

THE EFFECT OF ALKANES ON THE FORMATION OF ULTRAFINE
SILVER BROMIDE PARTICLES IN IONIC W/O MICROEMULSIONS

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ABSTRACT

Ultrafine AgBr particles formed in w/o microemulsions with different chain length of alkanes were studied by UV-VIS spectrophotometry, stopped-flow spectrophotometry and transmission electron microscopy. The ultrafine particles of AgBr (5-7 nm in diameter) were obtained by mixing two separately prepared microemulsion systems both containing AOT, n-hexane and an aqueous solution of either AgNO_3 or NaBr. The size distribution of the nearly spherical AgBr particles broadened from 5 to about 10 nm as chain length of alkane was increased from n-hexane to n-octane. When n-dodecane or a higher alkane was used, the microemulsion system became increasingly unstable causing precipitation of AgBr.

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INTRODUCTION

Very fine solid particles are extremely important to many industrial applications such as metal catalysts and photographic emulsions¹⁻³. It is, however, difficult to obtain fine and nearly monodispersed solid particles by conventional methods. Therefore, water-in-oil (w/o) microemulsions have attracted a considerable attention recently in view of their water pools (3-20 nm in diameter) which are ideal media for preparation of extremely fine particles. The ultrafine particles (3-8 nm) of rare metals⁴, metal borides⁵, metal oxides⁶⁻⁷ and metal carbonates⁸ have been successfully prepared in ionic and nonionic w/o microemulsions. The formation of ultrafine silver chloride particles (5-10 nm) has also been studied by reacting silver nitrate and sodium chloride in the w/o microemulsions^{9,10}.

The microdomains of microemulsions have been described as spherical droplets (10-60 nm) dispersed in the continuous medium within a certain composition range¹¹⁻¹⁶. Microemulsions may also exhibit bicontinuous structure¹⁶⁻¹⁸. Due to the dynamic nature of the microemulsion, the reacting species solubilized in the water pools of the microemulsion droplets can mix rapidly among different droplets¹⁹⁻²³. In principle, small and nearly monodispersed solid particles of various materials can be prepared by this method, if the solid particles produced can be protected from sintering.

This paper describes the general aspects of the ultrafine silver bromide particles prepared in the ionic w/o microemulsions consisting of sodium di-2-ethylhexyl sulfosuccinate (Aerosol OT), alkane (C₆-C₁₄) and an aqueous solution of either AgNO₃ or NaBr. It is well known that the dialkyl type AOT requires no cosurfactant, such as alcohol, in forming microemulsion because of its nearly balanced hydrophile-lipophile property²⁴⁻²⁶. Thus, the AOT-microemulsion system is suitable for preparing fine solid particles with lesser complications. Moreover, such a w/o

microemulsion with a given ratio of water and AOT can readily be diluted with the oil in the continuous phase with least modification of structure and composition of the different domains²⁷.

EXPERIMENTAL

Chemicals

Silver nitrate of spectropure was purchased from Engelhard Corporation. Sodium bromide (99.999%), n-nonane (99%) and n-tridecane (99%) were from Aldrich Chemical Company. Sodium di-2-ethylhexyl sulfosuccinate (AOT, >99%) was from Fluka Chemical Corporation. Other alkanes of 99% purity or reagent grade were obtained from Fisher Scientific Company. All reagents were used without further purification. Water was doubly distilled.

W/O Microemulsions

Except for transmittance measurements, the concentrations of AOT in all alkanes were prepared at 0.15M and the aqueous solutions of AgNO₃ and NaBr were at 0.4M. The microemulsion containing either AgNO₃ or NaBr was first prepared separately by mixing a certain amount of aqueous solution of AgNO₃ (e.g. 0.1mL) or NaBr (e.g. 0.1mL) to a certain amount of AOT/hexane solution (e.g. 8 mL). The resulting mixture was vigorously shaken by a vibrator until a clear solution (w/o microemulsion) was obtained. For the preparation of AgBr, an aliquot of the microemulsion containing AgNO₃ was rapidly mixed with an equal volume of the other microemulsion containing NaBr. From then on, all measurements were done on the microemulsion containing AgBr without further stirring.

