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C. Lee[a]; H. Tsai[a]
[a] DEPARTMENT OF MARINE ENVIRONMENT, NATIONAL SUN YAT-SEN UNIVERSITY KAOHSIUNG, TAIWAN, REPUBLIC OF CHINA

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Behaviors of Mixed Solutes in Surfactant Admicelles

C. LEE* and H. TSAI
DEPARTMENT OF MARINE ENVIRONMENT
NATIONAL SUN YAT-SEN UNIVERSITY
KAOHSIUNG, TAIWAN, REPUBLIC OF CHINA

ABSTRACT

Binary adsolubilizations of hexanol, phenol, and cyclohexanol in admicelles formed by sodium dodecylsulfate on aluminum oxide were studied. Calculations from the phase equilibrium model give sizable synergism of adsolubilizations in the presence of other solutes. In this work, however, all solutes behaved ideally up to a moderate adsorption density in all binary experiments. It is concluded that further modifications are necessary before these equilibrium calculations can be used to describe the effect of background solutes. Furthermore, significant deviations from ideal behavior in binary experiments due to competition adsolubilization were observed as the capacity of admicelles oversaturated.

INTRODUCTION

Nagarajan and Ruckenstein (1) addressed the concept of utilizing solubilization as a separation process in 1981, and the phenomenon of differential solubilization has recently been the subject of increasing research activity (2–12). Chaiko et al. (2) systematically studied binary solubilizations in different surfactants among benzene, hexane, and cyclohexane. A value as high as seven for the selectivity of solubilization among those solutes was observed. However, before more applications can be used, difficulties of separating the micellar phase and the aqueous phase by using micelle as separation media must be resolved. Harwell (13) proposed a novel separation process which can reduce this hindrance significantly by form-

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* To whom correspondence should be addressed.

ing aggregate-like micelles on metal oxides, called admicelles. By the characteristic of adsolubilization, similar to solubilization possessed by micelles, hydrophobic pollutants can be driven from the aqueous phase into an admicellar hydrocarbon core coated on the solid phase. Then the aqueous phase can be easily separated from the solid phase by solid/liquid separation. The scheme of this wastewater treatment process can be described as four steps (3): laydown of admicelles on a solid substrate, introduce wastewaters, remove the aqueous phase from the solid phase or remove the pollutants by chromatography, and finally recover the surfactant for recycling and obtain the concentrated waste solution. The capacity and effectiveness of this process do not compare with those of the activated carbon process in treating wastewater. Nevertheless, admicelle enjoys high selectivity while the capacity of activated carbon is sometimes wasted by adsorption of many kinds of nontargeted compounds. Also, the formation of admicelles is reversible; therefore, it can be regenerated quite easily after saturation of pollutants. Recovery of valued materials in the concentrated pollutant phase is also possible. These are definite advantages over the carbon adsorption process. Recently, by using different kinds of surfactants and solid substrates, this separation process has been quite successfully applied in treating artificial wastewaters and in separating isomers and enantiomers (3, 14–18).

Mixed pollutants in a wastewater during treatment might compete with each other for limited sites in the admicellar phase, or they might help each other and end up with the synergistic effect of adsolubilization. It is therefore quite important to predict the behaviors of mixed solutes in adsolubilization. With very little data in the literature dealing with mixed adsolubilization, it is quite difficult to make such predictions. Barton et al. (3) attempted an equilibrium calculation, referred to in this paper as the phase equilibrium model (PEM), to describe their results in separating isomers. This model assumed that the partition coefficient for a solute, defined as the mole fraction ratio in the aqueous phase to that in the admicellar phase, remains constant in the presence of other pollutants. The major drawback of this calculation is that there is no site-limiting component in the model. Their data are too sparse to verify the feasibility of this model. In this research, binary adsolubilization experiments with 1-hexanol, phenol, and cyclohexanol in the plateau adsorption of SDS (sodium dodecylsulfate) on aluminum oxide were carried out. Our results should not only lead to a better understanding of the structure and physical behavior of admicelles, but also add additional adsorption information for the basic phenomena involved in environmental systems associated with sediment, hydrophobic pollutants, and anionic surfactants, such as the surfactant aided subsurface remediation process (19).

EXPERIMENTAL

Degussa Aluminum Oxide C, a primary gamma alumina, was used as the solid substrate in all adsorption experiments. It has a narrow particle size distribution and a surface area of 100 ± 15 m^2/g (20). Sodium dodecylsulfate (99%) was purchased from Sigma; cyclohexanol (>99%) and phenol (99.5%) were from Merck; *n*-hexanol (98%) was from Riedel de-Haen; and HPLC grade methanol was from Mallinckrodt. All chemicals were used as purchased. The water used was generated by a Milli RO Plus/Milli Q water purification device.

