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Evolution and Growth of Oil Droplets in Emulsifier-free, Metastable Aqueous Solutions : A Light Scattering and Conductive Probe Study

Keiji KAMOGAWA^{*1,*2}, Toshio SAKAI^{*3}, Nobuyuki MOMOZAWA^{*2,*3},
Masuo SHIMAZAKI^{*3}, Masakazu ENOMURA^{*4},
Hideki SAKAI^{*2,*3}, and Masahiko ABE^{*2,*3}

*1 Ele. & Sec. Ed. Bureau, the Ministry of Education, Sports, Culture and Science
(Kasumigaseki, Chiyoda-ku, Tokyo 100-0013)

*2 Institute of Colloid and Interface Science, Science University of Tokyo
(1-3, Kagurazaka, Shinjuku-ku, Tokyo 162-0825)

*3 Faculty of Science and Technology, Science University of Tokyo
(2641, Yamazaki, Noda-shi, Chiba-ken 278-0022)

*4 M TECHNIQUE Co., Ltd. (3-3-8, Kamihigashi, Hirano-ku, Osaka-shi 547-0002)

Abstract : Metastable oil-in-water dispersed solutions were prepared by sonication or mechanical dispersion in the surfactant-free condition. Size distribution of oil droplets and their growth with time were studied at various oil concentrations, sonication times, and dispersion conditions, with the dynamic light scattering method and a conductive-probe technique. The droplet size distribution was found to be discrete with three classes having peaks around 10^{-1} , 10^{-2} , and 10^{-3} nm. The number fraction moved from the smaller classes to the larger ones during the first 10~50 min, while the size distribution in each class was almost unchanged. The results suggested transient generation of small oil droplets at a microemulsion-emulsion level and their subsequent growth process.

Key words : Oil droplets without surfactant, metastable dispersion systems, discrete growth of particles, dynamic light scattering, coalescence

1 Introduction

Oil and water mix with each other in the presence of surfactant to give a homogeneous dispersion, where droplets of one component involved are dispersed in another. Such dispersions are called emulsions or microemulsions, depending on the droplet size and thermodynamic stability. Emulsions have widely been used in the preparation of foods, cosmetics, etc., and they are recently used as microreactors for the synthesis of fine particles¹⁾, and in controlled polymerization and the recovery of oils and other pollutant materials. Since the positive interfacial energy forces oil droplets to combine with each other toward complete phase separation, surfactants are required in general for stabilization of their interfaces. The surface of these droplets is, however, covered with hydrophilic layers of hydrated parts of surfactant molecules accompanying water molecules into the interior.

If one can prepare small droplets in the form of emulsion or microemulsion in the absence of surfactant, the droplets would have a clear, discontinuous interface as well as a highly hydrophobic interior and show properties different from those of droplets in ordinary microemulsions. From an energetic viewpoint, such surfactant-free droplets should be thermodynamically unstable and can be prepared only transiently in solution, either by nucleation of supersaturated molecules²⁾ or by enforced dispersion of organic liquid in water. Surfac-

Corresponding author : Masahiko ABE

tant-free droplets are thus expected to exist just until they grow into larger visible droplets. In view of their dynamic characters, information on the nature and properties of oil droplets is extremely limited. Therefore, in the present study, evolution and growth of oil-droplets are investigated in the surfactant-free condition.

2 Experimental Section

2.1 Materials

Benzene (Wako), hexane (Hikotaro Shudzui), cyclohexane (Tokyo Kasei), fluorobenzene (Tokyo Kasei) and sodium dodecyl sulfate (SDS, Tokyo Kasei) are of GR-grade and used as received. Distilled and deionized water for injection, according to the Pharmacopoeia of Japan (Ohtsuka Pharmaceutical Co.) was used without further purification. Oils, weighted by volume with a syringe, were mixed with water in a flask and the mixtures were kept standing at 25°C. The mixtures were then sonicated for several min while standing the flask in an ordinary ultrasonic bath (Bransonic 220, 125 W at 40 kHz, Smithkline Company), temperature rise in which was almost negligible in these exposure conditions. Part of the sonicated solution was sampled for subsequent physical measurements.

