

Removal Rates of Major and Trace Components of an Organic Film Using Aqueous Nonionic Surfactant Solutions

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This work examines the cleaning of organic films composed of a primary component (abietic acid) mixed with trace amounts of a second contaminant (benzoic acid). Films were removed from a rotating disk in the presence of aqueous solutions of two poly(ethylene glycol) alkyl ether surfactants: C₁₂E₅ and C₁₆E₈. With C₁₂E₅ the abietic acid was removed from the disk in three successive cleaning stages—solubilization, shear removal, and rollup—whereas the benzoic acid was almost completely removed during the initial solubilization stage. Also, with C₁₂E₅ the results show that the micellar solubilization rate of the trace contaminant is directly proportional to its concentration in the film. The ratio of the molar removal rates of benzoic acid to abietic acid with C₁₂E₅ is an order of magnitude greater than the ratio of the mole fractions of the two components in the contaminant film. Solutions of C₁₆E₈ removed the abietic acid by only the solubilization and rollup stages. The ratio of the molar removal rates of benzoic acid to abietic acid with C₁₆E₈ was equal to the ratio of the mole fractions of the two components in the contaminant film. A mathematical model is proposed to quantify the simultaneous removal of benzoic acid and abietic acid during the micellar solubilization stage. The model takes into account the mass-transfer rate between the film and the bulk solution, as well as the micellization rates at the film/surfactant solution interface. The model adequately represents the experimental data.

Introduction

A common goal in cleaning processes is to achieve a desired degree of contaminant removal. During cleaning, a state of thermodynamic equilibrium does not exist. The rate of cleaning may be controlled by a complex series of steps which include solubilization, mass transfer, shear removal, and rollup. Previous work by our group has focused on examining the removal rates of a homogeneous organic contaminant film from a solid substrate.^{1–5} These studies helped to elucidate the mechanisms responsible for cleaning and to establish, under controlled shear and mass-transfer conditions, how changes in the surfactant molecular structure influence the cleaning rates. Industrial cleaning processes generally involve the removal of contaminants composed of multiple constituents. This work describes the cleaning of organic films containing a trace contaminant in order to understand how the cleaning mechanism determines the rates of removal of the major and minor components.

There has been little work done on the selectivity of surfactant-based cleaning processes. Thomas and Christian⁶ determined how the ratio of concentrations of species solubilized by micelles compares with their concentrations in the bulk solution. They examined the solubilization of benzene and cyclohexane in sodium deoxycholate micelles and found that the ratio of concentrations of each species solubilized was identical to that of their bulk concentrations in aqueous solution. Nagarajan and Ruckenstein⁷ argued that the results of Thomas and Christian⁶ were explainable because the molar solubilization ratios (MSR) of benzene and cyclo-

hexane were very similar in sodium deoxycholate micelles. The molar solubilization ratio is defined by the expression

$$\text{MSR} = \frac{C_{\text{sol}} - C_{\text{sat}}}{C_{\text{sur}} - \text{cmc}} \quad (1)$$

where C_{sol} is the concentration of organic species solubilized, C_{sat} is the aqueous solubility of the organic species, C_{sur} is the total surfactant concentration, and cmc is the surfactant's critical micelle concentration. The MSR represents the ratio of the moles of solute solubilized in micelles to moles of surfactant in micelle form. The application of this concept is approximate because it assumes no effect of solute concentration on cmc and no effect of the surfactant on C_{sat} . The MSR is not defined for submicellar conditions.

Nagarajan and Ruckenstein^{7,8} showed that the surfactant cetyl pyridinium chloride was 7 times more selective for benzene than for hexane. Aqueous solutions of octyl glucoside and sodium dodecyl sulfate also exhibited selective solubilization of benzene over hexane. These results were attributed to the higher MSR of benzene as compared to hexane. Additional experiments using benzene–hexane, benzene–cyclohexane, and hexane–cyclohexane as solubilizates confirmed the increase in solubilization with higher MSR.^{7,8}

Diallo et al.⁹ correlated the solubilities of small organic compounds with the hydrophile to lipophile balance (HLB) of nonionic surfactants. It was suggested in this work that the location of a solubilizate within a micelle can affect its solubility.

The goal of the present work is to measure the selectivity exhibited by aqueous solutions of nonionic surfactants in the rate of removal of two different

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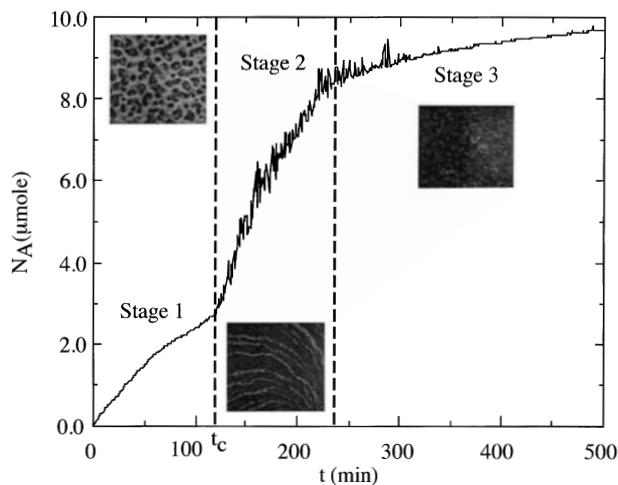


Figure 1. Typical cleaning curve of an abietic acid film from a rotating disk using a $C_{12}E_5$ surfactant. The cleaning mixture is an aqueous solution of $C_{12}E_5$ with a concentration of 6×10^{-5} M. The rotational speed of the disk is 1750 rpm. Insets show photographs of the film on the surface of the disk at the three stages of cleaning.

components from a surface film. This information allows for an improved understanding of the interactions between surfactant micelles and the interface during surface cleaning. The contaminants chosen consist of trace amounts of benzoic acid in a continuous film of abietic acid. The rate of removal of abietic acid by aqueous solutions of nonionic surfactants has been studied in detail, as described below. Only trace amounts of benzoic acid were introduced into the abietic acid film so that the presence of benzoic acid would not interfere with the previously determined mechanisms of removal of the abietic acid from the surface.

Prior Work

The rates of removal of abietic acid films from an epoxy laminate substrate in aqueous solutions of nonionic surfactants have been measured in a rotating disk apparatus.¹⁻⁴ Abietic acid is a primary component of solder flux and was chosen as the contaminant to simulate the removal of flux residues from printed circuit boards. The rotating disk apparatus allowed for controlled shear and mass-transfer rates.¹⁻³ These experiments used 10 μ m thick abietic acid films and alkyl ethoxylated surfactants, C_xE_y , with the following structure: $CH_3(CH_2)_{x-1}O(CH_2CH_2O)_yH$.⁴ It was found that abietic acid removal can occur by three different sequential cleaning mechanisms in the case of C_xE_5 surfactants such as $C_{12}E_5$. Figure 1 is a typical example of a cleaning curve that shows the total number of moles of abietic acid removed from the disk as a function of time using $C_{12}E_5$. The three stages of cleaning are characterized by differences in the rates of removal and the physical appearance of the film. Experiments with C_xE_8 surfactants only exhibited the first and third stages. Figure 2 is a typical cleaning curve for $C_{16}E_8$ and shows how the film morphology changes with time.