Adsorption isotherms of SDS on alumina were carried out by introducing 22.7 mL of various concentrations of SDS solutions into a series of 24-mL glass vials filled with 0.64 g alumina (pre-weighted). A solution of 0.1 N HCl was then gradually added to adjust the pH of the solution until equilibrium was reached at a specific pH value (4.0 ± 0.1 or 8.0 ± 0.1). Uniform contact between sorbent and solution was achieved by smoothly rotating the adsorption tubes on a rotating plate. The resulting solutions were centrifuged and filtered before the equilibrium concentrations of SDS were analyzed by high performance liquid chromatography using a conductivity detector (Hitachi L-6200/L-6294 with Hitachi L-3720 and a Shimadzu SIL-9A auto injector). The HPLC analytical procedure of SDS includes a solvent change from 20% methanol to pure methanol to avoid inorganic interference. Adsolubilization experiments were conducted in a manner similar to the procedure described above. Various concentrations of solutes were prepared from a stock solution with 20 mM SDS. The same amount (22.7 mL) of these solutions was introduced into a series of glass vials with 0.64 g alumina. For the practical application of admicelles to treat wastewaters, pH 8 was chosen in most of experiments instead of pH 4. After the same pH adjustment and equilibrium procedure, the solute concentrations were analyzed by gas chromatography using a flame ionized detector (Hitachi G-300) with a packed column (Supelco 80% carbopack, c/0.3% carbowax, 20 m, 15 g). Satisfactory results for mixed alcoholic compounds were obtained for a carrier gas flow rate of 31.3 mL/min by using oven temperature programming: 180°C, 0 minutes, 20°C/min; 200°C, 5 minutes, 10°C/min; 210°C, 2 minutes, 15°C/min; 225°C, 10 minutes.

All binary solute experiments for hexanol, phenol, and cyclohexanol were carried out in the following manner. One of the solutes served as a background pollutant while the other was a target pollutant. Serial concentrations of the target pollutant were prepared for adsolubilization experiments from a stock solution of fixed concentration of the background pollutant. This composed a set of experiments. Three levels of background pollutant concentrations were executed for each set of experiments in all mutual adsolubilization experiments.

RESULTS AND DISCUSSION

Because of electrostatic attraction or repulsion, the extent of adsorption of ionic surfactants on metal oxides is influenced by the surface charge of the sorbent. The surface charge of these metal oxides (e.g., aluminum oxide) is determined by the protonation or deprotonation of the adsorbed water molecules on the surface. When the pH of the solution is less than the point of zero charge (pzc) of the sorbent, the surface is positively charged and attracts electrostatically anionic surfactant. Therefore the lower the pH of the adjusted solution in our system, anionic dodecylsulfate adsorbed on aluminum oxide (pzc = 9.1), the higher the adsorption of the surfactant. As shown in Fig. 1, the plateau adsorption of the pH 4 isotherm is around 980 μmol/g, which is about twice that of the pH 8 isotherm. It is worthwhile noting that these two isotherms approach their plateau adsorption density in the 5–8 mM SDS range, which is about

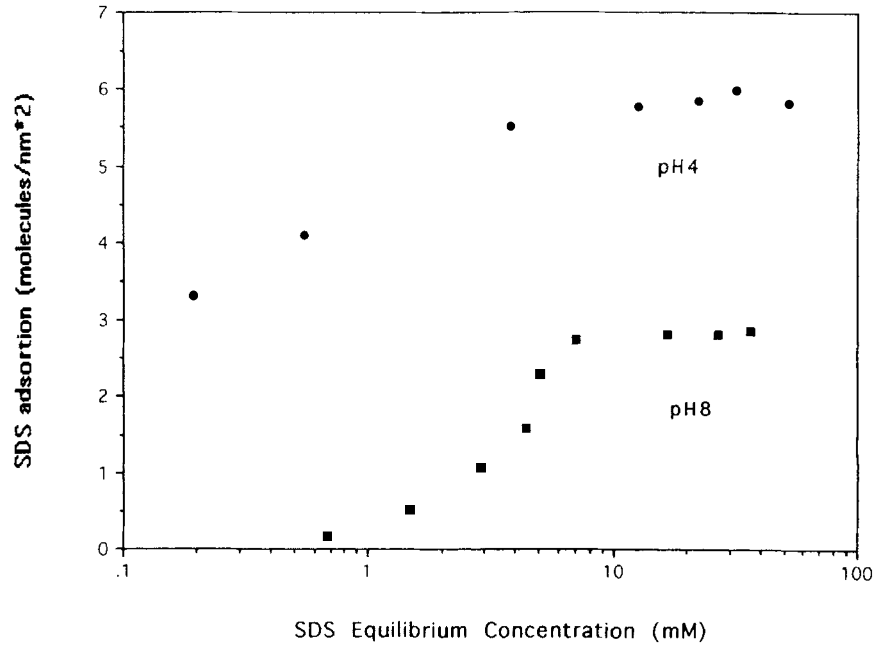

FIG. 1 Adsorption of SDS on alumina.

where its critical micellar concentration (cmc) is located. In other words, micelles begin to form beyond plateau adsorption. When a significant amount of micelles are formed, adsolubilization by admicelles competes with solubilization by micelles. Therefore, the best operating condition for treating wastewater is not only to have the best adsorption density for the greatest adsolubilization capacity, but also to avoid competition from micelles. Adsorption densities in the near-plateau adsorption region are good candidates for fulfilling both conditions. If the SDS adsorption density can be treated as a constant, the need to know the plateau adsorption density can be eliminated.

