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ORIGINAL CONTRIBUTION

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Effect of the structures of microemulsions on chemical reactions

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Abstract Two kinds of chemical reactions were studied in two different microemulsion systems: cetyltrimethylammonium bromide/1-butanol/10 and 25% *n*-octane/water and sodium dodecyl sulfonate/1-butanol/20% styrene/water. One reaction is a hydrolysis reaction, in which aspirin and 2,4-dinitrochlorobenzene were used as the hydrolysis substrates. The second reaction is the polymerization of styrene, which was initiated by using two initiators, water-soluble $K_2S_2O_8$ and oil-soluble 2,2′-azobis(isobutyronitrile), and, at the same time, the polymerization of acrylamide, which was initiated by $NaHSO_3$, was also studied. All the hydrolysis reaction experimental results show that the hydrolysis is greatly affected by the structures and the structural transitions of microemulsions. The hydrolysis rates are higher in water-in-oil (W/O) microemulsion media and decrease with the addition of water. The rates increase in bicontinuous (BC) microemulsions and decrease in oil-in-water (O/W) microemulsions. The transition points of the hydrolysis rates occurred at the two microemulsion structural transition points from W/O to BC and from BC to O/W. The polymerization relationships between the conversions of styrene, the molecular weights of polystyrene and the water contents of the microemulsion system were obtained. The effects of microemulsion structures on the sizes of the polystyrene particles and on the molecular weights of the polymers are discussed. Polystyrene particles with diameters of 10–60 nm were observed by microscopy. Our experimental polymerization results show that microemulsions are suitable as media for the production of polymers, the molecular weights and the particle sizes of which can be controlled and predicted by variations in microemulsion structures.

Key words Hydrolysis kinetics · Polymerization · Microemulsions · Aspirin · Styrene

Introduction

Micelles and microemulsions are important supramolecular assemblies which are formed in aqueous solutions of surfactants. Their structures and properties are changed on addition of cosurfactants or oil components. In recent years, microemulsion systems have been used as chemical reaction media in most of the studies described and the experimental results also seem to indicate the critical phenomena of chemical reactions in microemulsion media [1–3]. However, up to the present, no suitable theory exists to explain the connection between the chemical reaction medium variations and their effects on chemical reactions. The aim of the present paper is an attempt to enrich the information on chemical reactions in microemulsion media and to develop a relationship between chemical reactions and microenvironmental media, especially the structures and the structural transitions of microenvironmental media.

We report two kinds of chemical reactions in two microemulsion systems, cetyltrimethylammonium bromide (CTAB)/1-butanol/10 and 25% *n*-octane/water and sodium dodecyl sulfonate/1-butanol/20% styrene/water. One reaction is a hydrolysis reaction, in which aspirin and 2,4-dinitrochlorobenzene were used as the hydrolysis substrates. The second reaction is the polymerization of styrene, which was initiated by using two initiators; water-soluble $K_2S_2O_8$ and oil-soluble 2,2′-azobis(isobutyronitrile) (AIBN). The polymerization of acrylamide, which was initiated by $NaHSO_3$, was also investigated.

Experimental

Materials and instruments

CTAB and sodium dodecyl sulfonate (As) were recrystallized three times from ethanol and acetone mixed solvents and from ethanol, respectively. The hydrolysis reactants, aspirin and 2,4-dinitrochlorobenzene, were of especially pure grade (purity > 99.9%). Acrylamide was recrystallized three times from acetone and styrene was not purified further. The initiators, water-soluble $NaHSO_3$ for the polymerization of acrylamide, $K_2S_2O_8$ and oil-soluble AIBN for the polymerization of styrene, were all of especially pure grade and were used as received. All other chemicals were of analytical grade and were used as received.

A Shimadzu UV-3000 spectrophotometer was used to measure the absorption spectra during the hydrolysis reactions. Other instruments used included a DDS-11A electrical conductometer with a conductivity bridge, a Ubbelohde viscometer, a H-600 transmission electron microscope, and a 501 superior constant temperature container with an accuracy of ±0.1 °C.

Experimental methods

For phase diagrams, microemulsion structural regions (Fig. 1), measurements of the kinetics of hydrolysis reactions, polymerization of styrene and acrylamide in microemulsion systems, and the treatment of data see Refs. [4, 5]. Reaction solutions 5 ml were drawn after 90 min polymerization. The samples were observed under a H-600 transmission electron microscope.

