Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Enhanced Recovery of Nicotine from Tobacco Waste Using Sulfuric Acid and Microemulsion Medium

A. S. Chhatre[a]; N. K. Yadav[a]; B. D. Kulkarni[a]
[a] NATIONAL CHEMICAL LABORATORY, PUNE, INDIA

To cite this Article Chhatre, A. S. , Yadav, N. K. and Kulkarni, B. D.(1993) 'Enhanced Recovery of Nicotine from Tobacco Waste Using Sulfuric Acid and Microemulsion Medium', Separation Science and Technology, 28: 7, 1465 — 1477

To link to this Article: DOI: 10.1080/01496399308018051

URL: http://dx.doi.org/10.1080/01496399308018051

SEPARATION SCIENCE AND TECHNOLOGY, **28**(7), pp. 1465–1477, 1993

Enhanced Recovery of Nicotine from Tobacco Waste Using Sulfuric Acid and Microemulsion Medium*

A. S. CHHATRE, N. K. YADAV, and B. D. KULKARNI†
NATIONAL CHEMICAL LABORATORY
PUNE 411008, INDIA

ABSTRACT

Experimental data showing enhanced recovery of nicotine from a tobacco waste stream using sulfuric acid and suitably prepared microemulsion media are reported. The results are analyzed and indicate considerable enhancement in the reaction rate. The interfacial rate constant has also been evaluated by using an appropriate model for the system.

INTRODUCTION

Microemulsions are thermodynamically stable colloidal dispersions of either oil-in-water or water-in-oil stabilized by the addition of an amphiphile (1). On a microscopic scale these systems are heterogeneous, containing domains of water and oil separated by a monolayer of amphiphile, and the interface usually provides the meeting ground for the solubilized reactants to meet and interact. In view of the relative large interface, the reaction tend to proceed faster than in conventional heterogeneous systems. The interfacial properties, such as surface pressure and bending moment of the globule, affect the solubilization (2) of the reactant as also does the type of organic solvent used, the nature of the cations, and the electric charge state and hydrophobicities of the solute (3). These properties and their effect on the structure, dynamics, and interactions of the pseudo-phases have been studied and exploited in a variety of instances for facilitating and regulating the growth process for particles or polymers (4), in separation and purification (5), and in enhancing chemical reactions (6–8).

---

*National Chemical Laboratory communication 5434.
†To whom correspondence should be addressed.

Currently, nicotine is extracted from the macerated tobacco waste stream by using kerosene, and the extract is treated with sulfuric acid in a bubble column reactor (9) to form nicotine sulfate. Owing to mass transport limitations, the overall rate of the reaction is low. In the present paper we report and analyze the experimental results on the reaction of the extract with sulfuric acid in a suitably prepared microemulsion medium. For this purpose, we have made use of a Type I microemulsion system which is comprised of an excess kerosene phase in equilibrium with a microemulsion of kerosene in sulfuric acid. The phase behavior of systems comprised of kerosene sulfuric acid and three different surfactants along with pentanol as a cosurfactant were reported earlier (10, 11). A surfactant:cosurfactant ratio of 1:1 was used in the study of such a phase diagram.

MATERIALS

Cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulfate (LR grade), and Triton X-100 (isooctyl phenoxy polyethoxy ethanol) were obtained from SD Chemicals and were used as received. 1-Pentanol (AR grade) was a Fluka guaranteed material. Kerosene was obtained from local markets and was used without further purification. The approximate composition of the kerosene used (volume %) was aromatics [mononuclear (single ring aromatic hydrocarbons), 15%; dinuclear (double ring aromatic hydrocarbons), 6%], naphthenic rings [monocyclic (single ring aliphatic hydrocarbons), 26%; dicyclic (double ring aliphatic hydrocarbons), 9%], and paraffins [normal (straight chain aliphatic hydrocarbons), 25%; branched (aliphatic hydrocarbons with side chains), 19%]. Water used for the experiments was doubly distilled and deionized. Concentrated sulfuric acid and potassium sulfate crystals were obtained from SD Chemicals, and aqueous solutions of these were used. The exact concentrations of sulfuric acid were determined by titration with standard 0.5 and 1.0 N sodium hydroxide solutions.