With $C_{12}E_5$ the first stage exhibits a slow rate of removal and typically ends when approximately 10% of the abietic acid is removed. Cleaning in the first stage occurs by solubilization of the abietic acid. During the first stage surfactant partitions into the contaminant film, allowing water to penetrate the film. This liquefies the film and causes it to break and expose bare patches of substrate, as shown in Figure 1. Once the viscosity

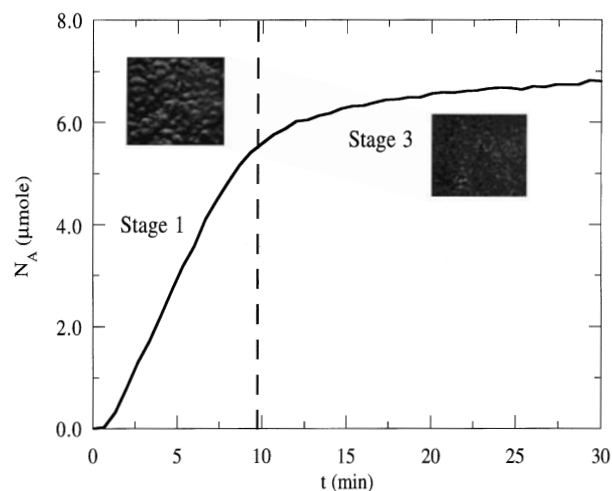


Figure 2. Typical cleaning curve of an abietic acid film from a rotating disk using a $C_{16}E_8$ surfactant. The cleaning mixture is an aqueous solution of $C_{16}E_8$ with a concentration of 1.84×10^{-2} M. The rotational speed of the disk is 1750 rpm. Insets show photographs of the surface of the disk at two stages of cleaning.

of the film is lowered because of the uptake of water and surfactant in the first stage, the second stage begins.¹⁻⁴ The second stage has a much faster rate of removal and accounts for the majority of the abietic acid removed. The second stage cleaning mechanism has been determined to be shear removal of the abietic acid film. This stage is characterized by the presence of rivulets whose curvature follows lines of constant stress (Figure 1).³ Droplets of the contaminant film are detached from the disk through the rivulets and are seen as spikes in the cleaning curve. The third stage is characterized by a very slow rate of removal dominated by rollup of isolated droplets created as the rivulets break apart.

At the same concentration (much higher than the $C_{12}E_5$ and $C_{16}E_8$ CMC values), $C_{16}E_8$ exhibits a faster first stage rate of abietic acid removal than $C_{12}E_5$. The first stage mechanism is the same for both types of surfactants, but with $C_{16}E_8$ the first stage accounts for at least 80% of the abietic acid removed. Also, as seen in Figure 2, $C_{16}E_8$ does not cause the contaminant film to coalesce or form rivulets. This is because not enough water partitions into the film to allow a sufficient reduction in film viscosity. As a result, $C_{16}E_8$ does not exhibit the second stage characteristic of the $C_{12}E_5$ behavior. The third stage removal rate for $C_{16}E_8$ is dominated by rollup of isolated droplets of material, similar to the third stage observed with $C_{12}E_5$.

Although $C_{12}E_5$ allows more water to partition into the contaminant film than $C_{16}E_8$, the first stage cleaning mechanism for both surfactants can be described in terms of the same transport and interfacial processes. These processes are (1) mass transfer of the surfactant from the bulk of the aqueous solution to the vicinity of the film surface; (2) adsorption of surfactant onto the interface; (3) formation of solute-laden micelles containing abietic acid molecules that desorb from the interface into the aqueous phase; and (4) mass transfer of micelles from the interface region to the bulk aqueous solution.

During the first stage both surfactant and water are simultaneously partitioning into the abietic acid (organic) phase, although more water partitions into the organic phase with $C_{12}E_5$ than with $C_{16}E_8$. As was shown in prior work,³ surfactant mass-transfer limitations are negligible in this process, which is controlled

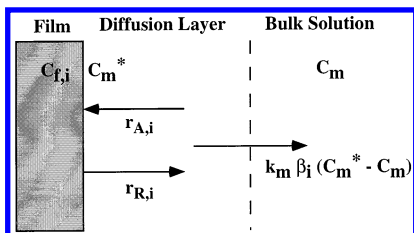


Figure 3. Proposed mechanism for the removal of contaminant from the film into the bulk solution.

by steps 3 and 4. Kabin et al.³ developed a mathematical model for the cleaning of abietic acid during stage 1 taking into account the net rate of removal of abietic acid micelles from the interface and their subsequent mass transfer into the bulk of the surfactant solution (steps 3 and 4). The model previously developed is extended in this work to the case of a contaminant film containing two components.^{3,10}

Model Development

It is important to note that, unlike traditional dissolution models, this model does not assume equilibrium at the solid/liquid interface. The model neglects diffusion limitations within the film and also considers that the rate of dissolution of abietic acid and benzoic acid into pure water is negligible compared to their rate of micellization by surfactant. This latter assumption was confirmed experimentally when mixed coated disks were spun in pure water. Virtually no abietic acid was solubilized, and the solubilization rate of benzoic acid was 3 orders of magnitude slower than that in the presence of surfactant. When surfactant is present, the solubilities of both the abietic acid and benzoic acid were significantly increased.

Figure 3 shows the mass fluxes in relation to the contaminant film. The contaminant film initially has a concentration of each species $C_{f,i}$. Abietic acid and benzoic acid are being solubilized in micelles at the specific rate $r_{R,i}$ (moles of i removed from the film surface per unit time and area). On the other hand, $r_{A,i}$ is the rate of adsorption of abietic acid and benzoic acid from the aqueous solution onto the interface. The concentration of solute-laden micelles at the film/solution interface is C_m^* . The concentration of solute-laden micelles in the bulk solution is C_m . Movement of each species from the film/liquid interface to the bulk of the aqueous phase is governed by the mass-transfer coefficient k_m ; the ratio of moles of component i micellized at the interface per unit mole of solute-laden micelles in the bulk solution β_i ; and the difference in concentration of the solute-laden micelles at the solid/liquid interface and the bulk solution. A steady-state molar balance of contaminant i (i = abietic acid or benzoic acid) yields the following expression for the cleaning rate in stage 1:

$$k_{1,i} = A(r_{R,i} - r_{A,i}) = k_m A \beta_i (C_m^* - C_m) \quad (2)$$

where A is the film surface area. The initial cleaning rate for component i in stage 1 ($k_{1,i}$) is therefore a function of surfactant concentration and all of the parameters that affect the mass-transfer coefficient and adsorption rate constant. In a rotating disk apparatus, the mass-transfer coefficient is given by¹¹

$$k_m = 0.6205 \nu^{-1/6} D_A^{2/3} \omega^{1/2} \quad (3)$$

where ν is the kinematic viscosity of the aqueous solution, D_A is the diffusion coefficient of the solute-laden micelles in the aqueous solution, and ω is the disk rotational speed.

