terms of a lower surface tension of the mixed system (see Figure 4), although the mixed surfactant system has a lower (almost half) adsorption capacity (0.114 μmol/g) than NP-9 (0.233 μmol/g).

Mixed surfactant systems may be useful for any remediation, enhanced oil recovery, and detergency process since they can reduce the loss of surfactants due to adsorption more so than that of single surfactants but show better organic removal efficiency from the solid surfaces.

4. Conclusion

The adsorption of non-ionic surfactants with different hydrophilic chain lengths has been studied in both batch and column experiments. With increasing hydrophilic chain length, since the head area of the surfactants increases as the maximum amount adsorbed decreases, the area occupied per molecule at the solid surface increases linearly with the number of EO groups. The adsorption rate constants obtained from the kinetic data show that they are very close for NP-9, NP-12, and NP-15 but have a slightly lower value for NP-40. The comparisons of the maximum amount adsorbed in both batch and column is shown to be the same. The effect of the EO group shows that with increasing the number of EO groups, the breakthrough begins very early as well as the time required for the equilibrium being less in column experiments. Desorption experiments show that complete removal of surfactants from the column is possible by eluting with pure water. Mixed surfactants with calculated average EO groups show similar amounts adsorbed in the batch to that of a single surfactant. The mixed surfactant system may be useful for remediation because it shows a lower adsorption density at the solid surface to that of a pure system but shows better solubilization efficiency of organics.

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