To eliminate the possibility of micellar interference and to test the sensitivity of variations of SDS equilibrium concentrations on adsolubilization capacity, two sets of phenol adsolubilization experiments were executed. These experiments were done under different initial concentrations of SDS, 20 and 30 mM, which give equilibrium concentrations at about 6 and 14 mM, respectively. As shown in Fig. 2, no significant difference was found between the two phenol adsolubilization isotherms. This indicates that no significant solubilization competition occurs at as high as 14 mM SDS equilibrium concentration. An initial concentration of 20 mM was then chosen for a fixed solid/liquid ratio for all adsolubilization experi-

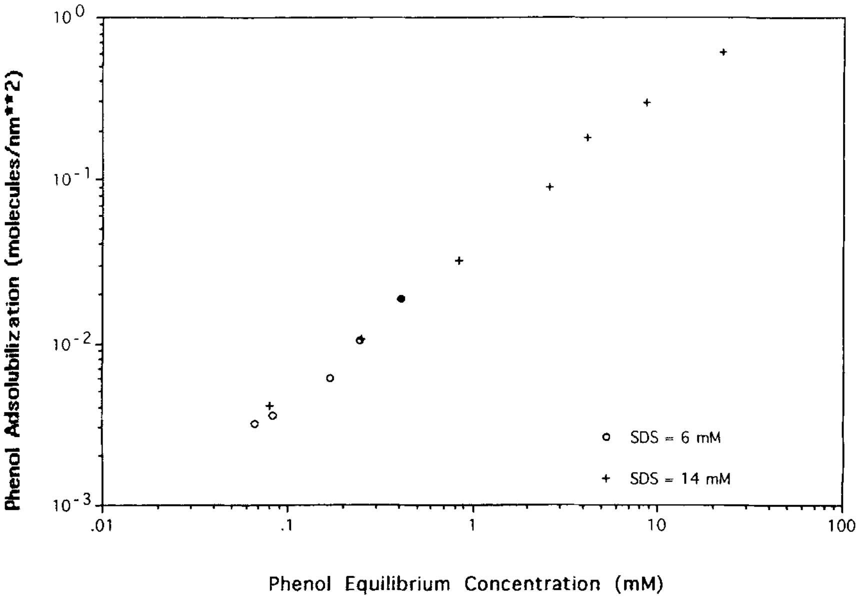

FIG. 2 Phenol adsolubilization under different SDS concentrations.

ments. The results of single adsolubilization isotherms of three solutes are presented in Figure 3(a). Theoretically, adsolubilization should have a linear isotherm at a low equilibrium concentration of solute, which can be referred to as Henry's law region. The ratio of adsorption amount and its equilibrium concentration, the partition constant K_h, is plotted against the whole range of concentrations in Figure 3(b) to examine the variation of H for each solute. Small variations from a constant for all three solutes were observed without any trend in any particular region. A good linear relationship was obtained between the average values of K_h for each compound and the solubility in water, as demonstrated in Fig. 3(c). The behaviors of single adsolubilizations of any other compounds with a similar structure can therefore be directly estimated from characteristic constants such as K_{ow} or water solubility without any additional experimental work. However, single adsolubilization experimental results may not be directly applicable to real world applications because many types of solutes in industrial wastewaters are commonly expected. As mentioned, PEM has been applied (3) for describing data in the separation of isomers. For this work, several sets of binary adsolubilization experiments were executed to justify the feasibility of using PEM for estimating the effect of the other solute on a specific pollutant. The derivation of this model is briefly introduced as follows.

For a system with multicomponent adsolubilizates, the total adsorption on the solid phase can be represented by

$$\Gamma_t = \Gamma_1 + \Gamma_2 + \cdots + \Gamma_{sp} \tag{1}$$

where Γ_i is the adsolubilization amount of i component per gram of sorbent and Γ_{sp} is the plateau adsorption of SDS, which is about 490 μmol/g alumina in this study. As mentioned, the basic assumption is that for a specific surfactant system the partition coefficient K_p for each pollutant is constant in the presence of other solutes. Since K_p is defined as the mole fraction ratio in the aqueous phase to the admicellar phase,

$$K_{pi} = Y_i/X_i \tag{2}$$

with

$$X_i = (18/1000V)(VC_{i,0} - \Gamma_i W) \tag{3}$$

and

$$Y_i = \Gamma_i/\Gamma_t \tag{4}$$

where V, $C_{i,0}$, and W are the volume of solution, initial concentration of solute, and weight of alumina, respectively. Therefore,

