

Reaction Kinetics in Water-in-Oil Microemulsions

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Over the past decade a concerted effort has been made to understand the structure, dynamics, and interactions of microemulsions (1,2), principally because of their unique properties as a reaction medium. The microemulsion droplet can be considered as a microreactor that provides a very small domain within which certain chemical reactions take place. Several authors (3-5) have reported that reaction rates and equilibria may be altered by several orders of magnitude in microemulsions as compared to reactions in homogeneous solutions. In particular, research efforts have examined the use of the aqueous droplets of water-in-oil microemulsions as a novel environment for enzyme-catalyzed reactions (6,7) and their potential for selective synthesis (8,9) and the synthesis of nanoparticles (10).

Reaction rates and equilibria in microemulsions depend on the microemulsion composition, structure of various components of the microemulsion and the hydrophobicity of the reactants (11). The droplets in microemulsions are continuously diffusing through the continuous phase, leading to collisions between droplets. These collisions are inelastic; they are often called *sticky* collisions, because they result in the coalescence of droplets and exchange of material between the droplets before they break apart (12,13). For a reaction in a water-in-oil microemulsion involving reactant species totally confined within the dispersed water droplets, a necessary step prior to their chemical reaction is transfer of reactants into the same droplet. When the chemical reaction is fast (close to being diffusion-controlled), the overall reaction rate is likely to be controlled by the rate of interdroplet transfer of reacting species, or "solubilize exchange" (12). Therefore, the nature of the collision process of droplets in microemulsions and the mechanism of transfer of reactants between two droplets (rate of coalescence of droplets) are of significance to the reaction kinetics. Fletcher et al. (14) have shown that for reactions on the nanosecond time scale (e.g., fluorescence measurements), droplets are essentially isolated, and no exchange occurs between droplets. For reactions in the microsecond to millisecond time scale, the interdroplet exchange is the rate-limiting step, and the reaction rate depends on the reactant concentrations in the aqueous droplets. For reactions occurring in longer times, the interdroplet exchange has no influence on the reaction rate (14).

Moya et al. (15) studied the oxidation of iodide ions by persulfate in water/sodium bis 2-ethylhexyl sulfosuccinate (AOT)/decane microemulsions. They reported reaction rates that followed second-order kinetics and were higher than those for the same reaction in an aqueous solution. The reaction rate decreases with an increase in water content but shows no dependence on surfactant concentration.

Lang et al. (16) systematically studied the effect of oil, surfactant, and cosurfactant alkyl chain length and temperature on the rate constant for reactions involving exchange of material between colliding droplets in water-in-oil microemulsions. Their results were in agreement with current theories on the stability of microemulsions. They found that the rate constant increased with increasing temperature or oil chain length but decreased with increasing surfactant or cosurfactant chain length.

Fletcher et al. (12) studied the exchange rates of aqueous solubilizates in AOT-based water-in-oil microemulsions as a function of droplet size, temperature, and oil chain length. Their results for electron transfer reactions indicated that these systems exhibited second-order reaction kinetics. These reaction rates were two to four orders of magnitude slower than the droplet collision rate as predicted from simple diffusion theory. The reaction rate increased with increasing temperature and oil chain length but decreased with increasing droplet size.

An experimental method commonly used for the study of reaction kinetics in microemulsions is stopped flow (12). This method permits the fast mixing of two reactants. The system derives its name from the fact that the flow of the sample is stopped immediately after mixing for monitoring the course of the reaction. The reactants to be mixed are placed in two syringes whose plungers are actuated by a pneumatic system. The reactants flow into a mixing chamber, where intimate mixing is achieved in 1 to 5 ms, and then into an observation chamber, where the reaction is usually monitored by conductivity or optical detection (UV-Vis absorption or fluorescence) (17).