Transmittance Measurements

For a relative stable system, the transmittance of the freshly prepared silver bromide microemulsion was measured at

298°K as a function of time at $\lambda=550$ nm with a Perkin-Elmer Spectrophotometer (model 575 UV-VIS). A stopped-flow spectrophotometer (Durrum Rapid Kinetics Systems Series D-100) with a cuvette of 2 cm path length was used for measuring the transmittance of a relatively unstable system. In this case, equal volume (0.2 mL) of the respective microemulsion containing AgNO_3 or NaBr was rapidly mixed (ca. 2 msec) in the cuvette by two drive syringes operated by a pressure actuator. The change in transmittance of the mixed microemulsion was monitored by a digital oscilloscope (Tektronix 468).

Electron Microscopy

The electron micrographs were taken by a JEOL 200CX transmission electron microscope. The samples were prepared by dropping a small amount of AgBr-microemulsion on a film substrate of Formvar (polyvinyl formal). The substrate supported by a copper or nickel grid was precoated with evaporated carbon.

RESULTS

Solubilization of Aqueous NaBr in W/O Microemulsion with Different Alkanes.

The solubilization capacity of the aqueous solution of NaBr or AgNO_3 in the w/o microemulsion was found to be similar to each other. It is expressed in terms of molar ratio of water to surfactant, n_w/n_s . The maximum water solubilization of the microemulsion increased markedly from C_6 to C_8 and then decreased steadily to C_{14} as shown in Fig. 1. The highest maximum-water-solubilization ($n_w/n_s=85.2$) was obtained for the n-octane system. As the concentration of NaBr was increased from 0.1 to 0.6M in the system containing either n-hexane, n-heptane, n-octane or

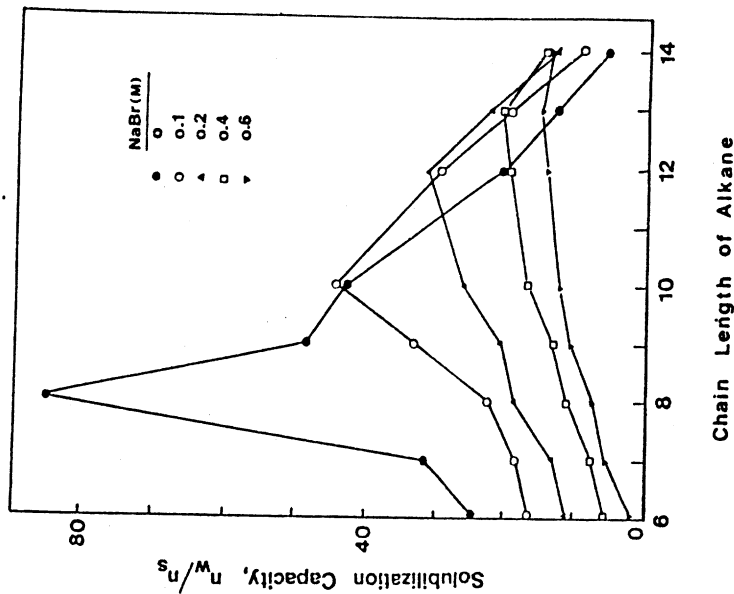


Fig. 1. Effect of chain length of n-alkane on maximum water solubilization capacity of AOT/n-alkane microemulsion. [AOT] in alkane = 0.15M, $T = 298^\circ\text{K}$.

n-nonane, all n_w/n_s decreased substantially. However, it increased first and then decreased in the system containing a higher alkane of either n-decane, n-dodecane, n-tridecane or n-tetradecane. Its maximum solubilization also shifted to a higher NaBr concentration as the chain length of alkane was increased, i.e., n-decane at 0.1M, n-dodecane at 0.15M, n-tridecane at 0.28M and n-tetradecane at 0.5M.