METHOD

The experiments were divided into two sets, each comprising of five different runs. In the first set (Runs 1–5), five different microemulsion systems were used for the reaction. The compositions of these systems are shown in Table 1. The microemulsion was prepared by equilibrating an excess of the organic solvent (kerosene) with a micellar aqueous solution of sulfuric acid, using 1:1 (wt/wt) surfactant–cosurfactant mixtures. Thus, a two-phase Type I system was formed wherein the upper organic layer was in equilibrium with an oil-in-water type of microemulsion. In the sec-

TABLE 1
Composition of Various Phases Used in Sets 1 and 2

Run no.	Surfactant mixture	Surfactant mixture		Kerosene		H_2SO_4		Strength of H_2SO_4 (mol/L)
		wt%	vol%	wt%	vol%	wt%	vol%	
1	CTAB + 1-pentanol	15	15.1	29	33.8	56	51.1	0.13
2	CTAB + 1-pentanol	12	11	43	49.1	45	39.9	0.26
3	CTAB + 1-pentanol	10	9.1	55	61	35	30	0.365
4	TX-100 + 1-pentanol	8	6.2	20	27.3	72	66.5	2.5
5	SDS + 1-pentanol	10	5.9	6	7.8	84	86.3	0.05

Composition of Excess Organic Phase for Set 1

Run no.	Surfactant mixture	Surfactant mixture		Kerosene	
		wt%	vol%	wt%	vol%
1	CTAB + 1-pentanol	1.1	0.9	98.9	99.1
2	CTAB + 1-pentanol	0.6	0.5	99.4	99.5
3	CTAB + 1-pentanol	0.6	0.5	99.4	99.5
4	TX-100 + 1-pentanol	1.2	0.6	98.8	99.4
5	SDS + 1-pentanol	1.0	0.4	99.0	99.6

Composition of Aqueous Phase for Set 2

Run 1, 0.13 mol/L H_2SO_4; Run 2, 0.26 mol/L H_2SO_4; Run 3, 0.365 mol/L H_2SO_4; Run 4, 2.5 mol/L H_2SO_4; Run 5, 0.05 mol/L H_2SO_4; negligible amounts of kerosene found in all the aqueous phases

Composition of Excess Organic Phase for Set 2

Runs 6–10: Kerosene containing negligible amounts of acid

ond set (Runs 6–10), pure aqueous sulfuric acid of corresponding strengths (as used in Runs 1–5) was equilibrated with excess kerosene and then used for the reaction after the excess kerosene was discarded. The excess organic layer as obtained above was used to prepare the organic phase for the reaction in all the runs by dissolving in it a known amount of nicotine. The initial concentration of nicotine was adjusted to around 4.748×10^{-5} mol/cm^3 for all the runs. Because the microemulsion was saturated with kerosene, most of the resistance to mass transfer of nicotine was expected to lie in the organic phase (12). The nicotine sulfate product is water soluble and remains in the aqueous phase. The contact between 50 cm^3 of the microemulsion and 50 cm^3 of the organic solution was achieved in a simple, jacketed, stirred cell reactor. The stirred cell reactor was maintained at

30°C by circulating thermostated water through its jackets. A four-blade stirrer was placed in such a way that half the widths of the blades were in the organic phase while the other half were in the microemulsion. The speed of rotation of the stirrer was maintained at 50 ± 2 rpm. The partition ratios of nicotine between the various phases were determined as follows. For determining the partition ratio of nicotine between the kerosene phase and the pure acid phase, equal volumes of the organic phase and aqueous solution of K_2SO_4 of appropriate molarity were equilibrated at 30°C by vigorous shaking in a separating funnel. The organic phase which separated from the aqueous phase was analyzed for its nicotine content. In the case of the determination of the partition ratio of nicotine between the kerosene phase and the surfactant phase, equal volumes of both phases were taken in a stoppered test tube and equilibrated at 30°C by vigorous shaking. The phases were separated by ultracentrifugation, after which the kerosene phase was analyzed for its nicotine content. The concentration of nicotine in the organic phase was determined by withdrawing small aliquots of the

