Effect of the structures of microemulsions on chemical reactions

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$_2$S$_2$O$_8$ 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 \( \text{K}_2\text{S}_2\text{O}_8 \) and oil-soluble \( 2,2' \)-azobis(isobutyronitrile) (AIBN). The polymerization of acrylamide, which was initiated by \( \text{NaHSO}_3 \), 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 \( \text{NaHSO}_3 \) for the polymerization of acrylamide, \( \text{K}_2\text{S}_2\text{O}_8 \) 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).