The objective of the experiments described in this chapter was to study the reaction kinetics in the microemulsion systems that we have previously used for the synthesis of nanoparticles of barium ferrite (18,19), zinc oxide-based varistors (20), and titanium dioxide (21) and to study the effect of the chemical structure of various microemulsion components on the reaction rate. However, precipitation reactions cannot be directly studied using stopped-flow photometry, because settling of particles and light scattering from particles would interfere with light absorbance measurements. Therefore, it is important to select reactants that do not precipitate while reacting but can be monitored by light absorption or transmittance. Keeping this in mind, we selected an electron transfer reaction between sodium hexachloroiridate(IV), Na_2IrCl_6 (abbreviated SHCl) and potassium ferrocyanide(II), $\text{K}_4\text{Fe}(\text{CN})_6$ (abbreviated PFC). Solutions of these two salts were used as aqueous phases in the two reactant microemulsions. We describe studies on the effect of droplet size, aqueous concentration, cosurfactant, and oil chain length on reaction kinetics in microemulsions.

Experimental Procedure

Materials

SHCl (99.9 % pure) and PFC (99 % pure) were purchased from Aldrich (Milwaukee, WI). Cetyl trimethyl ammonium bromide (CTAB), 1-butanol, isobutanol, 1-pentanol, isopentanol, 1-hexanol, 1-octanol, 1-decanol, *n*-hexane, *n*-octane, *n*-decane, *n*-dodecane, and *n*-tetradecane (all technical grade) were purchased from Fisher Scientific (Fairlawn, NJ). All reagents were used without further purification. Water was deionized and distilled before use. All experiments were carried out at room temperature.

Methods

A Perkin Elmer (Norfolk, CT) UV-Vis Spectrophotometer was used for absorbance measurements on three microemulsion systems. The first system was a reactant microemulsion containing 0.5 mM SHCl as the aqueous phase, 1-butanol as the cosurfactant, CTAB as the surfactant (0.5 M in octane), and octane as the oil phase. This microemulsion had a ω_o of 44.4 and a value of Z equal to 5, where

$$\omega_o = \frac{\text{Moles of water}}{\text{Moles of surfactant}} \quad (1)$$

$$Z = \frac{\text{Moles of cosurfactant}}{\text{Moles of surfactant}} \quad (2)$$

The second system was a reactant microemulsion similar to the first, except that the aqueous phase was a 0.5 mM solution of PFC. The third system was an equilibrium mixture of the first two and is therefore called the product microemulsion. Samples of all three systems were scanned for absorbance between wavelengths of 350 and 550 nm.

A DurrumDionex (Sunnyvale, CA) model D-110 Stopped-Flow Spectrophotometer was used to study the reaction kinetics in the microemulsions. This instrument is a complete system for rapidly mixing two liquid reactant solutions and measuring their change in optical transmission or absorbance as a function of time. The reaction is observed by photometrically monitoring the transmission of light through a port in the mixing chamber cuvette. The output level sensed by the photometer is applied to an oscilloscope, where it is displayed against a time base. This data is then transferred to a personal computer through a GPIB port for data analysis. Monochromatic light is used in the photometer system so that each reaction can be studied at its optimum absorption peak. For these microemulsion systems a wavelength of 490 nm was selected, based on the UV-Vis absorbance measurements. All stopped-flow experiments were monitored by measuring the transmittance of light at this wavelength.

To study the effect of droplet size and aqueous phase concentration, samples were prepared by varying ω_o and aqueous-phase concentration as required.

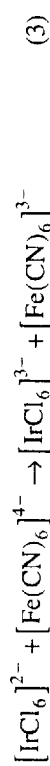
Concentration of CTAB in oil was kept constant at 0.5 M, and the molar ratio of cosurfactant to surfactant (Z) was kept constant at 5.

For experiments on the effect of alcohol and oil chain length, the concentration of CTAB in oil was kept constant at 0.5 M. A required amount of aqueous phase was added to this mixture, and then the cosurfactant (alcohol) was added drop by drop until the mixture became clear, signifying the formation of the microemulsion phase. The compositions for all these systems are given in Table 7.1.