As a first approximation, it is assumed that the rate of adsorption, $r_{A,i}$, is first order in the micellar aggregate concentration at the interface

$$r_{A,i} = k_{A,i} \beta_i C_m^* \quad (4)$$

where $k_{A,i}$ is a rate constant. Note that $\beta_i C_m^*$ represents the moles of species i per unit volume in the liquid phase at the interface. At the start of cleaning ($t = 0$), there is no contaminant in the bulk solution ($C_m = 0$). Substituting eq 4 into eq 2 results in

$$r_{R,i} - k_{A,i} \beta_i C_m^* = k_m \beta_i C_m^* \quad (5)$$

Solving for C_m^* yields

$$C_m^* = \frac{r_{R,i}}{\beta_i (k_{A,i} + k_m)} \quad (6)$$

Combining eqs 2 and 6 results in an expression for the rate of removal at the start of cleaning,

$$k_{1,i} = k_m A \beta_i C_m^* = \frac{k_m A r_{R,i}}{k_{A,i} + k_m} \quad (7)$$

The mass-transfer coefficient (from eq 3) can be rewritten in the form

$$k_m = \alpha \omega^{1/2} \quad (8)$$

where $\alpha = 0.6205 \nu^{-1/6} D_A^{2/3}$, which is independent of rotational speed. The rate of micellar solubilization of species i is assumed to be proportional to the concentration of solute species in the film,

$$r_{R,i} = k_{R,i} C_{f,i} \quad (9)$$

where $k_{R,i}$ is a rate constant and $C_{f,i}$ is the concentration of species i in the film. Combining eqs 7–9 results in the following expression for $k_{1,i}$:

$$k_{1,i} = \frac{k_{R,i} C_{f,i} A \alpha \omega^{1/2}}{k_{A,i} + \alpha \omega^{1/2}} \quad (10)$$

This expression does not assume equilibrium at the solid/liquid interface, as mentioned previously.

At equilibrium

$$r_{A,i} = r_{R,i} \quad (11)$$

so that according to eqs 4 and 9

$$k_{A,i} \beta_i C_m^* = k_{R,i} C_{f,i} \quad (12)$$

The thermodynamic partition coefficient for species i between the film and the micelles, K_i , can then be defined as

$$K_i = \frac{k_{A,i}}{k_{R,i}} = \frac{(C_{f,i})_e}{(\beta_i C_m^*)_e} \quad (13)$$

where, in eq 13, $(C_{f,i})_e$ is the amount of species i in the

contaminant film and $(\beta_i C_m^*)_e$ represents the amount of dissolved species i at equilibrium.

Substituting eq 13 into eq 10 and rearranging results in

$$\frac{1}{k_{1,i}} = \frac{K_i}{C_{f,i} A \alpha} \frac{1}{\omega^{1/2}} + \frac{1}{k_{R,i} C_{f,i} A} \quad (14)$$

According to this model, a plot of experimental values of $1/k_{1,i}$ vs $\omega^{-1/2}$ should result in a straight line. In this form, the contributions of mass transfer and solubilization kinetics can easily be distinguished:

$$\text{mass-transfer resistance} = \frac{K_i}{C_{f,i} A \alpha \omega^{1/2}} \quad (15)$$

$$\text{solubilization resistance} = \frac{1}{k_{R,i} C_{f,i} A} \quad (16)$$

The ratio between the first stage removal rates of benzoic acid and abietic acid, $k_{1,B}/k_{1,A}$, can be obtained by using eq 14:

$$\frac{k_{1,B}}{k_{1,A}} = \frac{K_A + \alpha \omega^{1/2} / k_{R,A}}{K_B + \alpha \omega^{1/2} / k_{R,B}} \frac{C_{f,B}}{C_{f,A}} \quad (17)$$

The ratio of concentrations of benzoic acid and abietic acid in the film, $C_{f,B}/C_{f,A}$, is equal to the ratio of film mole fractions $X_{f,B}/X_{f,A}$, so that

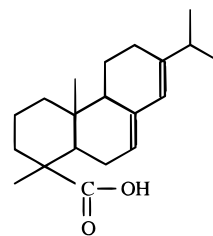
$$\frac{k_{1,B}}{k_{1,A}} = \frac{K_A + \alpha \omega^{1/2} / k_{R,A}}{K_B + \alpha \omega^{1/2} / k_{R,B}} \frac{X_{f,B}}{X_{f,A}} \quad (18)$$

This model predicts that the ratio of the removal rates in the first stage for the two components $k_{1,B}/k_{1,A}$ is proportional to the ratio of the mole fractions of the two components in the film $X_{f,B}/X_{f,A}$. It was mentioned that in stage 1 both the abietic acid and benzoic acid are removed from the film primarily in the form of solute-laden micelles. These solute-laden micelles can contain either (1) fractions of each species which are the same as their mole fraction in the contaminant film or (2) one species in a larger mole fraction and another species in a smaller mole fraction than those in the contaminant film. The experimental data for the simultaneous removal of abietic acid and benzoic acid are analyzed using this model.

Experimental Section

A detailed description of the experimental apparatus and measurement techniques is given elsewhere.^{1,3,4} This section summarizes the equipment and procedures for the simultaneous measurement of abietic and benzoic acid removal rates.

The disks used in the experiments were 2.1 cm in diameter consisting of circuit board material (FR-4 laminate), a fiberglass-reinforced brominated epoxy resin.¹ A solution to spin coat the disks was prepared by first dissolving ¹⁴C-labeled benzoic acid crystals in isopropyl alcohol (4.4, 8.7, or 17.4 M). Solid abietic acid crystals (1.68 g) were then added to the benzoic acid/isopropyl alcohol (IPA) solution (2.97 mL), and the mixture was sonicated until a homogeneous solution was obtained. The disks were coated with one application of the aforementioned solution using a spin coater



Abietic Acid

at 2000 rpm for 40 s (Specialty Coating Systems model P-6000). After the coating process, the disks were placed in a desiccator at room temperature for 24 h and then stored in a refrigerator at 5 °C. Disks containing three different benzoic acid mole fractions were used: 2.4×10^{-3} , 4.7×10^{-3} , and 9.4×10^{-3} (these compositions are based solely on the amount of abietic acid and benzoic acid in the film—they do not account for IPA). There is a limit to the amount of benzoic acid that could be added to the film. At film compositions above 1%, the benzoic acid crystallized upon desiccation, forming aggregates in the abietic acid film.