2.2 Methods

2.2.1 Differential refractivity

Differential refractivity measurements were performed with an RM-102 (Ohtsuka Electronics) under temperature control, using water as reference. Dispersed solution after ultrasonic irradiation was transferred into the refraction cell and left for a few min for stabilization before measurement. Two-phase solution was subjected to 24 hrs stirring before sampling to attain an equilibrium. Density was recorded with a Specific-gravity Meter DA-210 (Kyoto Electronics).

2.2.2 Dynamic light scattering

Ultrasonically dispersed solution was sampled for light scattering measurement after a few min delay. Particle size distribution was recorded with the dynamic light scattering method using a Submicron Analyzer System 4700 (Malvern Instruments Co.), based on digital correlator and equipped with an argon ion laser (Coherent Co. Ltd., at 5 W total power). Correlated data of the scattered light intensity were analyzed to get the diffusion rate and the corresponding hydrodynamic radii of the particles. Since droplet sizes are supposed to have wide and nonsymmetric distribution, a symmetric set of single diffusion functions derived for averaged particles is not appropriate for simulating the correlation function. In the 4700 system, the number density (%) distribution of particle sizes can be determined for polydispersed particles by fitting the observed curves to a set of decay functions. This mode assumes a spherical shape for the particles and their scattering activity related with the diameter. Precision of the number density analysis was checked as follows. Standard spherical latex particle samples have been provided as STADEx from JSR (Japan Synthetic Rubber Co. Ltd.), the available particle sizes of which are, for instance, at 309 ± 3.5 and 3248 ± 161 nm, the values determined by electron microscopy. The intensity mode for narrow-distribution resulted in 342 nm (width~500 nm) and 6332 nm (width~18000 nm), respectively, as an averaged diameters. On the other hand, the number density distributions were found to locate sharply at 330 ± 50 and 3220 ± 400 nm, respectively.

2.2.3 Electric conductivity

2.2.3.1 Batch type

Volumetrically weighted benzene was poured into an aqueous solution of SDS at 1 or 5 mM/L to make the concentration of benzene 40mM/L in the mixture, which was then sonicated for 2 min in a flask. Immediately after sonication, two electrodes (CG-511 B, TOA) were immersed into the mixture for conductivity measurement. Electric conductivity was recorded with a conductivity meter CM-60 S (TOA Electronics Co.) without temperature

compensation.

2.2.3.2 Continuous flow type

The setup is shown in Fig. 1.

Aqueous SDS solution at 5 mM/L concentration was introduced into a flask and then circulated with a pump without operating the homogenizer (CLEARMIX-CLM-0.8 S, M TECHNIQUE Co., Ltd.). The electric resistance of this solution was recorded with flow type electrodes (Horiba, Model 3562/10 D) connected to an LCR meter (ANDO, model AG-4303). Then, a weighted amount of benzene was added to the solution in the flask and the mixture was kept under circulation until the resistance reached at a constant value. After that, the mixture was rigorously homogenized for 2 to 20 min. Electric resistance was recorded during this homogenization and the following periods, and the data were finally converted to the specific conductivity values. Cold water was circulated around the homogenizing vessel, although the temperature of the outlet flow fluctuated around 20~35°C, due to heat evolution during the homogenization. This apparent temperature of the stream was monitored with a 100 ohm platinum resistor linked with four wires to a multimeter (ADVANTEST R 6551), which was located before the flow-type conductivity cell. The specific conductivity $L(t)$ at a given temperature t was converted to the corresponding value L_{REF} at the referring temperature $t_{REF}=25^{\circ}\text{C}$ using the following equation as applied to the CM-60 S,

$$L_{REF}=L(t)/[1+\alpha(t-t_{REF})] \quad (1)$$

The parameter $\alpha=0.02$ was chosen for this equation to fit to the observed values of aqueous SDS solution at other temperatures.

Fig. 1 Setup of the flow-type system for conductivity measurement. A) Flask for sample injection ; B) Magnetic stirrer ; C) Pump; D) Homogenizer ; E) Bubble Trap ; F) Platinum resistance sensor ; G) Flow-type conductivity cell ; H) Quartz thermometer ; I) Resistance detector, J) Shaft ; K) Cooling coil ; L) Pot and M) Cooling water bath.