$$\Gamma_i = VC_{i0}\Gamma_t K_{pi}(WK_{pi}\Gamma_t + 55.6V) \tag{5}$$

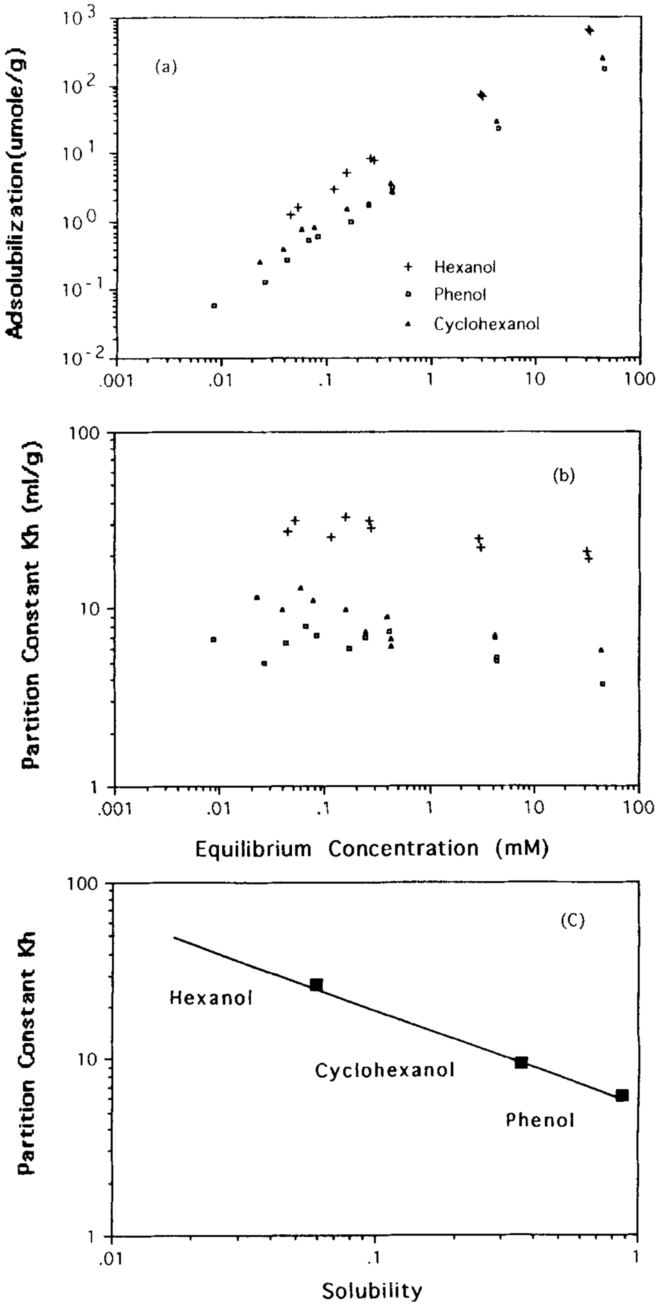

FIG. 3 Results of single solute adsolubilizations.

Γ_t can then be solved for by substituting this expression into Eq. (1) with a specified K_{pi} from single adsolubilization experiments. The value of K_{pi} for *n*-hexanol, for example, is about 2800, which is in good agreement with that in a micellar system (21). Values of K_{pi} for phenol and cyclohexanol obtained in this research are 690 and 750, respectively. Single adsolubilization isotherms for these three compounds can then be simulated with results close to experimental data (shown in Fig. 4). The above calculations can be applied to simulate multicomponent adsolubilization with a specified initial concentration of each solute to obtain adsorption isotherms for each component in solution. Figure 5 gives simulation results for binary adsolubilization of hexanol/phenol and phenol/hexanol. Other simulated results, not given here, are similar to these two cases. With increased initial concentrations of the background solute (like hexanol in Fig. 5b), the molar fraction of the targeted solute (like phenol in Fig. 5b) in the admicellar phase becomes lower. As such, the adsorption of phenol