Results and Discussion

Absorbance Measurements

Figure 7.1 shows the results of UV-Vis absorbance measurements on the two reactant and one product microemulsion systems. The first reactant microemulsion, containing SHCl as the aqueous phase, has two absorbance peaks at 425 nm and 490 nm. The second reactant microemulsion, containing PFC, has no absorbance peak in this range of wavelengths. The product (mixture) microemulsion had a very low absorption peak at 425 nm but no absorbance at 490 nm. The electron transfer reaction that had taken place in the aqueous phase of this microemulsion is as follows:



Because both the first reactant microemulsion and the product microemulsion system absorb light at 425 nm, the second microemulsion does not absorb light in this range, and only the first reactant microemulsion (SHCl) has absorbance at 490 nm, this wavelength was selected to study these reactions in various microemulsion systems using stopped-flow photometry. We were therefore monitoring the consumption of $[\text{IrCl}_6]^{2-}$ with time in the microemulsions.

TABLE 7.1

Compositions of Microemulsion Systems Used for Studying Effects of Alcohol Cosurfactants and Oil Chain Length

Alcohol	Oil	CTAB	ω_o
1-butanol (0.74 g)	Octane (5 mL)	0.9118 g	22.2
1-pentanol (0.62 g)	Octane (5 mL)	0.9118 g	22.2
1-hexanol (0.64 g)	Octane (5 mL)	0.9118 g	22.2
1-octanol (0.64 g)	Octane (5 mL)	0.9118 g	22.2
1-decanol (0.81 g)	Octane (5 mL)	0.9118 g	22.2
Isobutanol (0.9 g)	Octane (5 mL)	0.9118 g	22.2
Isopentanol (0.7 g)	Octane (5 mL)	0.9118 g	22.2
1-butanol (0.75 g)	Hexane (5 mL)	0.9118 g	22.2
1-butanol (1.02 g)	Decane (5 mL)	0.9118 g	22.2
1-butanol (0.64 g)	Dodecane (5 mL)	0.9558 g	22.2

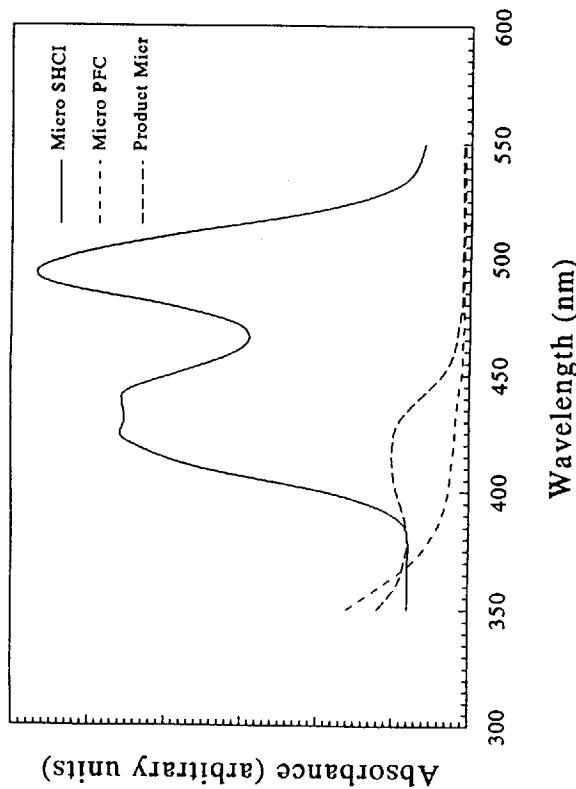


Fig. 7.1. UV-Vis absorbance for reactant and product microemulsions.

Experimental data for all reaction kinetics measurements were curve-fitted to obtain the order of the reaction. These results gave orders ranging from 0.8 to 1.2 for all experiments. It can thus be inferred that all reactions in these microemulsion systems are close to first-order.

Effect of Droplet Size

The results for effect of droplet size in aqueous phase/1-butanol/CTAB/*n*-octane microemulsions are shown in Fig. 7.2. When the aqueous-phase concentration was maintained at 0.5 mM, microemulsions with ω_o of 4.44 and 11.11 showed higher reaction rates than did microemulsions with less surfactant, ω_o values of 22.22 and 44.44. This result can be explained as follows: The droplets of all microemulsions have a bound layer of water (which cannot dissolve the reactant species) associated to the interface due to double layer formation (15). At high ω_o values the droplet size is large, so the volume of bound water will be small compared to the free water in the solution, and the effective concentration of reactant will be lower than in a small droplet, where a majority of the water is bound (15). Because effective concentration is higher in smaller droplets, fewer collisions and coalescence between droplets will be required for the reaction to reach completion. Therefore, the reaction will be completed more rapidly in these systems than in droplets with a low effective concentration.