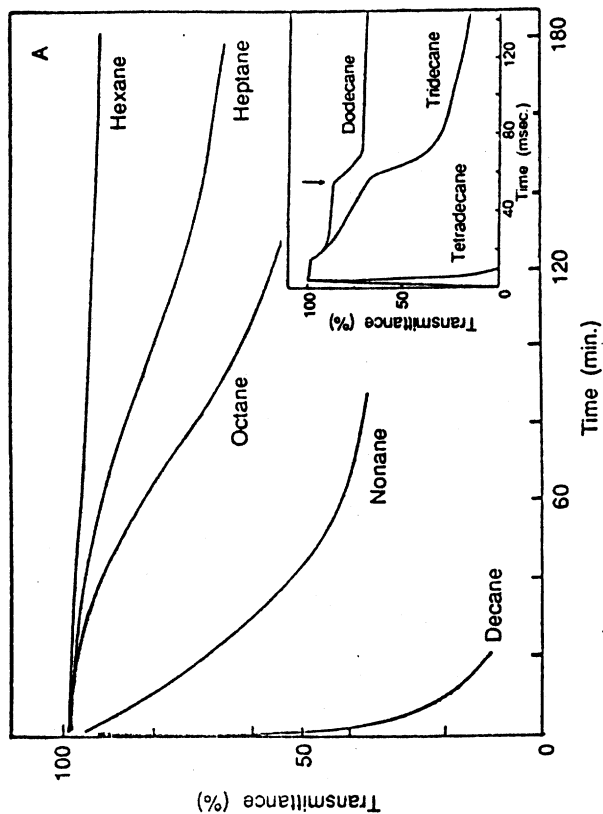


Fig. 2. Effect of chain length of alkane on variation of transmittance of w/o microemulsion as monitored by uv-vis/stopped-flow spectrophotometer at $\lambda=550$ nm, [AOT] in alkane = 0.3M, $n_w/n_s = 14$, $[\text{AgNO}_3] = [\text{NaBr}] = X$. (A) $X=0.1M$, Insert: $X=0.4M$. (B) $X=0.1$ to $0.4M$ /dodecane.

Transmittance Measurement

The effect of chain length of alkane on the transmittance of the silver bromide-microemulsion is shown in Fig 2A. The transmittance would be expected to decrease as the volume of particle increased due to growth or aggregation of AgBr microcrystals. The transmittance decreased faster for the system with an alkane of longer chain length. The dispersion of microcrystals was relatively stable in the system with either

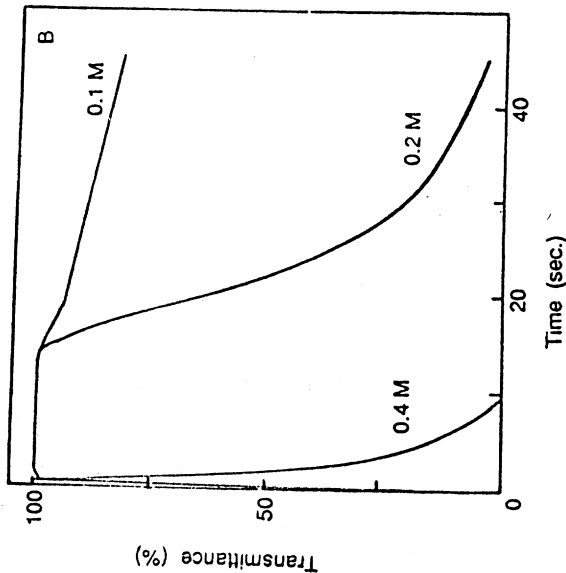


Figure 2 continued

n-hexane, n-heptane or n-octane. As the chain length of alkane was further increased from n-dodecane to n-tetradecane, the system became increasingly unstable that fast variation of the transmittance could only be monitored by a stopped-flow spectrophotometer. The transmittance for the system containing n-dodecane or n-tridecane showed an abrupt reduction at around 60 milliseconds after mixing the AgNO_3 - and NaBr-microemulsions. This indicates the transition between the completion of silver bromide reaction and the prevalence of flocculation (aggregation of microcrystals). Similar transition was also observed in the microemulsion system after mixing AgNO_3 and NaCl^{10} . For the n-tetradecane system, the profound flocculation of AgBr microcrystals was evidenced by a sharp drop in transmittance without passing through the 60 ms transition.