On the basis of the mass of abietic acid applied to the disk, it was determined that the initial thickness of a contaminant film was approximately 10 μm .¹ The dried film consisted of approximately 75 wt % solution of abietic acid in IPA with traces of benzoic acid. Both abietic acid and benzoic acid are solid at the conditions of the experiments, 24 °C and atmospheric pressure. The films on the disks were viscous liquids because of the presence of IPA. Films containing different amounts of benzoic acid were cast by changing the amount of benzoic acid dissolved in the IPA in the spin-coating mixture.

The coated disks were press-fit into a 4 cm diameter Teflon holder so that they were flush with the surface. The large diameter of the Teflon holder surface served to eliminate hydrodynamic edge effects. The disk holder was coupled to a shaft, leading to a precision rotator. Rotational speeds ranging from 250 to 1750 rpm were used in the cleaning experiments; all experiments were in the laminar flow regime.

The disks were cleaned in a reservoir containing 500 cm^3 of solution. Cleaning experiments were done with pure water as well as aqueous nonionic surfactant solutions of either pentaethylene glycol mono-*n*-dodecyl ether (C_{12}E_5) or octaethylene glycol mono-*n*-hexadecyl ether (C_{16}E_8), provided in monodisperse form by Nikkol Chemicals. The surfactant solutions ranged in concentration from 6×10^{-5} to 1.84×10^{-2} M. The lowest concentration employed (6×10^{-5} M) was slightly below the cmc of the C_{12}E_5 aqueous solution (6.4×10^{-5} M) and above the cmc of the C_{16}E_8 aqueous solution (1.6×10^{-6} M). All of the experiments were performed at 24 °C.

Quantities of the abietic acid removed from the disk were measured by recycling a 10 cm^3/min stream of the bulk cleaning solution through a UV detector and measuring UV absorbance changes at 254 nm. The residence time of the solution in the UV detector loop was approximately 1 min, appreciably lower than the characteristic times of the cleaning experiments. Hence, an essentially instantaneous measure of abietic acid concentration in the aqueous solution was obtained as a function of time.

Detection of ¹⁴C-labeled benzoic acid in the solution was accomplished by dissolving 1 mL samples of the

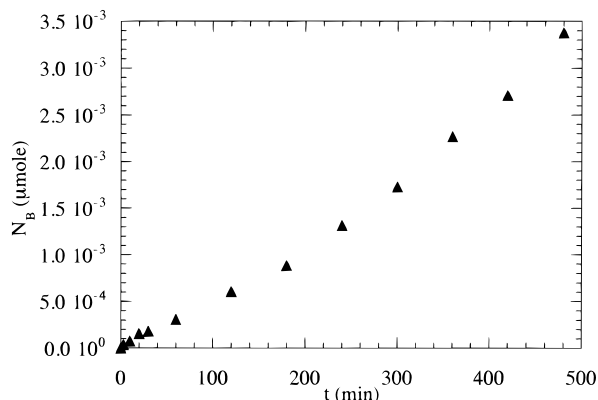


Figure 4. Cleaning curves for benzoic acid in pure water ($X_{f,B} = 4.7 \times 10^{-3}$ and 1000 rpm).

bulk cleaning solution in 10 mL of scintillation fluid (UniverSol liquid scintillation fluid obtained from ICN). Samples were counted for 5 min in a Packard 1500 Tri-Carb liquid scintillation analyzer. Approximately 50 samples were taken over the course of a cleaning experiment at appropriate times to obtain the full shape of the benzoic acid cleaning curve. The decrease in solvent volume due to the benzoic acid sampling technique was at most 10% (50 mL out of 500 mL). Abietic acid cleaning curves were compared for experiments with and without benzoic acid sampling. It was found that the benzoic acid sampling technique had a negligible effect on the experimental results. Error estimates were calculated for both the abietic acid and benzoic acid initial removal rates based on at least 10 experiments over the full range of rotational speeds examined.

The partition coefficient of benzoic acid between pure water and the contaminant film was determined by soaking coated disks in sealed jars containing 50 mL of distilled water. A total of nine disks were used, three at each of the three different ^{14}C -labeled benzoic acid mole fractions. The abietic acid does not dissolve in water, but the benzoic acid partitions between the film and the aqueous phase. Benzoic acid concentrations in solution were determined by liquid scintillation of 1 mL samples combined with 10 mL of scintillation fluid. After 7 days of continuous stirring, the solution was deemed at equilibrium when the average benzoic acid concentration in the aqueous phase did not change for 3 days. The concentration of benzoic acid in the contaminant film at equilibrium was determined by soaking each disk in 10 mL of IPA for at least 5 min to dissolve the film. A 1 mL sample of the benzoic acid/IPA solution was combined with 10 mL of scintillation fluid so liquid scintillation could be used to determine the initial amount of benzoic acid in the film.

Results and Discussion

1. Pure Water. Disks coated with films containing both abietic acid and benzoic acid were cleaned using pure water as the solvent. Abietic acid is water-insoluble, but the solubility of benzoic acid in water at 25 °C is 3.4 g/L of water.¹² Only the benzoic acid was removed from the disks in these experiments. A benzoic acid cleaning curve at 1000 rpm is shown in Figure 4 using pure water as the solvent. Over the 500 min duration shown, the rate of benzoic acid removal is constant and relatively slow (1.2×10^{-7} μmol/s). Other rotational speeds and benzoic acid mole fractions were

also studied in the same manner, and all of these experiments exhibited linear benzoic acid cleaning curves over long time periods (500 min). As will be seen later, the rate of benzoic acid removal increases substantially when surfactants are added to the solution.

The benzoic acid removal into pure water solutions can be controlled by one or a combination of the following: mass-transfer limitations, kinetics of solubilization, and diffusion limitations. Assuming that benzoic acid removal is mass-transfer-limited, the concentration of benzoic acid in the film, $(C_{f,B})_e$, would be in equilibrium with the concentration of benzoic acid at the interface, $(C_B^*)_e$. The equilibrium partition coefficient for benzoic acid between the film and pure water is given by

$$K_B = (C_{f,B})_e / (C_B^*)_e \quad (19)$$

Experimentally, $(C_{f,B})_e$ and $(C_B^*)_e$ were measured in partitioning experiments where coated disks were allowed to equilibrate in sealed containers initially filled with pure water. The concentration of benzoic acid in the film at equilibrium, $(C_{f,B})_e$, was determined by dissolving the equilibrated film in IPA and measuring the amount of benzoic acid in a sample of the resulting solution. The equilibrium partition coefficient was determined to be 3500.