3 Results and Discussion

The oils used in this study are all partially miscible with water at 25°C. Increasing the concentration beyond saturation caused the solution to become opaque, indicating two phase separation at the equilibrium. Slightly above saturation, the mixture is thought to form a metastable or supersaturated solution. Such metastable solution has recently been studied for an oxygen/water system after fast chemical decomposition reaction²⁾. On the other hand, as observed with the oils used in the present study, surfactant free droplets can also be formed when an oil-in-water mixture is homogenized with a high shear-rate disperser or ultrasonic agitation. In these treatments, the oil molecules are once dispersed into small droplets but they aggregate with each other to grow into larger visible droplets as is well known^{3~5)}.

At the same time, the particle size distribution in emulsions is expected to be dependent on the homogenizing procedure. For example, there might be some difference in size distribution between emulsions prepared with sonication and those prepared with mechanical homogenization³⁾. Hence, size distribution and growth of oil droplets were also compared in this study among the solutions prepared with sonication and a high-shear rate homogenizer.

3.1 Density and Refractivity

Fig. 2 gives the differential refractivity (Δn) and density (ρ) of benzene solutions as a function of oil concentration.

In a stirred solution, each quantity varied smoothly with benzene concentration until it showed a small jump, after which approaching an almost constant value. The discontinuity observed at about 23 mM/L was coincided with the saturating concentration. Slight changes in Δn and ρ continued above this point, suggesting contribution from large droplets suspended in the mixture under stirring. Both solutions gave almost no difference in Δn below the discontinuity point. However, ρ of sonicated solution continued to decrease with benzene concentration even above the saturating point. Since the mixtures became opalescent at 40 mM/

Fig. 2 Optical and volumetric behavior of benzene-in-water dispersed mixtures at 25°C, as a function of benzene concentration at the time of preparation. The mixture was stirred gently (○) or rigorously agitated (●) in a supersonic bath. (a) differential refractive index and (b) density.

L, refractivity measurement was impossible about this concentration. The curvature of ρ was smaller below this concentration for the sonicated solution than for the stirred solution. Both quantities for the sonicated solution approached the zero intercept as those for the stirred solution. This means that sonication did not affect the bulk water properties but the vicinity of benzene molecules. In a mixed solution, the density ρ can be related to the partial molar volumes of the components as follows.

$$V = M_{av}/\rho = V_{BZ}X_{BZ} + V_W X_W = (V_{BZ} - V_W)X_{BZ} + V_W \quad (2a)$$

$$M_{av} = M_{BZ}X_{BZ} + M_W X_W \quad (2b)$$

where V , M_{av} and ρ are the volume, averaged molecular weight and density of the mixture, respectively. V_{BZ} , M_{BZ} , and X_{BZ} are the partial molar volume, molecular weight and molar fraction of benzene in the mixture, respectively. Similarly, those labeled with W indicate the corresponding quantities of water. When oils are only weakly miscible with water like benzene, $X_{BZ} \approx m_{BZ}M_W/1000$ (m_{BZ} : the molar weight concentration) stands and eq. 2 c is obtained.

$$V = (V_{BZ} - V_W)m_{BZ}M_W/1000 + V_W \quad (2c)$$

The fluctuating point at about 23 mM/L corresponds to $X_{BZ} 4.1 \times 10^{-4}$. We applied these equations to V of stirred and sonicated solutions obtained from the density data in Fig. 2. The volume gave to the sonicated solution $V_{BZ} = 79$ cc/mol, which is smaller than 89.4 cc/mol of pure benzene. In the stirred solution, a slightly smaller value of 76~78 cc/mol was obtained. These smaller values suggest that benzene molecules are surrounded by the neighboring molecules more closely than in pure liquid.

3.2 Droplet size distribution

Fig. 3 shows typical profiles of the droplet growth in several oil-in-water dispersed solutions after sonication.