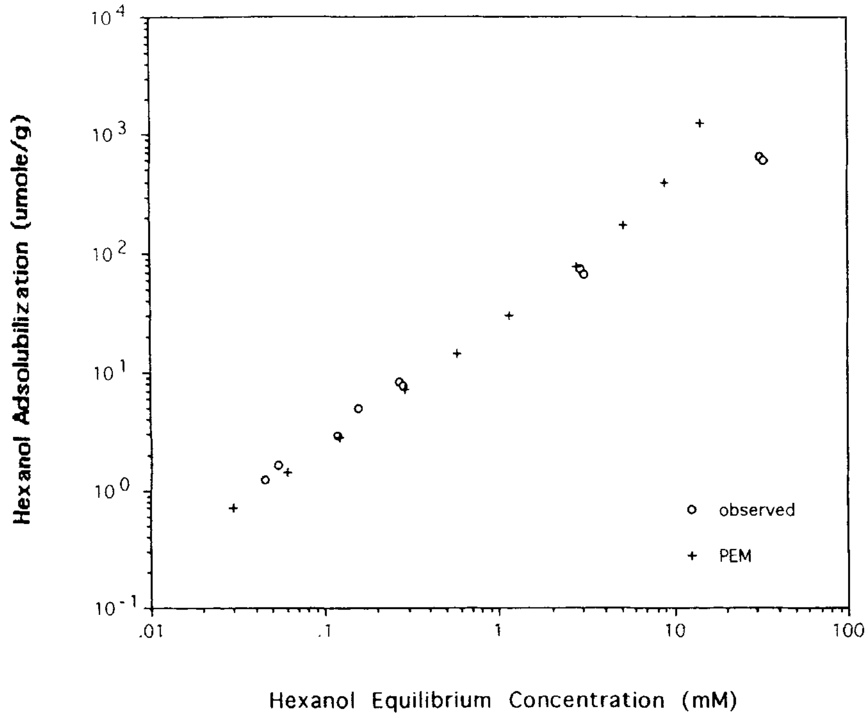

FIG. 4 Comparison of hexanol adsolubilization between PEM calculated and observed results.

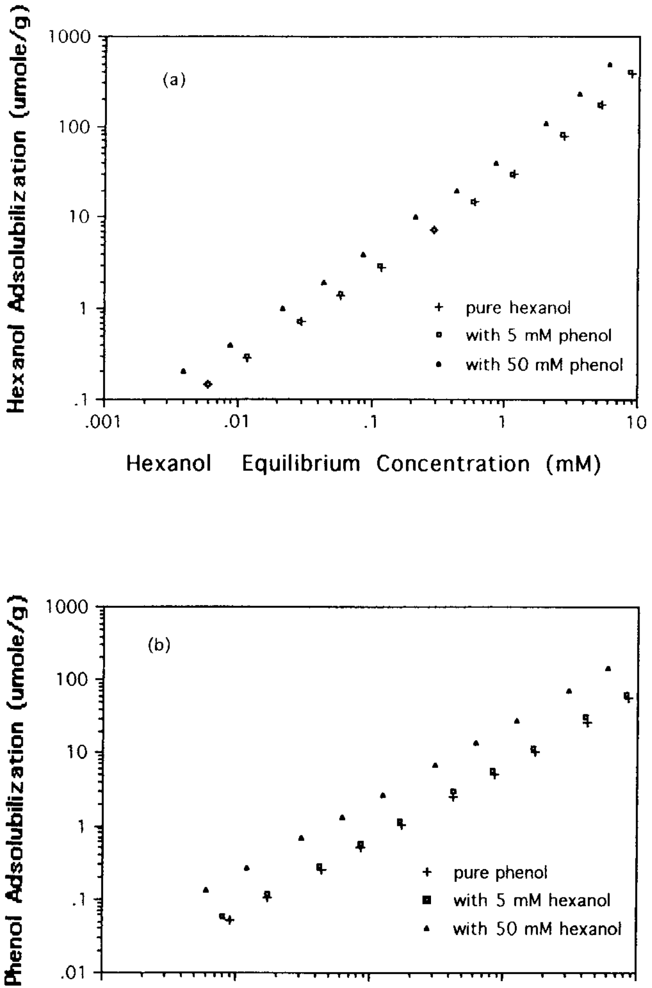

FIG. 5 Binary adsolubilizations results predicted by PEM calculations.

must be raised to lower X of phenol, and the K_p of phenol can then be held constant to fulfill the basic assumption of the model. This synergistic effect has been reported in some mixed solubilization systems (2). However, this model does not consider site limitation; therefore, no competition effect was observed from these simulation results. As shown in Fig. 6, the binary experimental results of phenol/hexanol, with background