Results and discussion

Hydrolysis reactions of aspirin and 2,4-dinitrochlorobenzene in microemulsions

The different microemulsion media were chosen in accordance with the phase diagram in Fig. 1A. The compositions of the microemulsion media for which hydrolysis reaction rates were determined are indicated in Fig. 1A. The relationship between the hydrolysis reaction rate constants ($k\psi$) and the compositions of the microemulsions was measured at 40 °C. The experimental results are shown in Fig. 2. From the curve of $k\psi$ of aspirin hydrolysis (curve 1) in Fig. 2, it can be seen that the different microemulsion structures have different effects upon $k\psi$ of aspirin hydrolysis. The hydrolysis rates are much higher in the water-in-oil (W/O) microemulsion media and decrease with increasing water content. When the water content amounts to 20 wt%, the reaction rates of aspirin hydrolysis increase with the addition of water. When the water content amounts to 59 wt%, the reaction rates of aspirin hydrolysis decrease again with increasing water content. The variations observed in Fig. 2 (curve 1) indicate two points, at 20 and 59 wt% water, at which the reaction rates of aspirin hydrolysis are changed. Significantly, the two points correspond to the transitions of the structures of microemulsions from W/O to bicontinuous (BC) and from BC to oil-in-water (O/W) (Fig. 1A).

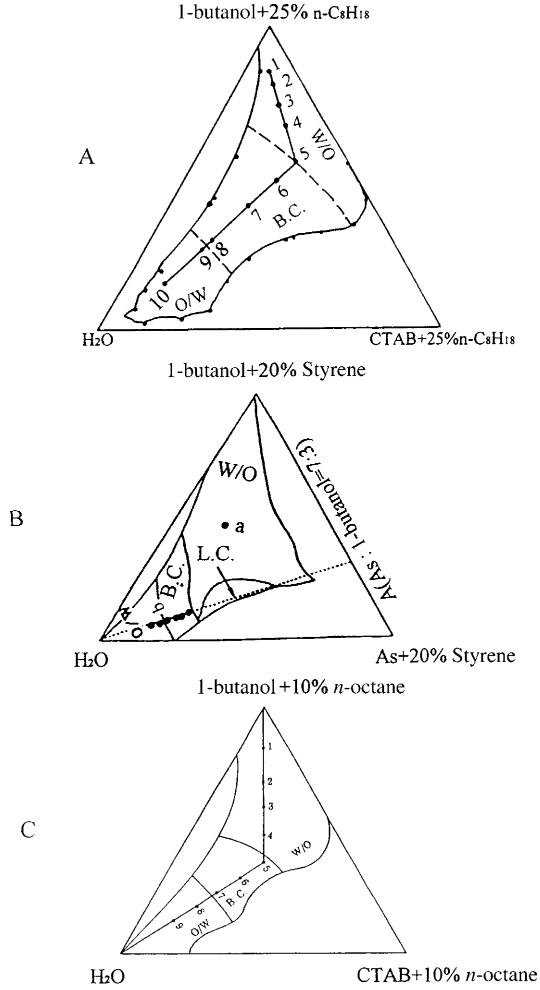

Fig. 1A–C Phase diagrams and microemulsion structures. The composition of the microemulsion media for the chemical reactions are indicated in these phase diagrams. The different phases are oil-in-water (*O*/*W*), water-in-oil (*W*/*O*), bicontinuous (*BC*) and liquid crystals (*L.C.*). **A** Cetyltrimethylammonium bromide (*CTAB*)/1-butanol/25% *n*-octane/water system. **B** Sodium dodecyl sulfonate (*As*)/1-butanol/20% styrene/water system. **C** CTAB/1-butanol/10% *n*-octane/water system

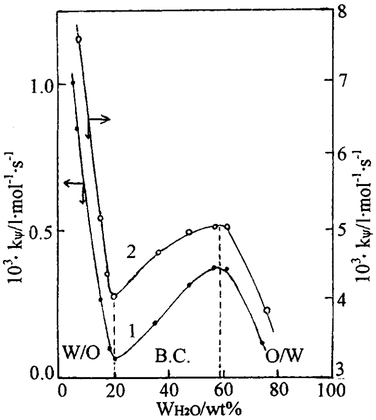

Fig. 2 The relationship between the hydrolysis reaction rate constants ($k\psi$) and the structure of the microemulsions at 40 °C. *1* Aspirin, *2* 2,4-dinitrochlorobenzene

In order to confirm the experimental results for aspirin hydrolysis, we also measured the hydrolysis of 2,4-dinitrochlorobenzene under the same conditions as for aspirin. Extremely similar experimental results were obtained. (Fig. 2, curve 2). Mishra et al. [2], Friberg et al. [6] and Hao et al. [7] also observed such similar catalysis or inhibition induced by the structures and the structural transitions of microemulsions.

At the present time, no suitable theory exists to explain these observations, however, we attempt to connect the critical points of a microemulsion system with the chemical reaction rates and to explain them by considering the different hydrolysis mechanisms in the different microemulsion media and the variation of the polarity in "the interfacial films" of microemulsions [4].