In benzene solution at 30 mM/L, small droplets first appeared at around 30~100 nm were classified as of the fine class. About 20 min after sonication, the fine class droplets were replaced by larger droplets around 200~1000 nm, which were classified as of the middle class. The larger droplets were finally replaced by visible droplets around 3000~4000 nm diameter in ~30 min. Fluorobenzene-in-water mixture also gave fine and middle class droplets around 20~100 nm and 100~1000 nm, respectively, just after sonication. Although their population lasted longer (~50 min) than those in the other three solutions, these droplets were finally replaced by visible class droplets at around 3000 nm.

On the contrary, n-hexane solution at 4 mM/L concentration first gave in most cases a wide distribution around 200~1000 nm containing droplets classified as middle class ones. Fine class droplets was only able to be observed occasionally at 40~100 nm. The total fractions fluctuated between the fine and middle classes during ~20 min, but all droplets finally transferred to visible class droplets at around 3000 nm. For cyclohexane-in-water mixture at 3 mM/L concentration, the initial population was found only in the middle class around 100~1000 nm for ~10 min. The total population then transferred to that of visible class around 3000~5000 nm.

In these observations, the three classes of droplets were characteristically identified for the oils except cyclohexane as the fine class (10^1 nm), middle class (10^2 nm) and visible class (10^3 nm). All of the three classes would be found for benzene-in-water mixture. Irregularity of class fractions was noticeable for fluorobenzene. This irregularity can be attributed to limited numbers of smaller class droplets as follows. The lower solubility of the oil in water, compared to those in surfactant-rich solutions at concentrations such as at 100 mM/L, significantly reduces the number density of oil droplets in the observing space and time window of light scattering. It would result in an enhanced fluctuation of the number density, to an extent that fine class droplets are transiently observed even after the appearance of middle class droplets. This interpretation is partly supported by the regular droplet size order found

Fig. 3 Oil droplet size distribution for oil-in-water dispersed solutions slightly above the saturation at 25°C at various elapsed times after 2 min sonication. The size distribution curves were expressed in number (%) density on semilogarithmic scale of diameter. (a) benzene 30 mM/L, (b) fluorobenzene 17 mM/L, (c) n-hexane 4 mM/L and (d) cyclohexane 3 mM/L.

for benzene, which has a larger solubility than fluorobenzene. It should also be noticed that the principal distribution appeared at different sizes for different kinds of oils. This supports the physical existence of such fine and middle class droplets.

Fig. 4 shows the droplet growth in benzene-water mixture at 40 mM/L oil after sonication in the same condition as that for the 30 mM/L oil mixture shown in **Fig. 3**.

At this concentration, middle class droplets were first observed only weakly and visible class droplets dominated the entire population around 3000~5000 nm through the time course. Absence of fine and middle class droplets may suggest insufficient dispersion of the oil. Actually, visible droplets showed a peak in the number density at 3000 nm, as in the case of 30 mM/L oil mixture. **Fig. 5** shows the droplet growth in benzene-in-water mixture at 40 mM/L oil after prolonged sonication.

Clearly, only fine class droplets were found in every profile, exhibiting fractions of 30~100 nm diameters. The population of these fine droplets was so stable as to last for 20 min. This indicates that the oil can be dispersed transiently in water without surfactant, if sonication is performed for an appropriate time at a given oil concentration. Even with prolonged exposure of 40 mM/L oil solution to sonication in **Fig. 5**, the size distribution in the fine class was almost invariant with time and similar to that of 30 mM/L oil solution in **Fig. 3**. This stability is thus indicative of the real existence of fine droplets.

Size distribution is also plotted in **Fig. 6** for the mechanically dispersed solutions.

Fig. 4 Concentration dependence of droplet size distribution for benzene-in-water dispersed solutions at 25°C at various elapsed times after 2 min sonication. (a) benzene at 30 mM/L from Fig. 3, (b) benzene at 40 mM/L.

While population appeared around 100 nm first, discrete populations were again observed at about 30, about 300 and about 3000 nm at later times for 30 mM/L benzene solutions. Drift of the peaks was almost negligible in each population. Irregularity in the appearance may be noticed for the whole fraction of fine and middle class droplets. Additionally, even at 40 mM/L oil concentration, about 30 and about 300 nm populations was able to be distinguishable for 15 min. Formation of the fine droplets was only slightly incomplete, as compared with the case of prolonged sonication. Therefore, the discrete distribution was also common in this kind of dispersion preparation.