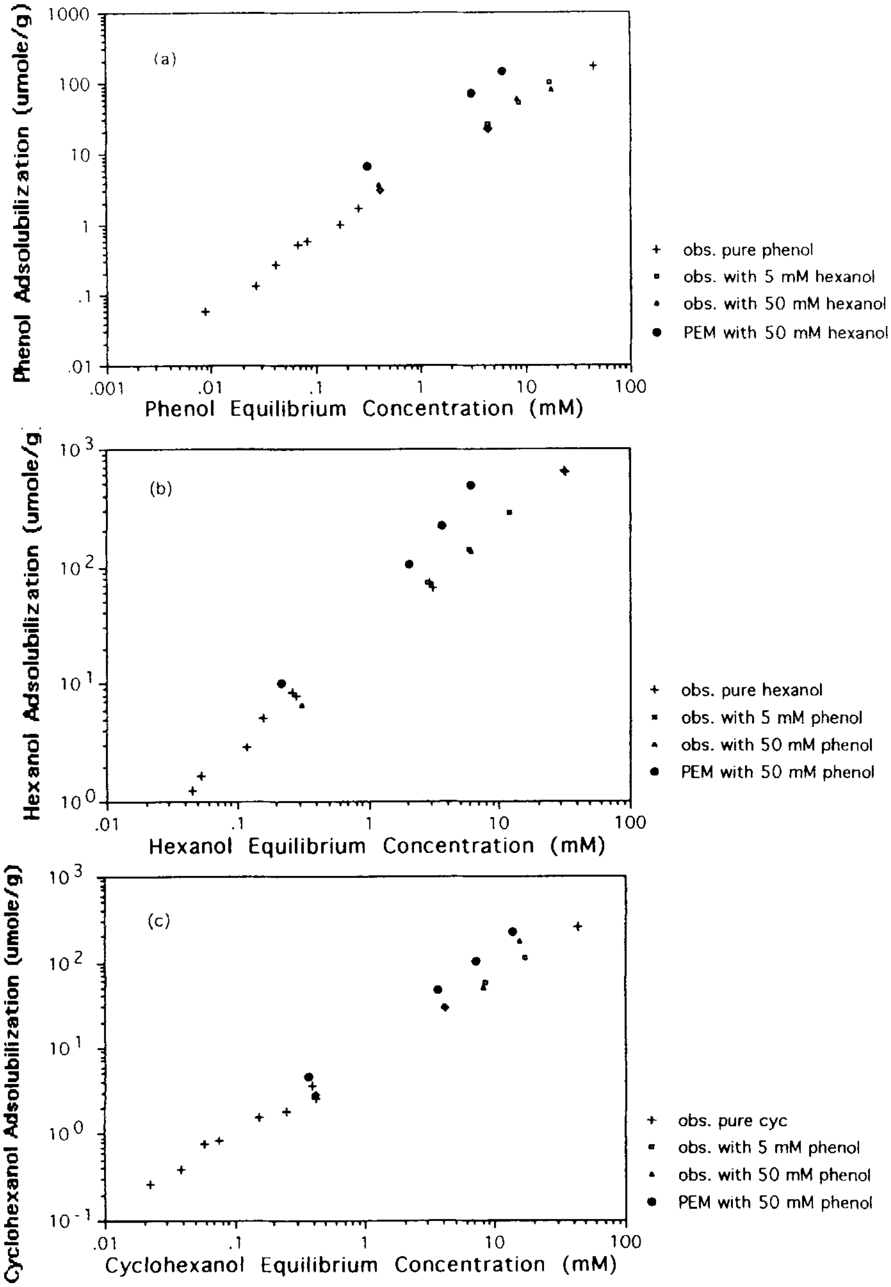

FIG. 6 Binary experimental results in comparison with PEM calculations.

solute concentrations up to 50 mM, show neither competition nor a synergism effect. Similar results were observed for hexanol/phenol (Fig. 6b), cyclohexanol/phenol (Fig. 6c), and other combinations among these three solutes. The PEM results shown here were calculated with observed SDS adsorption densities, which are assumed to be constant in Fig. 5. Those binary data are fitted much better by the ideal adsolubilization model (IAM), which represents no interaction between solutes during adsolubilization, than by PEM. The values of selectivity for each solute over phenol were not varied much against initial concentration ratios, as shown in Fig. 7, and this is a good indication for the stability of plateau adsorption of SDS. One of the combinations in the above binary experiments, phenol/hexanol, were done under a different pH, 4. Results shown in Fig. 8 give the same conclusion for pH 8 as mentioned above. Therefore, reasonable prediction of the efficiency of removing hydrophobic pollutants from wastewaters with multicomponent solute is possible by applying the IAM for both pH 4 and pH 8. Nevertheless, deviations from the IAM were observed as the amount of solutes adsolubilized approach the capacity of

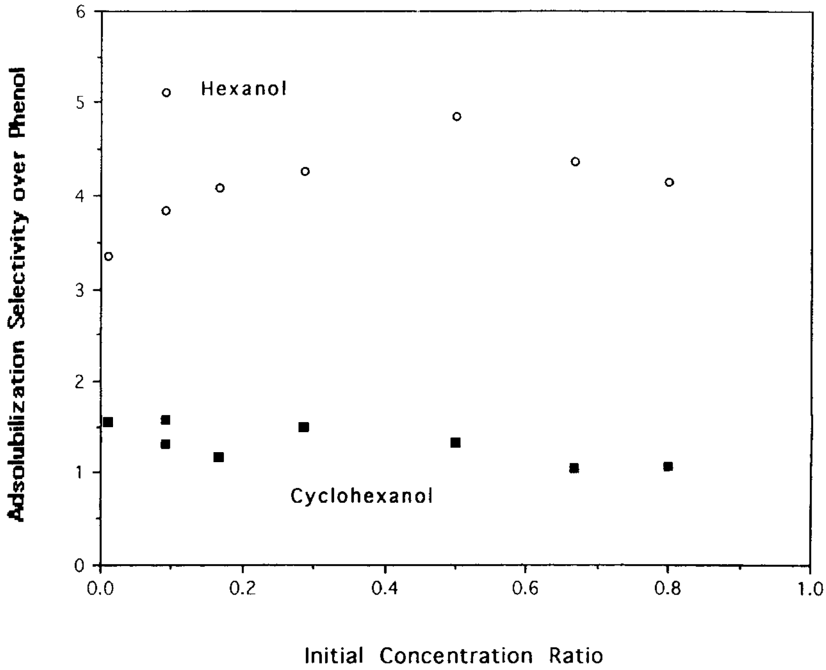

FIG. 7 Adsolubilization selectivity of hexanol and cyclohexanol over phenol.