For a mass-transfer-limited process, the benzoic acid removal can be described by the expression

$$-V_f k_{1,B} = k_m A [C_B^* - C_B] \quad (20)$$

where V_f is the volume of the film (3.46×10^{-9} m³), $k_{1,B}$ is the initial rate of benzoic acid removal, C_B^* is the concentration of benzoic acid at the interface, C_B is the concentration of benzoic acid in the bulk solution, and $A = 3.46 \times 10^{-4}$ m². Using ν for water (1×10^{-6} m²/s) and D_A for benzoic acid in water (1.21×10^{-9} m²/s)¹³ and a rotational speed of 1000 rpm, eq 3 yields an estimate for the mass-transfer coefficient $k_m = 7.2 \times 10^{-5}$ m/s. Furthermore, if there are no mass-transfer limitations, $C_B^* = K_B^{-1}(C_{f,B})_e$ and the benzoic acid concentration in the bulk solution is negligible ($C_B \approx 0$) relative to C_B^* . Under these conditions, eq 20 predicts that 99% of the benzoic acid should dissolve in pure water in only 37 min assuming a mass-transfer-limited process. This was not observed experimentally. As shown in Figure 4, after 500 min less than half of the benzoic acid was solubilized. This indicates that the benzoic acid removal rate is not mass-transfer-limited.

If there were diffusion limitations in the film hindering the removal of benzoic acid, the rate of removal would be directly proportional to the square root of time. Because the slope of the cleaning curve in Figure 4 does not change for long periods of time (i.e., greater than 500 min), we can conclude that the benzoic acid removal is not diffusion-limited. Because neither mass-transfer nor diffusion limitations are present during benzoic acid removal from the film, the interfacial kinetics of the solubilization process must be controlling. Because diffusion limitations do not exist for the removal of benzoic acid using pure water as the solvent, there cannot be diffusion limitations in the presence of surfactant (which increases the benzoic acid diffusion coefficient in the film). This will again become evident during the discussion of the cleaning results with surfactants in the sections that follow.

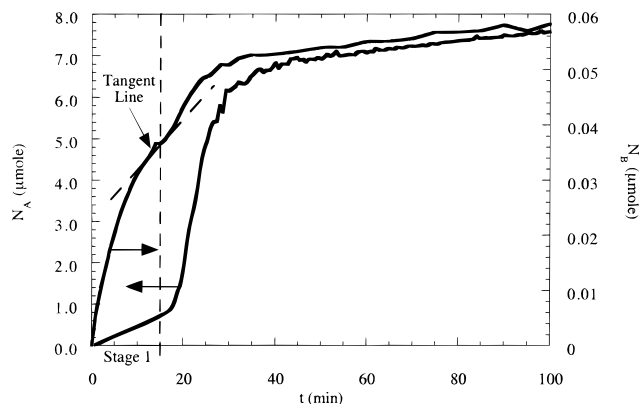


Figure 5. Cleaning curves of abietic acid and benzoic acid from a film on a rotating disk. The cleaning mixture is an aqueous solution of $C_{12}E_5$ with a concentration of 1×10^{-3} M. The rotational speed of the disk is 1000 rpm, and the mole fraction of benzoic acid in the film is 4.7×10^{-3} .

2. Aqueous $C_{12}E_5$ Solutions. Figure 5 shows cleaning curves for the simultaneous removal of both abietic acid and benzoic acid at 1500 rpm and 1×10^{-3} M $C_{12}E_5$. Notice that after 40 min most of the benzoic and abietic acid are removed from the disk. These results are quite different from those using pure water as the cleaning solvent. Figure 4 shows that only a negligible amount of the benzoic acid was removed after 40 min and that at these conditions the abietic acid is virtually insoluble in pure water.

As shown in Figure 5, during the first stage, only about 10% of the abietic acid is solubilized in $C_{12}E_5$. However, in the same time period, 62% of the benzoic acid is solubilized. Both the benzoic acid and abietic acid cleaning curves are initially linear, but the benzoic acid curve exhibits a more pronounced downward concavity during the first stage. This is because the benzoic acid is removed much faster from the film, based on its initial relative mass, and the film becomes depleted of benzoic acid earlier than it gets depleted of abietic acid.

A transition from the first to second stage in the benzoic acid cleaning curve is evident in Figure 5 by the slight increase in slope of the cleaning curve. The transition is more pronounced in the abietic acid cleaning curve than in the benzoic acid removal curve. This transition from the first to second stage in the benzoic acid cleaning curve is more easily seen when the experimental cleaning curve is compared to a line drawn tangent to the data at the end of the first stage (see Figure 5). It was earlier established that the second stage is dominated by a shear-driven removal of aggregates of contaminant film.¹⁻⁴ For abietic acid, approximately 75% of the material is removed during the second stage under the conditions shown in Figure 5. Because benzoic acid is still present in the contaminant film, it is expected that it is also being removed with the abietic acid aggregates.

Figure 6 shows the influence of rotational speed on the benzoic acid cleaning curves. All three curves exhibit the same behavior, consisting of an initial linear increase in the amount of benzoic acid removed with time followed by a decrease in the removal rate. These benzoic acid cleaning curves exhibit smaller initial slopes at lower rotational speeds. This is consistent with changes in the initial slopes of the abietic acid cleaning curves with variations in rotational speed.¹⁻⁴

The effect of surfactant concentration on the benzoic acid cleaning curve at 1000 rpm is shown in Figure 7.

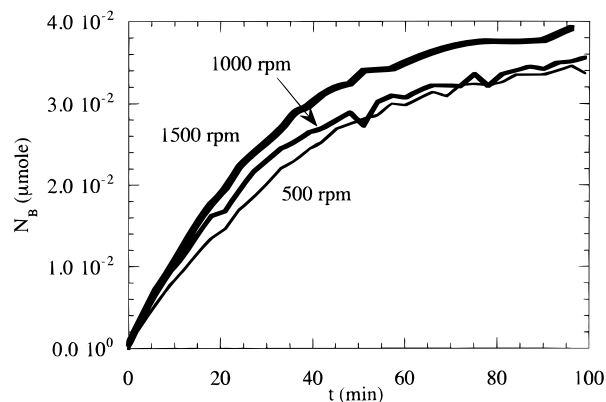


Figure 6. Benzoic acid cleaning curves for the removal of abietic acid–benzoic acid films with a benzoic acid mole fraction of 4.7×10^{-3} in a 6×10^{-5} M $C_{12}E_5$ solution. Disk rotational speeds of 500, 1000, and 1500 rpm are shown.