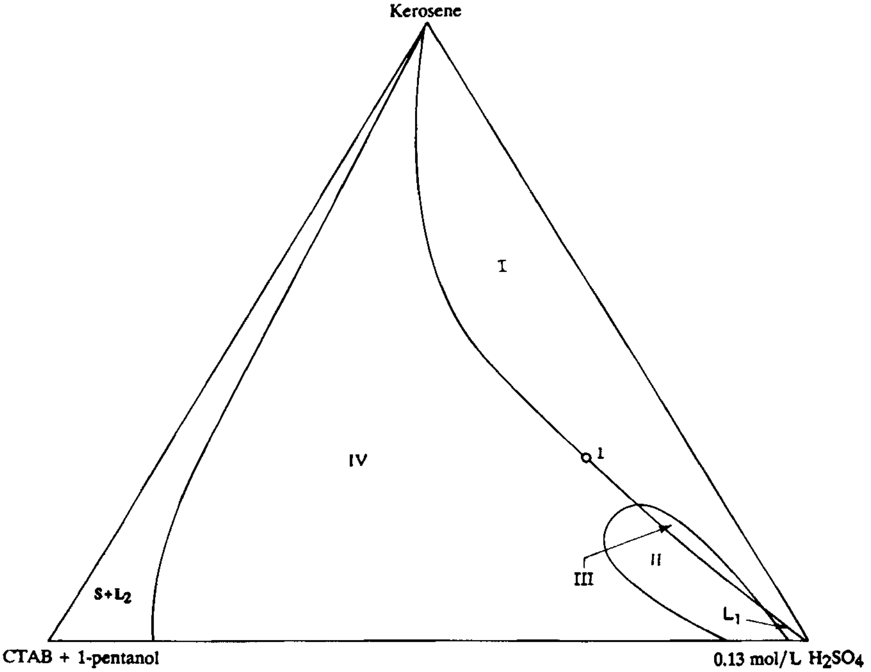

FIG. 1 Pseudoternary phase diagram of the system CTAB + 1-pentanol/0.13 mol·L^{-1} H_2SO_4/kerosene at 30°C. I–IV: Types I–IV systems. L_1: O/W emulsion. S + L_2: Solids + W/O emulsion.

organic phase, diluting the aliquot with kerosene, and analyzing the diluted solution by UV spectrophotometric methods at $\lambda_{max} = 281$ nm. A Shimadzu-made UV-visible spectrophotometer was used for this purpose. It was estimated that the average relative uncertainty in the measurement of the organic phase concentration in Set 1 was less than about 2%, and that in Set 2 was about 1%.

RESULTS AND DISCUSSION

Figures 1–5 show the actual phase diagrams for the various microemulsion systems used. Points marked 1 to 5 on the respective phase diagrams denote the actual compositions used in Runs 1–5. Table 2 shows concentration values of the organic phase measured with time. A plot of log concentration of the organic phase versus time for Runs 6–10, shown in Fig. 6, reveals the first-order nature of the reaction. Figure 7 shows a plot of log concentration versus time for Runs 1–5. Considering the rates of

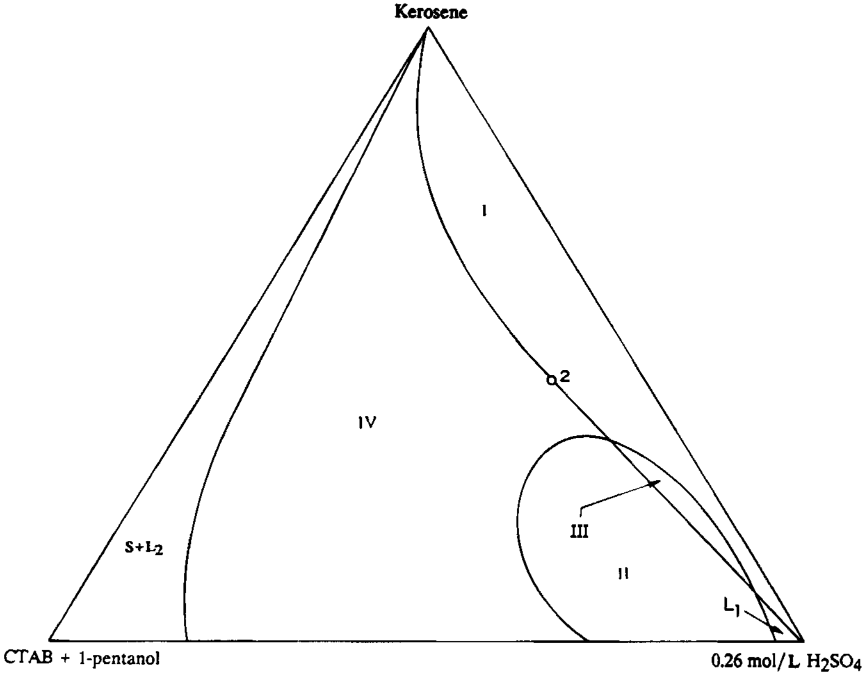

FIG. 2 Pseudoternary phase diagram of the system CTAB + 1-pentanol/0.26 mol·L^{-1} H_2SO_4/kerosene at 30°C. I–IV: Types I–IV systems. L_1: O/W emulsion. S + L_2: Solids + W/O emulsion.