On the other hand, at low aqueous-phase concentrations the effective concentration does not change appreciably with droplet size. Therefore, at low aqueous-phase concentrations (0.25 mM and 0.1 mM) the reaction rate is not increased in small

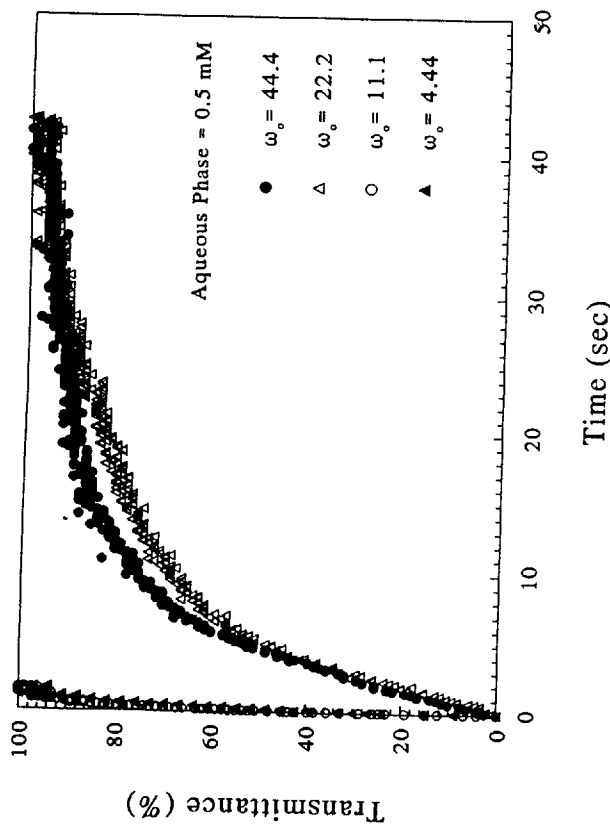


Fig. 7.2. Effect of droplet size of microemulsion on reaction rate for an aqueous-phase concentration of 0.5 mM.

droplets, as can be seen by comparing Fig. 7.2 with Fig. 7.3, where results for $\omega_o = 11.11$ at different aqueous-phase concentrations are plotted.

Effect of Alcohol Chain Length

Figure 7.4 shows the effect of alcohol chain length on the reaction rates in various microemulsion systems (compositions shown in Table 7.1). The reaction rates for microemulsions containing 1-butanol, 1-pentanol, and 1-hexanol and similar to each other. Therefore, we can infer there is very little increase in the fluidity of the microemulsion as the cosurfactant chain length is changed from C_4 to C_6 . However, when 1-octanol is used as cosurfactant, the reaction rate decreases significantly. This can be attributed to the high rigidity of the interface for this system due to the *chain length compatibility effect* (22–24), which arises when

$$L_s = L_o + L_a \quad (4)$$

where L_s is the carbon number of the surfactant, L_o is the carbon number of the oil, and L_a is the carbon number of the alcohol (24). Both 1-octanol and *n*-octane have eight carbon atoms in their hydrophobic chain, and the hydrophobic chain of CTAB contains 16 carbon atoms, so Eq. (4) is fulfilled in this case. Chain length compatibility allows the chains to pack very well at the interface, making it very