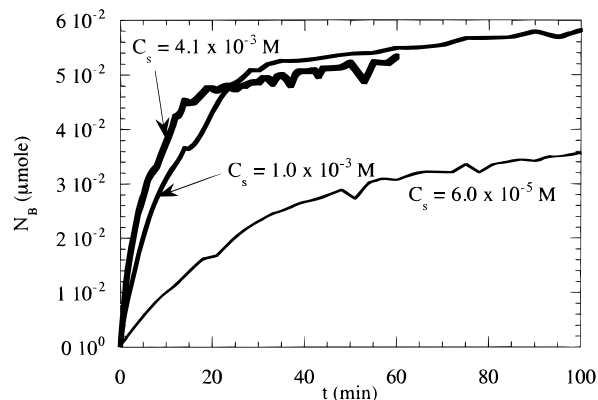


Figure 7. Benzoic acid cleaning curves for the removal of abietic acid–benzoic acid films with a benzoic acid mole fraction of 4.7×10^{-3} at 1000 rpm. Surfactant concentrations of $C_{12}E_5$ used were 6×10^{-5} , 1×10^{-3} , and 4.1×10^{-3} M.

All three cleaning curves eventually plateau at the same value of benzoic acid removal. However, for the submicellar case shown ($C_s = 6 \times 10^{-5}$ M), this plateau occurs at 250 min and cannot be seen in Figure 7. As the concentration of surfactant increases, the initial slopes of the benzoic acid cleaning curves increase as well. The fact that solubilization was observed for submicellar surfactant concentrations exposes a problem in using the concept of the MSR (eq 1) as a measure of solubilization capacity.

Initial abietic acid removal rates were calculated from the slopes of experimental cleaning curves. Equation 14 indicates that a plot of the inverse of the initial cleaning rate vs $\omega^{-1/2}$ should be a straight line. Experimental abietic acid removal rates were found to obey this relationship as shown in Figure 8. The error bars correspond to average deviations obtained for each surfactant concentration by using a total of more than 10 repeated experiments over the whole range of rotational speeds. The scatter is magnified for the lower surfactant concentrations because initial removal rates are smaller, and their reciprocal is shown in Figure 8. In the presence of benzoic acid, these abietic acid removal rates are comparable to the rates obtained in prior work in the absence of benzoic acid.³

Figure 9 shows $1/k_{1,B}$ values for benzoic acid plotted as a function of $\omega^{-1/2}$. The benzoic acid data sets at the three surfactant concentrations exhibit trends similar to those of abietic acid. However, the magnitudes of the initial removal rates for benzoic acid ($k_{1,B}$) are at least

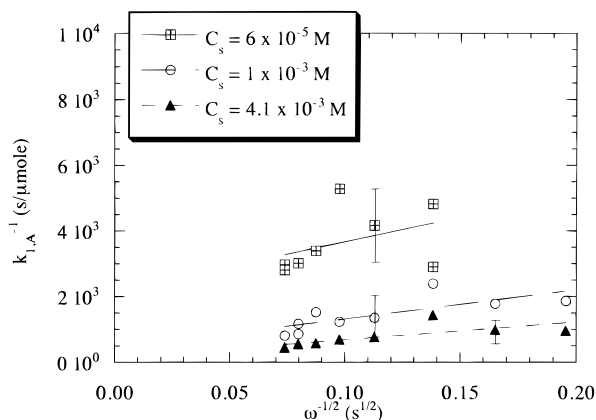


Figure 8. Scaling of stage 1 abietic acid removal rates with rotational speed at three different concentrations of $C_{12}E_5$.

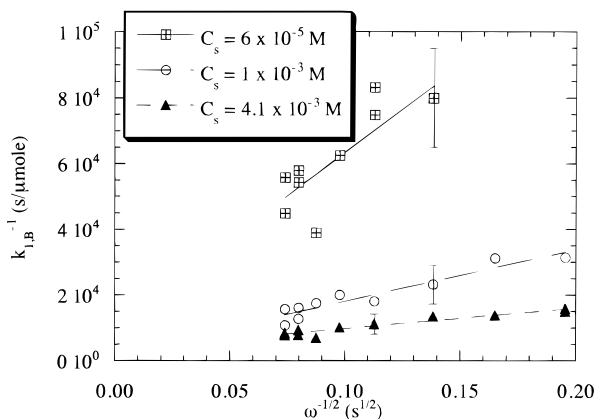


Figure 9. Scaling of stage 1 benzoic acid removal rates with rotational speed at three different concentrations of $C_{12}E_5$ at an initial benzoic acid film mole fraction of 4.7×10^{-3} .

Table 1. Dependence of Abietic Acid and Benzoic Acid Stage 1 Removal Rates and Readsorption Coefficient on Surfactant Concentration ($X_{f,B} = 4.7 \times 10^{-3}$)

C_s (M)	$r_{R,A}$ ($\mu\text{mol}/\text{m}^2 \cdot \text{s}$)	$r_{R,B}$ ($\mu\text{mol}/\text{m}^2 \cdot \text{s}$)	$r_{R,B}/r_{R,A}$	$k_{A,A}/\alpha$ ($\text{s}^{-1/2}$)	$k_{A,B}/\alpha$ ($\text{s}^{-1/2}$)
6.0×10^{-5}	1.3	0.27	0.21	6.9	49
1.0×10^{-3}	6.8	1.28	0.19	21	70
4.1×10^{-3}	21.7	0.87	0.04	41	19

an order of magnitude different from those of abietic acid. The initial removal rates for benzoic acid follow the model developed in eq 14. This suggests that in the presence of $C_{12}E_5$ solutions both solubilization kinetics and mass-transfer limitations are controlling. This is consistent with the order of magnitude analysis using eq 14 at the end of the Pure Water section. It was stated that surfactant would cause an increase in K_B , making mass-transfer limitations significant.