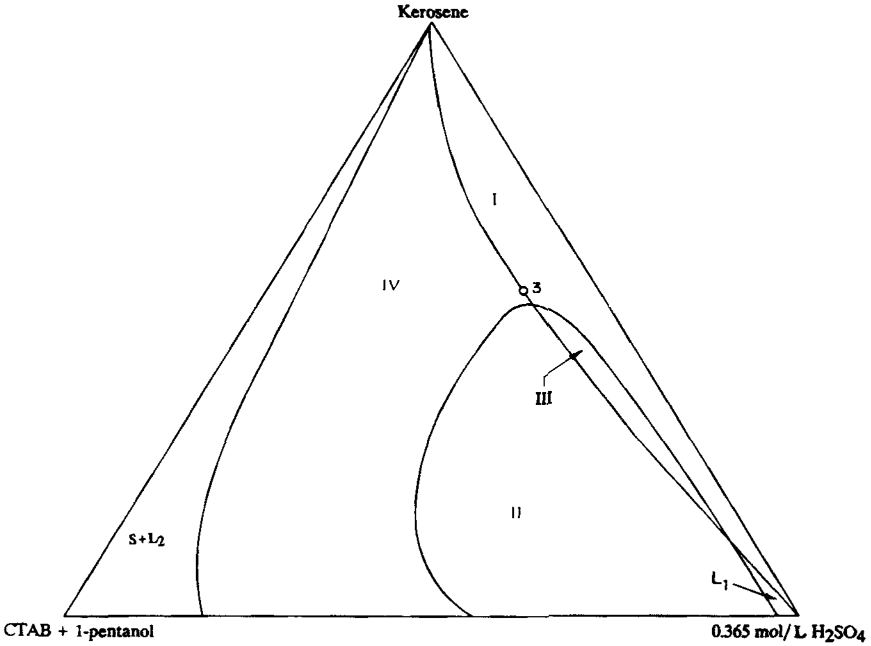

FIG. 3 Pseudoternary phase diagram of the system CTAB + 1-pentanol/0.365 mol·L^{-1} H_2SO_4/kerosene at 30°C. I–IV: Types I–IV systems. L_1: O/W emulsion. S + L_2: Solids + W/O emulsion.

reaction obtained in the case of microemulsions (Runs 1–5) as compared to those obtained in the corresponding case of no surfactant (Runs 6–10), we have defined an enhancement factor *E* as

$$E = \frac{(d[B]/dt)_{[B]}^{\text{microemulsion}}}{(d[B]/dt)_{[B]}^{\text{no surfactant}}} \tag{1}$$

where $(d[B]/dt)_{[B]}^{\text{microemulsion}}$ is the rate at a known value of $[B]$ in the case of a microemulsion (Runs 1–5), and $(d[B]/dt)_{[B]}^{\text{no surfactant}}$ is the rate of reaction at that concentration in the case of no surfactant (Runs 6–10). Figure 8 shows a plot of the enhancement factor thus obtained versus the concentration of the organic phase.

The influence of micelles in enhancing the reaction rate is currently of significant interest, and models appropriate for hydrophilic or hydrophobic solutes have been formulated (13–16). These models treat the micellar solution as a multiphase system wherein the reacting species distribute