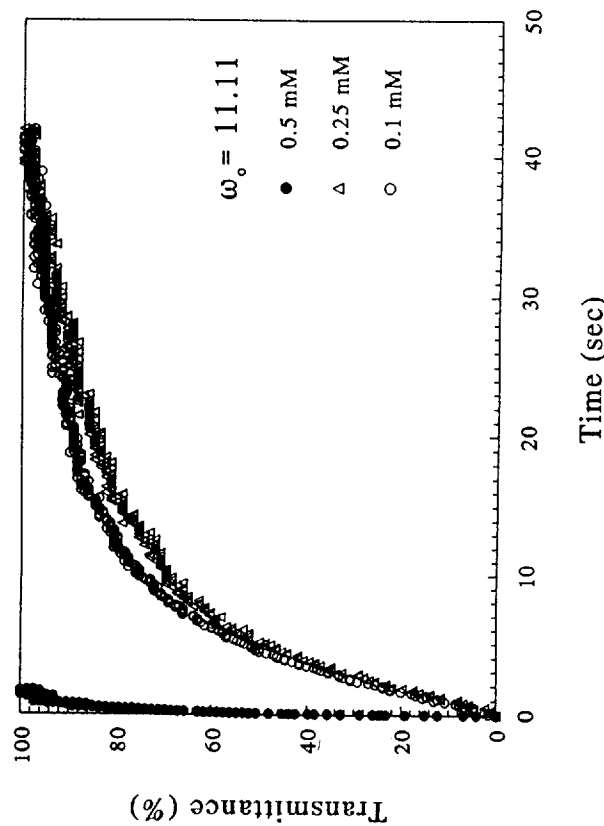


Fig. 7.3. Effect of aqueous-phase concentration on reaction rate in microemulsions for $\omega_0 = 11.11$.

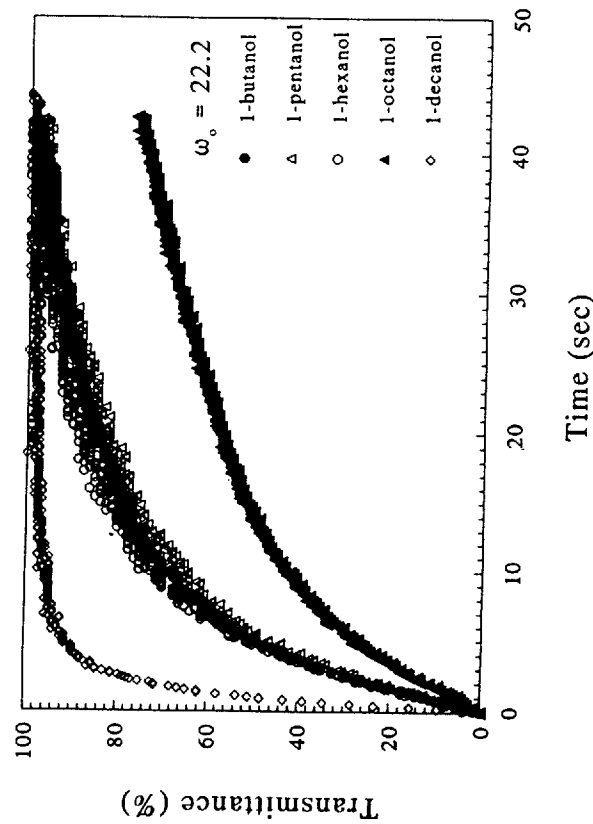


Fig. 7.4. Effect of straight-chain alcohols on rate of reaction in microemulsions.

rigid; as a result, collisions of microemulsion droplets are less likely to result in coalescence and to bring reactants into contact with each other, so the reaction rate is reduced. On the other hand, the microemulsion system having 1-decanol as the cosurfactant has a very fluid interface and therefore a very high coalescence rate of microemulsion droplets, as shown by its high rate of reaction.

Figure 7.5 shows the effect of branched-chain alcohols. It can be seen that there is very little change in reaction rates in these systems. Therefore, branched-chain alcohols do not increase the fluidity of the interface significantly.

Effect of Oil Chain Length

Results for the effect of oil chain length are shown in Fig. 7.6. A chain length compatibility effect can be seen in these results too for the microemulsion system that has dodecane as its oil phase (24). Dodecane has 12 carbon atoms; the cosurfactant, 1-butanol, has four; and the surfactant, CTAB, has 16. Therefore, this system had a very high interfacial rigidity and therefore a lower reaction rate.