In microemulsion media, chemical reactions are considered to occur at the phase structure interface of the microemulsions [8]. In the W/O microemulsions, aspirin molecules solubilize in the inner core (water phase) and the head groups for α, β, γ and $^+N(CH_3)_3$ in CTAB molecules. The concentration of OH^- in the inner core of the microemulsions is high, the probabilities of collisions between OH^- ions and the ester bond of the aspirin molecules are high, and so the hydrolysis reaction rates are much higher. In addition, the reaction rates of aspirin hydrolysis in the microemulsions are high compared to the rate in pure water, because the amount of solubilization of aspirin in the inner core of the microemulsions is much higher than the solubility of aspirin in pure water [9]. With the increase in the water content, however, the microdrops of the W/O microemulsions increase in size and the relative concentrations of OH^- decrease, which gradually results in a decrease in the rates of aspirin hydrolysis. When the water content reaches 20 wt%, the structures of the microemulsions are changed from W/O to BC. Water and oil phases intersect each other [10, 11] and the collisions between OH^- ions and aspirin molecules become more frequent, which results in an increase in the rates of aspirin hydrolysis in BC microemulsions. When the water content reaches more than 59 wt%, the microemulsion structure is changed to O/W. The microdrops of the microemulsions are much bigger, the surface electric charges are lower than in the W/O microemulsions, the molecules of aspirin are submerged into "the surface layers" of the microemulsions, the ground state of aspirin is stable, the ester group in the aspirin molecules is not easily split and the rates of aspirin hydrolysis decrease again. The experimental results for 2,4-dinitrochlorobenzene hydrolysis can be explained in the same way as for aspirin hydrolysis.

Polymerization of styrene in W/O microemulsion media

The W/O microemulsion media were prepared with the compositions of microemulsions indicated in Fig. 1B (e.g. point a). The polymerization was initiated by $K_2S_2O_8$ at 70 °C. The styrene content decreased with the progress of the polymerization and the insoluble product, polystyrene, adhered to the wall of the glass flask. The product is not soluble in water and cold methanol, however, it is soluble in toluene and chloroform. In the W/O microemulsions, styrene is in the continuous oil phase and a little styrene (0.031 wt%) solubilizes in the inner-core water where the soluble-water initiator, $K_2S_2O_8$, exists. Thus, in accordance with the investigation carried out by Guo et al. [12] for the polymerization mechanism of styrene in W/O microemulsions, we guessed that the polymerization mechanism of styrene initiated by $S_2O_8^{2-}$ ions may be that the initiator, $S_2O_8^{2-}$, produces the free-radical ion, $SO_4^{-}\cdot$, in the inner-core water, and the free-radical ion, $SO_4^{-}\cdot$, can initiate a little styrene by solubilizing in the inner-core water the monomer free radicals which can polymerize into polystyrene free radicals of lower molecular weights. The polystyrene free radicals can return into the continuous oil phase (styrene phase) by diffusion, and polymerization in the continuous oil phase can be carried out.

We did not obtain quantitative data for the polymerization of styrene in W/O microemulsions because it was difficult to obtain the polystyrene during the progress of the experiment. Thus, we give the possible phenomena of the polymerization in W/O microemulsions.

Polymerization of styrene in BC and O/W microemulsions

The relationship between the degree of conversion of styrene and the water content of the microemulsion system was obtained and the results are shown in Fig. 3A. The microemulsion media for the polymerization were prepared according to the compositions indicated in Fig. 1B, As→H_2O was the inverstigation route and it passed through the BC and O/W microemulsion regions. The polymerization temperature was 70 °C, and the water-soluble $K_2S_2O_8$ and the oil-soluble AIBN were used as the initiators. The polymerization was carried out under a nitrogen atmosphere and the reaction times were 90 min.

The variations (curve A, B) observed in Fig. 3A indicated conversions were the highest when the water content was 73 wt%, with either $K_2S_2O_8$ or AIBN as initiators. Significantly, this water content corresponded to the transition from BC to O/W microemulsions (see Fig. 1B). The results show that the transition points of microemulsion structures have an important effect on the polymerization. In other words, the polymerization is sensitive to the critical points of microemulsions.

In BC microemulsions, water and oil (styrene) phases intersect each other [10, 11]: in other words, O/W and W/O microemulsions coexist, and styrene is neither inner-core oil phase for O/W microemulsions nor continuous oil phase for W/O microemulsions. The polymerization of styrene is rapid when styrene is regarded as the inner-core oil phase, which was similar to the polymerization in the O/W microemulsions. At the same time, the polymerization was also similar to that in the W/O microemulsions when styrene was the continuous phase, and so the polymerization in BC microemulsions was greater than that in W/O microemulsions. With the increase in water content, O/W-structures were formed in the BC-microemulsions and the polymerisation rate was increasing. The structures of the microemulsions are transferred from BC into O/W microemulsions when the water content reaches 73 wt%. The polymerization rate was the highest at this water content. With further addition of water, the number of microdrops of the O/W microemulsions and the concentrations of the initiators ($K_2S_2O_8$ and AIBN) all decreased. The polymerization rate also decreased with the increase in water content.