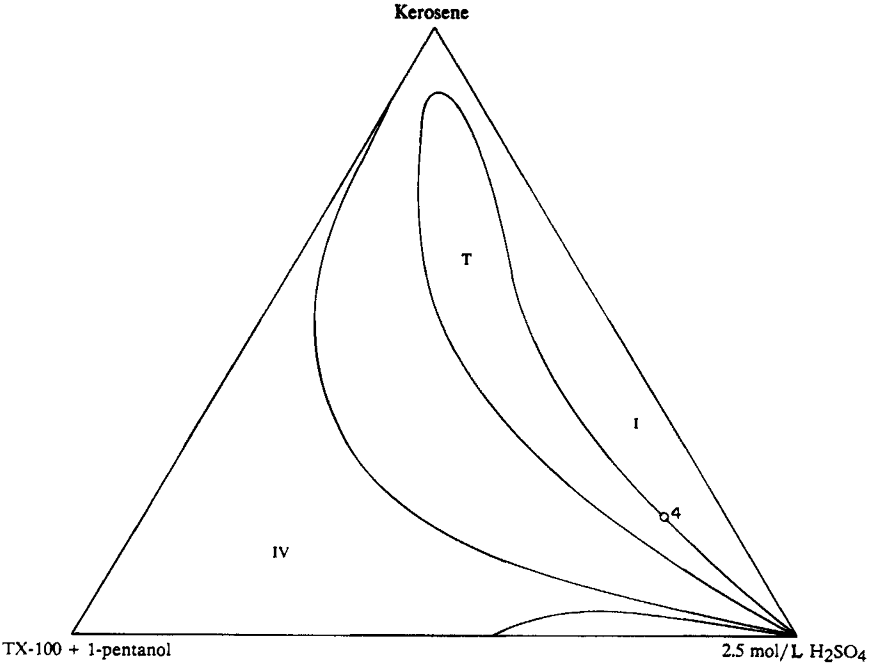

FIG. 4 Pseudoternary phase diagram of the system TX-100 + 1-pentanol/2.5 mol·L^{-1} H_2SO_4/kerosene at 30°C. I: Type I system. T: Three-phase system. IV: Type IV system (microemulsion).

themselves between various phases. The presence of micelles influences the rates of reactions due to the simultaneous course of the reaction in all the pseudophase subvolumes. It is possible to divide the micellar solution into three subvolumes: the organic phase volume (o), the interfacial volume (s), and bulk aqueous phase volume (w), and a reaction may proceed in all the three subvolumes. The scheme for such reaction can be given as

$$\begin{array}{ccccccl} A_o & + & B_o & \rightarrow & P_o & & \text{(oil phase)} \\ \uparrow\downarrow & & & & \uparrow\downarrow & & \\ A_s & + & B_s & \rightarrow & P_s & & \text{(interface)} \\ \uparrow\downarrow & & & & \uparrow\downarrow & & \\ A_w & + & B_w & \rightarrow & P_w & & \text{(water phase)} \end{array}$$

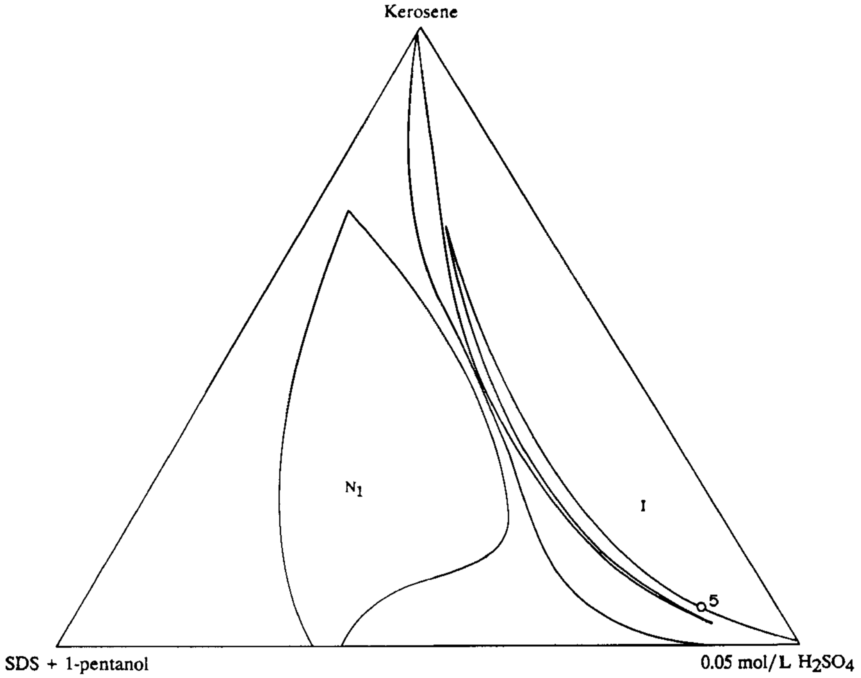

FIG. 5 Pseudoternary phase diagram of the system SDS + 1-pentanol/0.05 mol·L^{-1} H_2SO_4/kerosene at 30°C. I: Type I system. N_1: Single phase (microemulsion). B: Mesophasic region.

where A (here sulfuric acid) is assumed to be predominantly water-soluble and B (nicotine) is the oil-soluble reagent. The overall balance of species such as B can then be written as

$$n_B = n_B^o + n_B^s + n_B^w \tag{2}$$

$$= V_o[B]_o + V_s[B]_s + V_w[B]_w \tag{3}$$

where o, w, and s denote the respective phases and the brackets represent concentrations. The rate law for the irreversible reaction is expressed by a change in n_B, the number of moles of organic reagent, as

$$-dn_B/dt = V_o k_o [B]_o [A]_o^2 + V_s k_s [B]_s [A]_s^2 + V_w k_w [B]_w [A]_w^2 \tag{4}$$