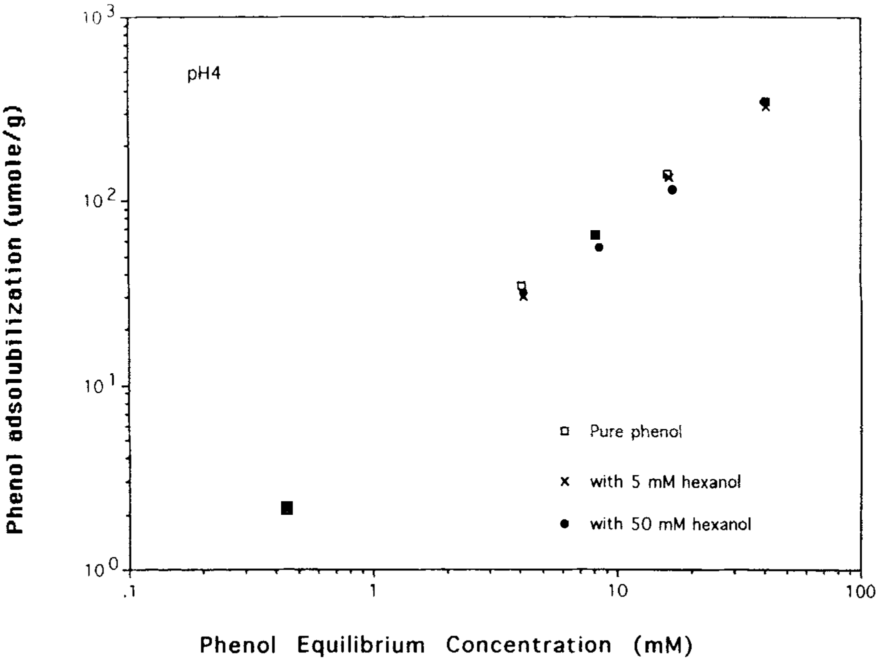

FIG. 8 Binary adsolubilization of phenol in the presence of hexanol at pH 4.

admicelles. Figure 9(a) shows systematically dropping of the extent of hexanol, the target solute, adsorption density as doses of phenol, the background solute, increased. However, no significant deviation of mixed adsolubilization from single adsolubilization was found, as shown in Fig. 9(b), if the adsorption density ratios of hexanol to SDS were used instead of the hexanol adsorption density with the initial concentrations of phenol up to 300 mM from this figure. Figure 10 provides a likely reasoning of what is happening in the above observations. Some amount of the adsorbed SDS was substituted for by alcoholic compounds and expelled from the adsorbed phase to the aqueous phase when the alcohol concentrations in the aqueous phase became high enough. In other words, this mechanism helped keep the partition constant (Γ/C) of the solute (hexanol) from varying during the site-limiting process by sacrificing the adsorption density of SDS. This phenomenon sounds contradictory to the fact that the adsorption of alcohol helps the adsorption density of SDS (22). Very likely, the physical structure of admicelles under this mechanism is similar to that of the two-site adsolubilization model proposed by Lee et al. (22). As such, some alcohol molecules occupy some of the skeleton positions