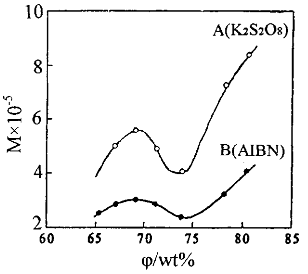

Fig. 3A, B The relationship between the conversions, polymerization rates in the microemulsions and the water contents given in Fig. 1 B and C. *A* Styrene, with $K_2S_2O_8$ initiator and *B* Acrylamide, with 2,2′-azobis(isobutyronitrile), (*AIBN*) initiator. The concentration of $NaHSO_3$ was 3.9101×10^{-3} M. The ratio of the microemulsion volume to acrylamide weight was 10 ml:2g

Polymerization of acrylamide in microemulsions

Figure 3B shows that the polymerization rates of acrylamide vary with water content in the microemulsion system for CTAB/1-butanol/10% *n*-octane/water at both 30 and 45 °C. The variations observed in Fig. 3B also indicated two points, at 27 and 56 wt% water content, at which the rates of polymerization are enhanced. Significantly, these points correspond to the transition from W/O to BC and from BC to O/W (see Fig. 1C). The experimental results of acrylamide polymerization are similar to those of styrene.

Effect of microemulsion structures on polystyrene molecular weights

The relationship between the molecular weights of polystyrene and the water content of the system is shown in Fig. 4. It can be seen from Fig. 4 that the molecular weights of polystyrene in BC-microemulsions changed less both for the oil soluble initiator AIBN (2,4-2,9·10^5 g/mol) and for the water soluble initiator $K_2S_2O_8$ (4,22-5,6·10^5 g/mol). The structures of the microemulsions changed from BC to O/W when the water content was 73 wt% under these condition the molar weight of polystyrene increased significantly.

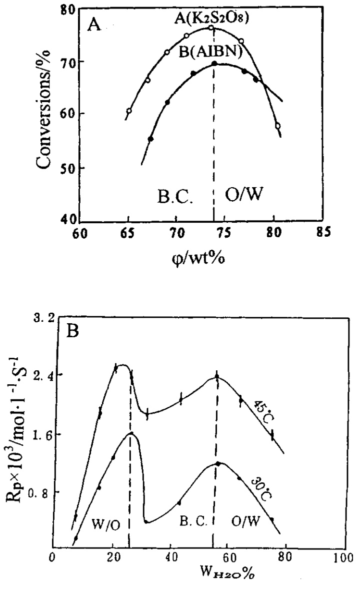

Fig. 4 The effect of the microemulsion structures on the molecular weights of polystyrene

Table 1 Effect of microemulsion structures on polyacrylamide molecular weights at 30 °C. The ratio of the concentrations of acrylamide and $NaHSO_3$ constant

Microemulsion compositions ($M \times 10^5$)	Water-in-oil				Bicontinuous			Oil-in-water	
	1	2	3	4	5	6	7	8	9
	6.58	9.65	9.58	7.34	5.75	3.68	2.92	5.60	4.57

Effect of microemulsion structures on the molecular weights of polyacrylamide

The molecular weights of polyacrylamide in the different microemulsion media are listed in Table 1. The microemulsions for 1, 2, 3 and 4 are W/O microemulsion media, 5, 6 and 7 are BC microemulsion media and 8 and 9 are O/W microemulsion media (see Fig. 1C). Table 1 shows that the molecular weights of polyacrylamide are different in the different microemulsion media. The highest molecular weights were obtained in W/O microemulsion media, the lowest in BC-microemulsion media and intermediate molar weights in O/W microemulsions what is similar to the results for polystyrene. So microemulsions were shown to be suitable as media for the production of polyacrylamide in which molecular weights can be controlled and predicted by variations in microemulsion structures.

Transmission electron microscopy observation of polystyrene

With TEM micrographs we found after a polymerisation time of 90 min that the sizes of the polystyrene particles were 10–15 nm in BC-microemulsions and 15–20 nm in W/O-microemulsions, respectively. The sizes are fairly well distributed. The polystyrene sizes in W/O microemulsions are much higher, and are 30–50 nm and 50–60 nm and are also relatively well distributed. The results of TEM observation of polystyrene also indicated the suitability for controlling and predicting the production of polymers.

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