By assuming that the hydrophilic reagent A cannot penetrate into the oil phase, the above equation reduces to

$$-dn_B/dt = V_s k_s [B]_s [A]_s^2 + V_w k_w [B]_w [A]_w^2 \tag{5}$$

TABLE 2
Measured Values of Nicotine Concentration (mol·cm^{-3} × 10^{-5}) with Time (seconds)

Time	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
0	4.7501	4.7492	4.7466	4.7513	4.7533	4.7488	4.7474	4.7487	4.7485	4.7499
120	2.8660	3.2057	3.0646	1.4657	2.7262	4.0391	4.0379	4.0422	4.0319	4.0433
240	1.8888	2.3023	2.2863	0.4690	1.6536	3.4356	3.4335	3.4409	3.4234	3.4428
360	1.2814	1.7383	1.7558	0.1530	1.0130	2.9222	2.9196	2.9290	2.9067	2.9315
480	0.8693	1.3323	1.4020	0.0536	0.6144	2.4856	2.4826	2.4932	2.4680	2.4961
600	0.6011	1.0366	1.1410	0.0182	0.3727	2.1142	2.1110	2.1223	2.0956	2.1254
720	0.4168	0.8105	0.9445	0.0061	0.2283	1.7983	1.7951	1.8066	1.7793	1.8098

Under pseudofirst-order conditions, $[A]_w \gg [B]_w$, giving $K_w = k_w[A]_w^2$ and $K_s = k_s[A]_s^2$. Further, defining the distribution ratio of the organic reagent between the aqueous and oil phase as

$$R_{w,o} = \frac{V_w[B]_w}{V_o[B]_o} = \frac{n_B^w}{n_B^o} \tag{6}$$

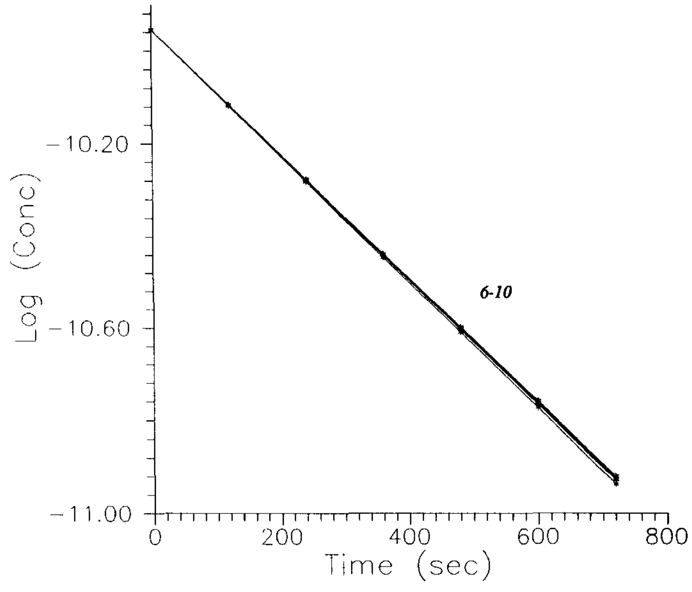

FIG. 6 Plot of log (conc) versus time (second) for Runs 6–10.

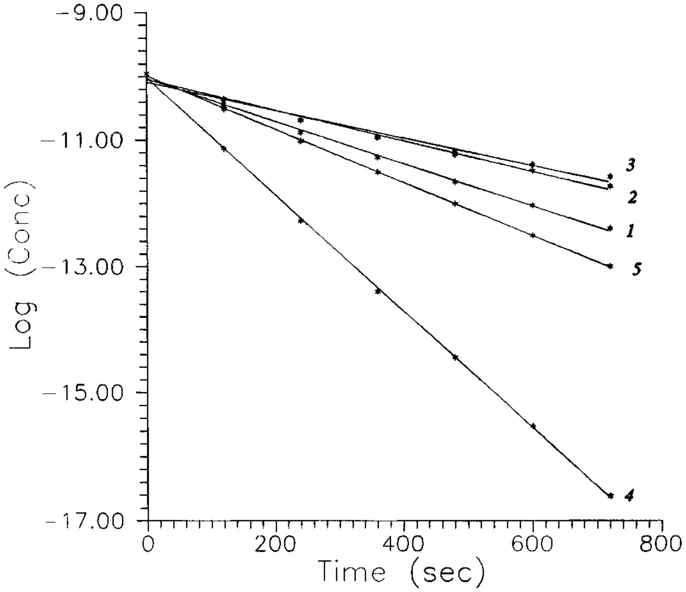

FIG. 7 Plot of log (conc) versus time (second) for Runs 1–5.