Conclusions

This chapter's study of the effect of several variables (droplet size, aqueous-phase concentration, cosurfactant chain length, and oil chain length) on reaction rates in microemulsion systems leads to two main conclusions:

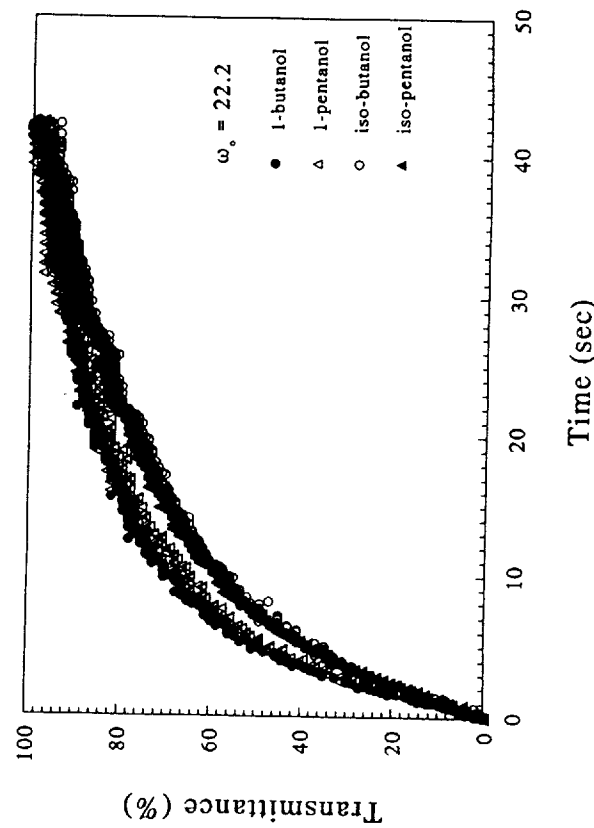


Fig. 7.5. Effect of branched-chain alcohols on rate of reaction in microemulsions.

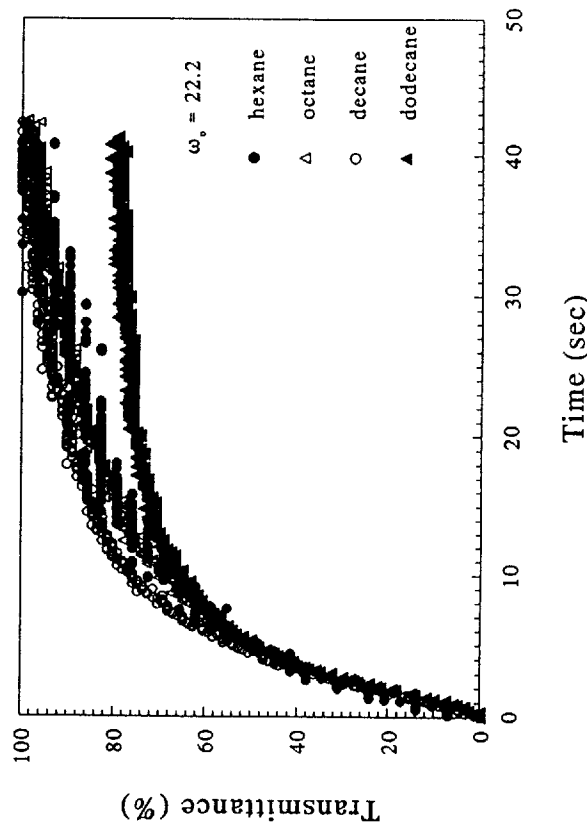


Fig. 7.6. Effect of oil chain length on rate of reaction in microemulsions.

1. As the droplet size in microemulsions decreases, the rate of the reaction increases if the aqueous-phase concentration is sufficiently high. This result has been explained on the basis of an enhanced effective concentration of the aqueous phase in small droplets (15).
2. Chain length compatibility among the cosurfactant, oil, and surfactant plays a significant role in determining the interfacial rigidity in microemulsion systems (22-24). This rigidity decreases the reaction rates in the 1-octanol/CTAB/octane and the 1-butanol/dodecane/CTAB microemulsion systems significantly.

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