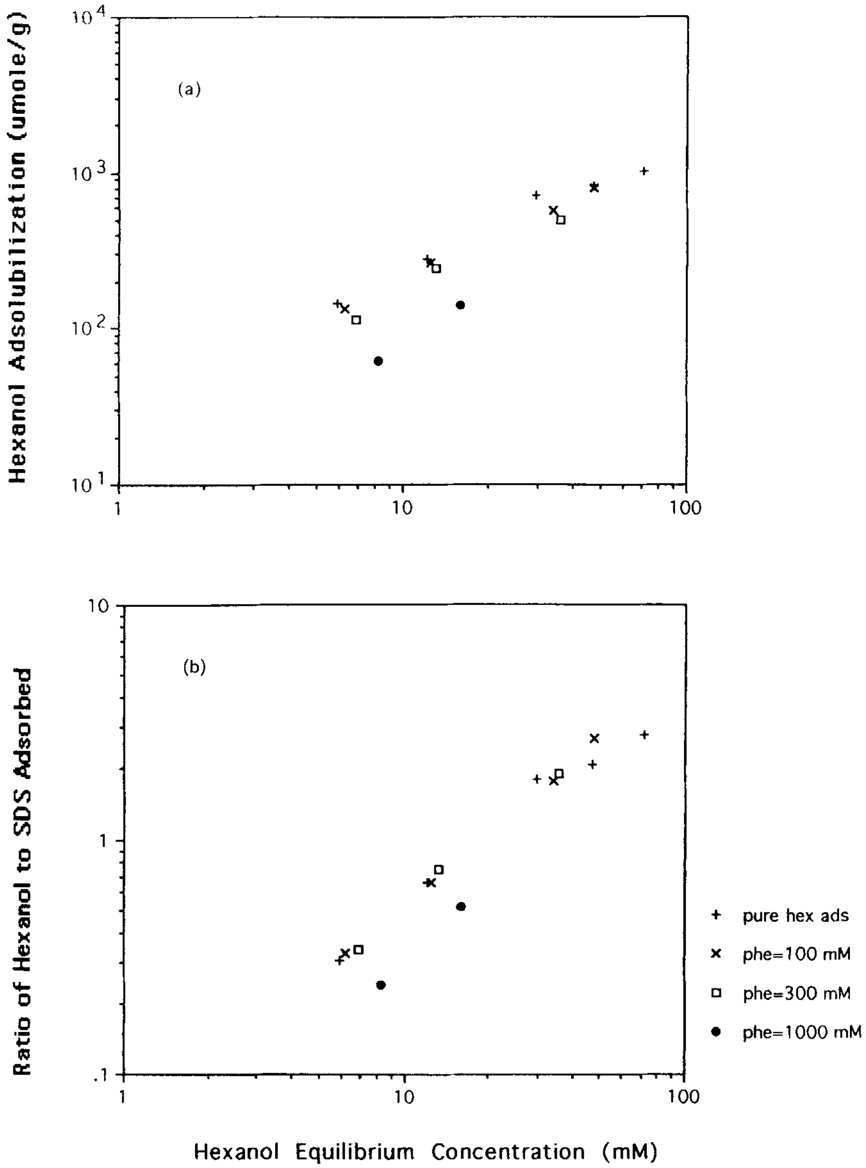

FIG. 9 Observed binary adsolubilizations results of hexanol in the presence of phenol.

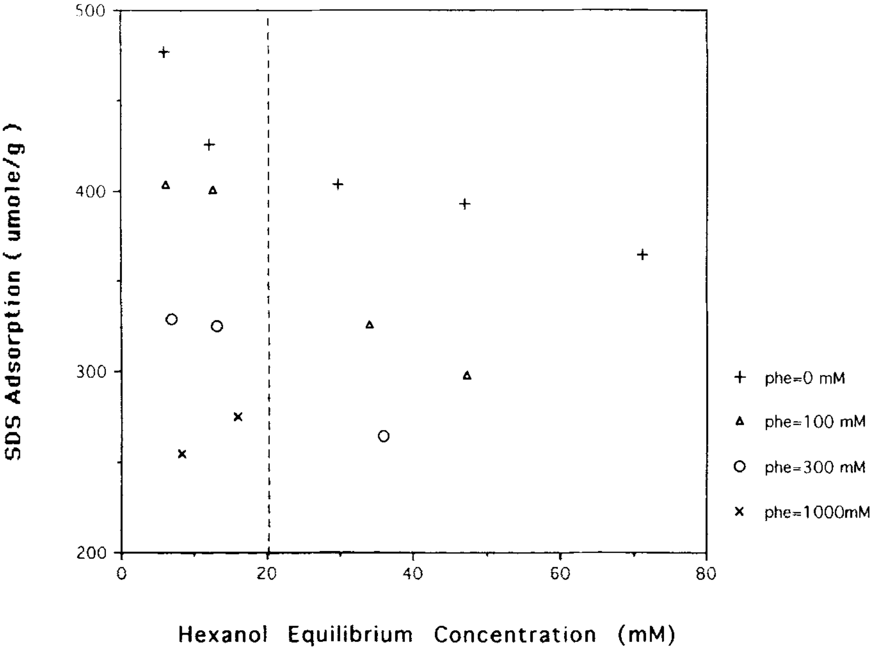

FIG. 10 Variation of SDS adsorption density in the presence of organic solutes.

in the bilayer structure of admicelles while others are adsolubilized deeper into the hydrocarbon core of admicelles. It can also be concluded that the driving force of this substitution depends on the hydrophobicity and the liquid-phase equilibrium concentration of alcohols. This phenomenon was not described before, and should draw attention in the study of the behavior of adsolubilization.

CONCLUSION

New experimental data are presented on the adsolubilization isotherms of single and binary mixtures of hexanol, phenol, and cyclohexanol under plateau adsorption of SDS on aluminum oxide. Theoretical binary adsolubilization isotherms based on the concept of phase equilibrium were also calculated. Comparisons between these isotherms and the experimental data are not good. In most cases, all solutes behave ideally in binary experiments. As the concentrations of solutes were increased, the driving force of an adsolubilizing solute into the admicellar phase becomes so strong that the adsorbed SDS molecules are even substituted for by alcohol molecules. A further increase of the concentrations of the background solutes will significantly decrease the adsolubilization density of the target solute. This phenomenon has great impact on the efficacy of removing a dilute target toxicant in a wastewater with highly concentrated nontargeted solutes.

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