From the intercepts of the three data sets shown in Figures 8 and 9, the intrinsic removal rates, $r_{R,i}$, were estimated for abietic and benzoic acid (eq 14). These parameters are listed in Table 1. Because this parameter is obtained from an extrapolation, there are large deviations in r_R . There is an apparent increase in r_R for abietic acid with increasing surfactant concentration and a much smaller dependence of r_R on surfactant concentration for benzoic acid. Even though the error associated with the r_R values is large, an order of magnitude increase with increasing surfactant concentration can be seen in the data for abietic acid but is difficult to see with benzoic acid because of the approximate nature of these values (see Table 1). The

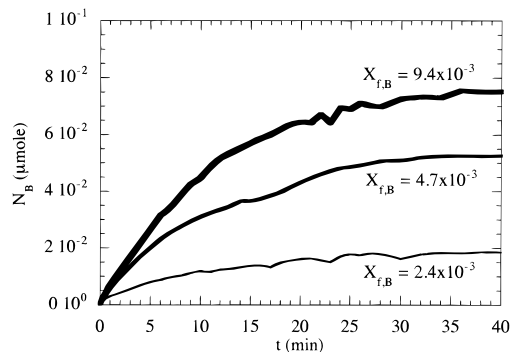


Figure 10. Benzoic acid cleaning curves for the removal of abietic acid-benzoic acid films in a 1×10^{-3} M $C_{12}E_5$ solution at 1000 rpm. Three different benzoic acid mole fractions are shown.

trend of increasing $r_{R,A}$ with increasing surfactant concentration observed here is similar to that obtained in prior work in the absence of benzoic acid.³

The ratio of $r_{R,B}/r_{R,A}$ in Table 1 is much greater than $X_{f,B}/X_{f,A}$ (the ratio of benzoic acid to abietic acid mole fractions). Because $X_{f,A} \approx 1$, $X_{f,B}$ is approximately equal to $X_{f,B}/X_{f,A}$. The fact that $r_{R,B}/r_{R,A}$ is much greater than $X_{f,B}/X_{f,A}$ suggests that the solute-laden micelles forming are not only of the type in which the mole fractions of the abietic acid and benzoic acid match that of the contaminant film. The solute-laden micelles forming seem to contain a greater fraction of benzoic acid and a smaller fraction of abietic acid than their mole fraction in the contaminant film. This latter type of micelle is probably more easily formed because of increased water in the film with $C_{12}E_5$ and the higher water solubility of benzoic acid compared to abietic acid. Formation of this latter type of micelle most likely causes the experimentally observed selectivity in removal rates between the two species.

The slopes of the data sets shown in Figures 8 and 9 increase with decreasing surfactant concentration. From the slopes and intercepts, the ratio $k_{A,i}/\alpha$ was calculated using eqs 13 and 14, and these values are shown in Table 1. The ratio $k_{A,i}/\alpha$ depends only on surfactant concentration through the adsorption rate constant $k_{A,i}$. The error associated with the $r_{R,i}$ values is propagated when $k_{A,i}/\alpha$ is calculated, causing $k_{A,i}/\alpha$ to also have a large error. As shown in Table 1, a trend of increasing $k_{A,i}/\alpha$ with surfactant concentration is seen for the abietic acid but is difficult to see with the benzoic acid because of the approximate nature of these values.

Experiments were done with rotational speeds ranging from 250 to 1750 rpm at 1×10^{-3} M $C_{12}E_5$ for disks with initial benzoic acid mole fractions ($X_{f,B}$) of 2.4×10^{-3} , 4.7×10^{-3} , and 9.4×10^{-3} . Figure 10 shows the influence of the initial benzoic acid mole fraction in the film on the benzoic acid cleaning curves at 1000 rpm. For all three benzoic acid concentrations, similar behavior is seen in the cleaning curves. The initial rate of benzoic acid removal increased with increasing benzoic acid mole fraction in the film. Here, the dependence of $k_{1,B}$ on $X_{f,B}$ is more easily seen than that for the pure water case presented earlier in Figure 4. When $1/k_{1,B}$ is plotted vs $\omega^{-1/2}$ for films at each of the three benzoic acid mole fractions, the linear trend predicted by the model in eq 14 is observed as shown in Figure 11.

The model developed in this work shows that the ratio of the first stage removal rates for benzoic and abietic acid should be proportional to the ratio of the initial film concentration of each component using $C_{12}E_5$ as the

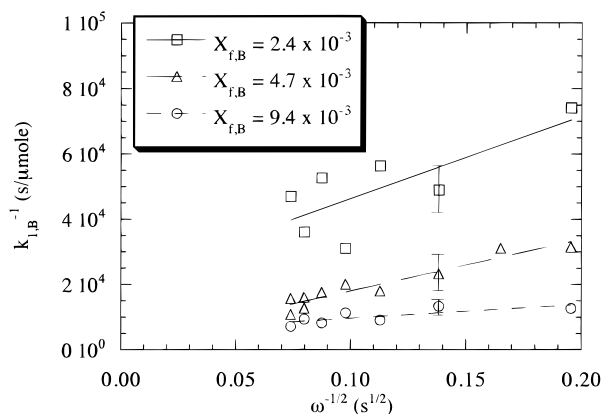


Figure 11. Scaling of stage 1 benzoic acid rates with rotational speed for films of different benzoic acid compositions at a surfactant concentration of 1×10^{-3} M $C_{12}E_5$.

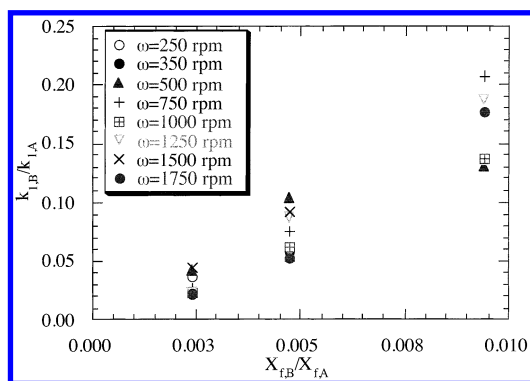


Figure 12. Comparison of experimental data with models at seven different rotational speeds and three different benzoic acid mole fractions (2.4×10^{-3} , 4.7×10^{-3} , and 9.4×10^{-3}). A 1×10^{-3} M $C_{12}E_5$ surfactant solution was used.

surfactant (eq 17). In Figure 12, experimental cleaning rate data are shown at each of the three different film compositions for the seven different rotational speeds examined in this work. Over the range of experimental conditions examined, the linear trend predicted by eq 17 is followed approximately. The data also appear to exhibit a zero intercept, which is consistent with eq 17. It is interesting to note that the data in Figure 12 do not show a change in slope with rotational speed. According to eq 17, this observed independence of the slope in Figure 12 on rotational speed can only result if the mass-transfer resistance and solubilization resistance for the two components are of the same order of magnitude. This was indeed verified with an order of magnitude analysis of the terms in eq 17 based on the rotational speed dependence of the cleaning rates of benzoic and abietic acid.