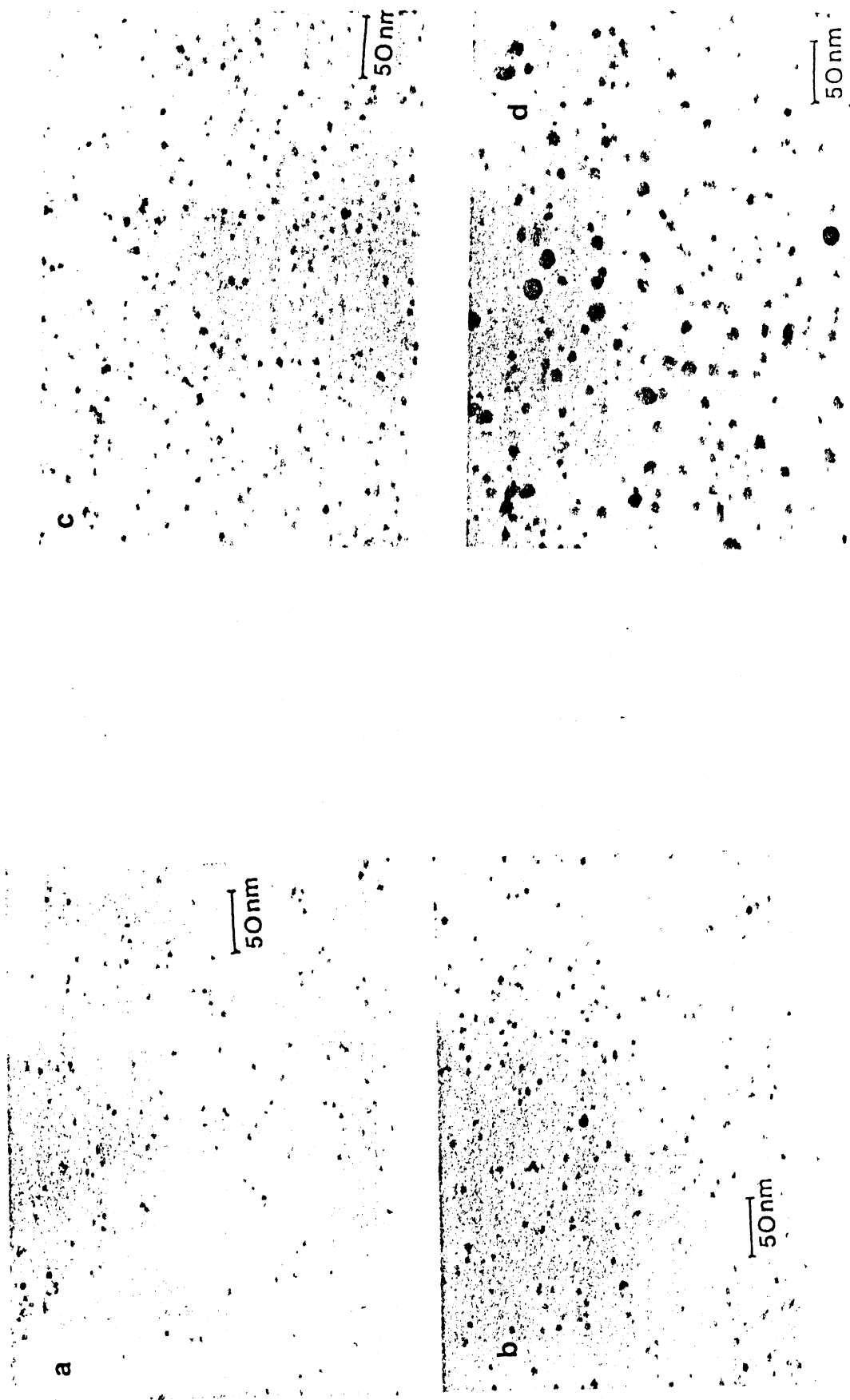


Fig. 3. TEM of AgBr microcrystals in alkane-microemulsion, $n_v/n_s = 4.63$. (a) n-hexane, (b) n-heptane, (c) n-octane, (d) n-hexane and $n_v/n_s = 7.9$.