and that between the surfactant phase and the oil phase as

$$R_{s,o} = \frac{V_s[B]_s}{V_o[B]_o} = \frac{n_B^s}{n_B^o} \tag{7}$$

we get

$$-dn_B/dt = n_B^o(R_{w,o}K_w + R_{s,o}K_s) \tag{8}$$

where K_w now is regarded as the pseudofirst-order rate constant of the reaction between the oil phase and the pure aqueous phase, and K_s that between the oil phase and the surfactant phase.

On integrating the above equation, we get

$$n_{B,i}^o = n_{B,f}^o \exp\{-K(t_f - t_i)\} \tag{9}$$

where $n_{B,i}^o$ and $n_{B,f}^o$ are the moles of B at times t_i and t_f, respectively, and K represents the overall rate constant observed for the reaction, given as

$$K = R_{w,o}k_w[A]_w^2 + R_{s,o}K_s \tag{10}$$

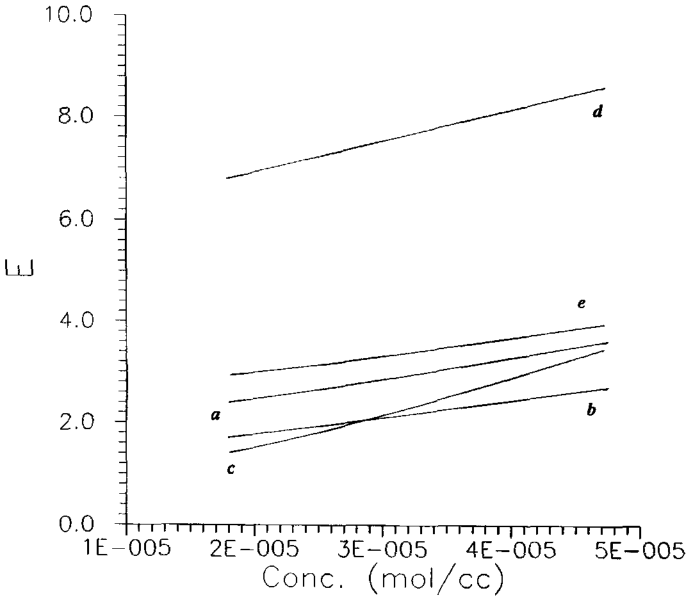

FIG. 8 Plot of enhancement (E) versus concentration of organic phase (mol/cm^3). a: CTAB + 1-pentanol/0.13 mol·L^{-1} H_2SO_4/kerosene. b: CTAB + 1-pentanol/0.26 mol·L^{-1} H_2SO_4/kerosene. c: CTAB + 1-pentanol/0.365 mol·L^{-1} H_2SO_4/kerosene. d: TX-100 + 1-pentanol/2.5 mol·L^{-1} H_2SO_4/kerosene. e: SDS + 1-pentanol/0.05 mol·L^{-1} H_2SO_4/kerosene.

K_w is calculated from the experimental data of the reaction between the oil phase and pure acid. Knowing the values of $R_{w,o}$, $R_{s,o}$, and K, we can determine the values of K_s as

$$K_s = \frac{K - R_{w,o}k_w[A]_w^2}{R_{s,o}} \tag{11}$$

Equation (11) implies that the presence of micelles may influence the rate of chemical reactions in two different ways: 1) the rate constants in the interface region, K_s, differ from those in the bulk aqueous region, K_w; and 2) the reacting species A and B partition into the aqueous and surfactant subvolumes to different extents, thus increasing or decreasing the overall rate of the reaction. In the later case, the equilibrium is also influenced. Using the concentration–time data, and the values of $R_{w,o}$, $R_{s,o}$, K, and K_w reported in Table 3, the rate constant K_s has been estimated.