3. Aqueous $C_{16}E_8$ Solutions. In our prior work, C_xE_8 surfactants were found to clean abietic acid by only the first and third stages while C_xE_5 surfactants were found to exhibit all three stages.¹⁻⁴ This is because in the C_xE_5 series studied the shorter alkyl chain favors surfactant and water partitioning into the film over longer alkyl chain lengths. The enhanced surfactant and water partitioning characteristic of the C_xE_5 surfactants enables the film to be liquefied to the extent that it flows under the shear stress of the bulk cleaning solution. Such a decrease in film viscosity does not occur with the C_xE_8 surfactants, as evidenced by the lack of a second stage.⁴ Figures 13 and 14 show the results of cleaning experiments for 1.84×10^{-2} M solutions of

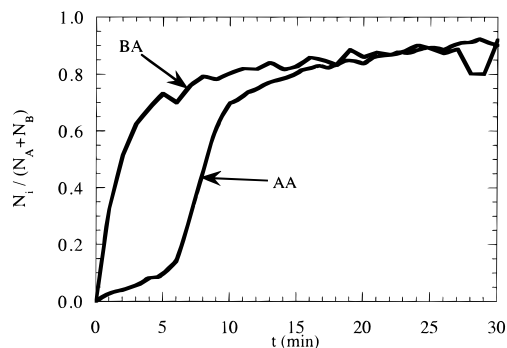


Figure 13. Cleaning curves of abietic acid and benzoic acid from a film on a rotating disk. The y axis corresponds to the fraction of each species removed. The cleaning mixture is an aqueous solution of $C_{12}E_5$ with a concentration of 1.84×10^{-2} M. The rotational speed of the disk is 750 rpm, and the mole fraction of benzoic acid in the film is 4.7×10^{-3} .

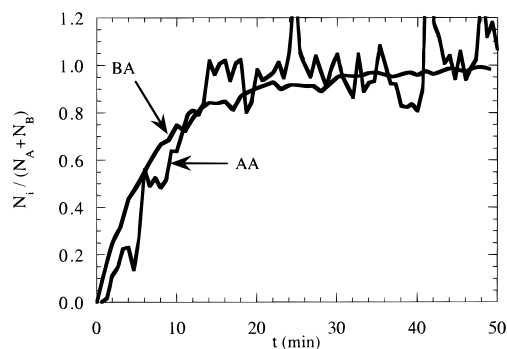


Figure 14. Cleaning curves of abietic acid and benzoic acid from a film on a rotating disk. The y axis corresponds to the fraction of each species removed. The cleaning mixture is an aqueous solution of $C_{16}E_8$ with a concentration of 1.84×10^{-2} M. The rotational speed of the disk is 750 rpm, and the mole fraction of benzoic acid in the film is 4.7×10^{-3} .

Table 2. Initial Rates ($\mu\text{mol/s}$) of Abietic Acid and Benzoic Acid Removal from Disks Rotating at 750 rpm in 1.84×10^{-2} M Surfactant Solutions ($X_{f,B} = 4.7 \times 10^{-3}$)

contaminant/surfactant	$C_{12}E_5$	$C_{16}E_8$
abietic acid	3.0×10^{-3}	8.2×10^{-3}
benzoic acid	1.1×10^{-4}	4.0×10^{-5}

$C_{12}E_5$ and $C_{16}E_8$ at 750 rpm. At this surfactant concentration, both surfactants remove the abietic acid after 20 min.³

Table 2 shows the initial rates of abietic acid and benzoic acid removal at 750 rpm in 1.84×10^{-2} M surfactant solutions ($X_{f,B} = 4.7 \times 10^{-3}$). It can be seen that the initial rate of abietic acid removal is faster with $C_{16}E_8$ than with $C_{12}E_5$. However, at the same surfactant concentration, the initial rate of benzoic acid removal is faster with $C_{12}E_5$ than with $C_{16}E_8$. Figure 13 shows that with $C_{12}E_5$ most of the benzoic acid is removed from the film before significant abietic acid removal. The ratio of the initial rates of removal of benzoic acid to abietic acid is 3.6×10^{-3} . With the $C_{16}E_8$ cleaning curve, shown in Figure 14, the fraction of benzoic acid and abietic acid removed is constant with time as evidenced by the superimposition of the cleaning curves. Also, the ratio of the initial rate of benzoic acid removal to abietic acid removal is 4.8×10^{-3} , which is within 2% of the ratio of the initial concentrations in the film. Under these conditions, there does not appear to be any selectivity of benzoic acid removal over abietic acid. Experiments were also performed on disks with $X_{f,B} = 4.7 \times 10^{-3}$ at 250 and 500 rpm and a disk with $X_{f,B} = 9.4 \times 10^{-3}$ at

Table 3. Dependence of the Ratio $k_{1,B}/k_{1,A}$ on Rotational Speed and Initial Benzoic Acid Mole Fraction

rotational speed (rpm)	$k_{1,B}/k_{1,A}$ ($X_{f,B} = 4.7 \times 10^{-3}$)	$k_{1,B}/k_{1,A}$ ($X_{f,B} = 9.4 \times 10^{-3}$)
250	6.3×10^{-3}	
500	6.8×10^{-3}	
750	5.0×10^{-3}	9.9×10^{-3}

750 rpm using 1.84×10^{-2} M $C_{16}E_8$. The $k_{1,B}/k_{1,A}$ values experimentally determined are listed in Table 3. For all of the experiments with $C_{16}E_8$ as the surfactant, the ratio of $k_{1,B}/k_{1,A}$ is approximately equal to $X_{f,B}/X_{f,A}$. This confirms that initial rates of removal are proportional to the film composition and also implies that $K_A = K_B$ and/or $k_{R,A} \approx k_{R,B}$.

The behavior described above likely results from a larger amount of water partitioning into the film with $C_{12}E_5$ than with $C_{16}E_8$. It was mentioned earlier that because water partitions into the film, it is possible to form solute-laden micelles that are richer in benzoic acid than abietic acid or that increase the rate of benzoic acid dissolution into water. This is more likely to happen with $C_{12}E_5$. The $C_{16}E_8$ is likely solubilizing both the abietic acid and benzoic acid from the contaminant film surface in solute-laden micelles without discriminating between its components.

Conclusions

Using solutions of $C_{12}E_5$, over the range of experimental conditions studied, fractional removal rates of benzoic acid were faster than those of abietic acid. The trends in benzoic acid removal rates were found to correlate with the model developed, suggesting that benzoic acid is removed by micellar solubilization in the first stage. The aforementioned model was also used to compare relative rates of removal of abietic acid and benzoic acid with their concentration in the contaminant film, using $C_{12}E_5$ solutions. It was found that the rate of removal of a species from the contaminant film is proportional to its concentration in the film. Solutions of $C_{16}E_8$ gave the same fractional removal rates for benzoic acid and abietic acid. The selectivity of solubilization $C_{12}E_5$ exhibits for benzoic acid is attributed to enhanced surfactant and water partitioning into the film with $C_{12}E_5$. This enhanced partitioning enables benzoic acid to be more readily incorporated into micelles.

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