Figure 3 continued

The concentration effect of AgNO_3 and NaBr on the stability of *n*-dodecane microemulsion is shown in Fig. 2B. When the concentrations of both reactants were increased to 0.4M or even higher, the system became highly unstable resulting in rapid precipitation of AgBr .

Electron Microscopy Study

The effects of alkanes and n_w/n_s on the particle size of AgBr microcrystals were examined with a transmission electron microscope. All the transmission electron micrographs (TEM) were taken after 24 hours of mixing the microemulsions of AgNO_3 and NaBr . Volume fraction (ϕ) was kept at 0.07 and n_w/n_s at 4.63 for most of the cases.

The TEM of Fig. 3 show that the shape of the ultrafine AgBr microcrystals appeared to be nearly spherical. The particle size seemed to increase slightly from the system of *n*-hexane to that of *n*-octane. It was rather uniform (5-7 nm) in the *n*-hexane system. In the heptane and octane systems, they ranged from 5 to 8 nm and 5 to 10 nm respectively. The particle size distribution of AgBr also broadened (5-20 nm) in the hexane-microemulsion system when its n_w/n_s was increased from 4.63 to 7.94.

The hexane microemulsion system at $n_w/n_s=4.63$ was stable up to many weeks. Its stability is very sensitive to the detrimental effect of added electrolyte. Flocculation of AgBr microcrystals can also be induced by adding small amount of ethanol or propanol to the microemulsion system.

DISCUSSION

The Solubilization Behaviour of Aqueous NaBr in The W/O Microemulsions

Water solubilization in a w/o microemulsion depends on the molecular structure of the various components of a microemulsion²⁸.

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It is well known that its maximum solubilization of hydrocarbon and water is obtained with less surfactant when hydrophile-lipophile property of the surfactant system is balanced²⁹⁻³¹. HLB³² also depends strongly on type of surfactant, cosurfactant, oil, electrolyte concentration and temperature.

The solubilization behaviour of aqueous NaBr as shown in Fig. 1 can also be viewed to be limited by the spontaneous curvature of the interface and the attractive interaction among the microemulsion droplets³³⁻³⁸. In turn, they are strongly influenced by the molecular structures of the interfacial layer and the continuous phase^{28,39,40}. At a very low interfacial tension such as in microemulsion, an interface would assume an optimum curvature, $1/R^0$, known as spontaneous curvature³⁹ at an equilibrium condition. For a small volume fraction of water, the droplets of a w/o microemulsion with radii $R < R^0$ are formed. The minimum curvature energy is attained as R reaches R^0 at an optimum water solubilization. When excess water is added to the system, it results in phase separation with the coexistence of microemulsion phase and aqueous phase. For systems where the phase instability is mainly induced by the curvature effect, the radius of spontaneous curvature would decrease as the chain length of alkane is decreased, or the size of the polar head of surfactant is decreased²⁸. Consequently, a lower water solubilization capacity for the system containing shorter alkane is observed.

The solubilization behaviour is also influenced by the attractive interaction among droplets. It has been reported that attraction among the droplets also increases with the increase of the chain length of oil used resulting in the instability of the system⁴¹⁻⁴⁴. Phase separation may arise from strong attractive interdroplet interactions because of the increasing interfacial fluidity. It should be noted that the factors affecting the radius of spontaneous curvature have the opposite effect on the fluidity of interface⁴⁴⁻⁴⁵. Therefore, the maximum water solubilization for a given system is the result of the compromise

between the two opposite effects. This compromising effect is clearly manifested in the microemulsions without NaBr as shown in Fig. 1. With small oil molecule such as n-hexane, the deep penetration of oil into the interface favors the formation of small radius of spontaneous curvature of droplets and results in low water solubilization. This is consistent with the observation that oil-water interfacial tension in brine/ $C_8H_{17}(C_6H_5)_2SO_4Na$ /hydrocarbon system was the lowest for hexane as compared to that of decane and dodecane³¹. The decrease in radius of spontaneous curvature can also be explained as due to the increase of the packing ratio of interface by oil penetration. The packing ratio⁴⁶ is described by v/a_0l_c , where v is the volume of the hydrocarbon chain of the surfactant, a_0 is the optimum cross-sectional area per polar head group of the surfactant and l_c is approximately 80-90% of the fully extended length of the surfactant chain.