It is evident from Fig. 8 that the enhancement obtained in the case of TX-100 + 1-pentanol is the greatest, whereas that obtained in the case of CTAB + 1-pentanol is the lowest. This is because $R_{s,o}$ is predominantly

TABLE 3
Measured Values of K, $R_{w,o}$, $R_{s,o}$, and K_w, and estimated values of K_s

No.	k_w × 10^3 s	K × 10^3 s	$R_{w,o}$ × 10^4	$R_{s,o}$ × 10^{-4}	K_w × 10^{10} s	K_s × 10^7 s
1	1.35	3.30	8.236	1.2812	0.228	2.58
2	1.35	2.40	7.79	1.2812	0.913	1.87
3	1.34	2.13	7.68	1.2812	1.78	1.67
4	1.36	9.16	7.03	1.9938	85.21	4.59
5	1.34	4.19	9.08	1.0163	0.0335	4.11

greater in the case of the TX-100 + 1-pentanol/2.5 mol·L^{-1} H_2SO_4/kerosene system as that in comparison with the CTAB + 1-pentanol/H_2SO_4/kerosene system. However, upon comparison of the plots of E versus concentration in the cases of SDS + 1-pentanol and CTAB + 1-pentanol, it becomes evident that $R_{s,o}$ is not the only factor that decides the enhancement E. Besides the volume fraction of the surfactant phase of the microemulsion system, the mechanism of reaction taking place at the interface also decides the magnitude of E. Since the value of K_s is entirely decided by these factors, the trend shown by K_s matches exactly with that shown by E.

NOTATION

$[A]$, $[B]$	concentration of species A, B (mol/cm^3)
E	enhancement factor as defined by Eq. (1)
k_o, k_s, k_w	rate constants of reaction in the organic, surfactant, and aqueous phases, respectively
K_s, K_w	pseudo-order rate constants of reaction in the surfactant and aqueous phases, respectively (second^{-1})
K	overall pseudo-order rate constant of the reaction
n_B^o, n_B^s, n_B^w	moles of species B in the organic, surfactant, and aqueous phases, respectively (g-mol)
$n_{B,i}^o$	moles of Species B in the organic phase before reaction (g-mol)
$n_{B,f}^o$	moles of Species B in the organic phase after reaction (g-mol)
$R_{w,o}$	partition ratio of Species B between the aqueous and organic phases
$R_{s,o}$	partition ratio of Species B between the surfactant and organic phases

t	time (second)
t_i	initial time (second)
t_f	final time (second)
V_o, V_s, V_w	volumes of organic, surfactant and aqueous phases, respectively (cm^3)

ACKNOWLEDGMENTS

We are thankful to Mr. B. R. Bhanage for his help in UV measurements. A.S.C. would also like to thank the University Grants Commission for a fellowship.

REFERENCES

1. P. G. de Gennes and C. Taupin, *J. Phys. Chem.*, *86*, 2294 (1982).
2. E. B. Leodidis and T. A. Hatton, *Ibid.*, *94*, 6400 (1990).
3. M. Adachi, M. Harada, A. Shioi, and Y. Sato, *Ibid.*, *95*, 7925 (1991).
4. P. Lianos and J. K. Thomas, *J. Colloid Interface Sci.*, *117*, 505 (1987).
5. P. D. I. Fletcher and J. Parrot, *J. Chem. Soc.*, *Faraday Trans. 1*, *84*, 1131 (1988).
6. M. Menger and A. R. Elrington, *J. Am. Chem. Soc.*, *113*, 9621 (1991).
7. M. L. Moya, C. Izquierdo, and J. Casado, *J. Phys. Chem.*, *95*, 6001 (1991).
8. R. Schomacker, K. Stickdorn, and W. Knoche, *J. Chem. Soc.*, *Faraday Trans.*, *87*(6), 847 (1991).
9. E. L. Griffin Jr., G. W. M. Phillips, J. B. Claffey, J. J. Skalamera, and E. O. Strolle, *Ind. Eng. Chem.*, *44*, 274 (1952).
10. A. S. Chhatre and B. D. Kulkarni, *J. Colloid Interface Sci.*, In Press.
11. A. S. Chhatre and B. D. Kulkarni, *J. Chem. Res.*, In Press.
12. A. P. Colburn and D. B. Welsh, *Trans. Am. Inst. Chem. Eng.*, *38*, 179 (1942).
13. I. V. Berezin, I. Martinek, and A. K. Yatsimirskii, *Dokl. Akad. Nauk SSSR*, *194*, 840 (1970).
14. L. S. Romsted, in *Micellization, Solubilization and Microemulsions* (K. L. Mittal, Ed.), Plenum Press, New York, 1977.
15. V.-R. Hanke, W. Knoche, and E. Dutkiewicz, *J. Chem. Soc.*, *Faraday Trans. 1*, *83*(9), 2847 (1987).
16. R. Schomacker, K. Stickdorn, and W. Knoche, *Ibid.*, *87*(6), 847 (1991).

Received by editor June 1, 1992