The highest solubilization capacity was observed for the system containing n-octane at the compromise of the two opposite effects. As the chain length of alkane was further increased from n-nonane to n-tetradecane, the larger attractive interaction among droplets (high interfacial fluidity) played the decisive role in decreasing the solubilization capacity of water.

Addition of electrolyte to w/o microemulsion decreases the attractive interaction among droplets. This is because the interfacial layer becomes more rigid due to closer packing of polar groups^{41,47}. Consequently, the degree of interpenetration among droplets is reduced during collision. However, the increase of salinity also causes the radius of spontaneous curvature to decrease because of the compression of the electrical double layer and hence exhibiting a smaller area per polar group of surfactant²⁸. The curvature effect thus dominated the system with an alkane of shorter chain length, such as n-hexane, n-heptane, n-octane or n-nonane. Therefore the solubilization capacity decreased as the concentration of NaBr was increased.

But the solubilization behaviour was much different for the system with a higher alkane, such as n-decane, n-dodecane, n-tridecane, or n-tetradecane. It first increased and then decreased with the increase of NaBr concentration. This clearly illustrates the compromise of the two opposite effects under the influence of electrolyte towards different alkanes used in the w/o microemulsion.

Stability of AgBr Microcrystals Formed in The W/O Microemulsions

Very fast reaction between the ionic species of Ag^+ and Br^- in the w/o microemulsion was estimated to complete within 60 milliseconds from the stopped-flow measurements. This short time scale may not be surprising in view of the exchange of the reactants in water pools of a w/o microemulsion requires only less than one microsecond^{22,48,49}. After completion of the reaction, it is envisaged that the growth of AgBr microcrystals took place inside the microemulsion droplets through collision, fusion and split of droplets. This is because the mass of Ag^+ and Br^- in each microemulsion droplet before reaction was calculated to be only 1/300 of the amount required to grow a AgBr particle of 5 nm in diameter.

The hexane-microemulsion system containing AgBr microcrystals remained clear and stable up to several weeks without any precipitation. This was probably due to the rigid interfaces arising from the penetration of short chain hexane and the effect of electrolyte $NaNO_3$. As the ratio of n_w/n_s was increased from 4.63 to 7.94, the particle sizes of AgBr also varied broadly from 5 to 20 nm. The similar trend was also observed from the other microemulsion systems that produced $CaCO_3$ particles^{50,51}. At a higher n_w/n_s , the microemulsion system was less stable and it could be due to the deficiency of surfactant molecules to protect the larger droplets. They might thus undergo slow flocculation resulting larger aggregation of AgBr particles.

When n-hexane in the microemulsion was replaced by n-heptane or n-octane, the AgBr particles became slightly larger ranging from 5-8 nm for the former and 5-10 nm for the latter, and yet they were still stable. This was not the case for systems with a higher alkane ranging from n-dodecane to n-tetradecane. An attractive interaction among the microemulsion droplets might prevail in those systems arising from the interfacial fluidity. The effectiveness of mass exchange of the components in the water pools of a w/o microemulsion is strongly dependent on the fluidity of the interfaces of the microemulsion droplets^{49,52}. A more fluid interface of a w/o microemulsion droplet would increase the frequency of its sticky collision which facilitates the exchange of the contents in a water pool. Hence, flocculation of AgBr microcrystals occurred readily in those microemulsions.

Our results on the stability of the w/o microemulsion containing AgBr microcrystals are consistent with many studies on the dynamics and the inter-droplet interactions of microemulsions^{42,53,54}. This means that the droplet interface becomes more fluid and the inter-droplet interactions more attractive when the chain length of an alkane is increased.

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