The above results were almost the same for the two mixing procedures. If the preparation conditions serve as an unstable droplet formation without any favorable size, the peak position in size distribution would shift continuously to the larger size side with standing time. This did not happen, suggesting the metastable nature of oil droplets. Furthermore, if there is a natural tendency for the droplets to attain particular diameters, a certain correspondence may be found between surfactant-free and surfactant-assisted emulsions and microemulsions. Benzene droplets of fine class size were found at 30~100 nm. This is comparable with 100~250 nm diameter of a toluene emulsion supported by SDS-hexadecane in water, prepared with a sonifier and measured with the capillary hydrodynamic fractionation

Fig. 5 Droplet size distribution after 2 min- and 8 min sonication for 40 mM/L-benzene solution at 25°C. (a) 2 min exposure time from Fig. 3 and (b) 8 min exposure time.

(CHDF) method⁶). In such a way, stable submicron-micron sized emulsions have been prepared^{7),8)}. Although this similarity in size between these emulsion droplets and the fine and middle class of oil droplets may be eventual, it seems to suggest that the size of stable surfactant-supported emulsions are correlated with the stability of transient oil droplets.

In addition to the discrete profiles, the peak position was almost invariant in each class of population. The about 30 nm peak for benzene droplets seems to remain at its original position while the peak height decreases, as does the about 300 nm peak. When the number density monotonously decreased in one class, that in the next larger class increased. For example, the small class of benzene droplets having a tail over 100 nm seems to approach the second class starting at about 200 nm. These monotonous decreases may indicate a fractal nature of particle aggregation^{9),10)}, in which larger aggregates are smaller in the number density. This suggests a growth mechanism that smaller droplets aggregate until a certain critical size is attained, at which the aggregate is instantaneously fused into a larger droplet, as depicted in Fig. 7.

Similar aggregates can be found at micrometer-order with hexadecane emulsion droplets, prepared in the gentle conditions with the aid of 50 mM/L cesium dodecylsulfate⁸⁾. The surface structure of aggregated droplets may probably be responsible for such critical nature of droplet fusion. This fusion model is different partly from the simple Ostwald ripening and continuous fractal aggregation. In the Ostwald scheme, droplets grow uniformly through

Fig. 6 Comparison of droplet size distribution between 30 mM benzene-in-water dispersed solution prepared by sonication and that prepared by high speed homogenization at 25°C. (a) sonication from Fig. 3 and (b) homogenization.

the adsorption of single molecules coming from smaller droplets^{7),11)}. The Ostwald ripening is referred to as one of possible mechanisms for the droplet growth of water-soluble oils such as toluene in water¹¹⁾. Hence, the mechanism would be more expectable for benzene. The scheme is distinguished by a drift of the peak size in one class but this was not the case. It may be partly operative for droplet growth within one class. This is because fractal aggregation prepares much closer approach of droplets with each other. Diffusion of oil molecules through the interface would be fast inside the aggregating region, accelerated by the short distance between the adjacent droplets. The mechanism seems to be also operative within a droplet aggregate. In the fractal scheme, aggregates also grow gradually via coalescence, decreasing their population as observed in each droplet class. Therefore, a drift of the peak is again expected.

Furthermore, shrinkage of visible class droplets to about 3000 nm size is another characteristic finding. Of course, the limit of resolution must be taken into consideration in the semilogarithmic analysis of the correlated data from dynamic light scattering measurements. Because the time window is finite in length, slowly diffusing particles will be cut off

Fig. 7 Proposed model for discrete size distribution and growth of oil droplets. Small class droplet (A) is generated first on dispersion. Droplets of this class associate until a certain critical aggregate (B) is formed, which fuses to a middle class droplet (C). Droplets of this class aggregate again (D) and then fuse to form a visible class droplet (E) and so on. Since each of the fundamental droplets (A, C, E) can often be detected accordingly to their number density, the size distribution becomes discrete.

in the analysis. Although the apparent tendency is in contrast to that in two phase separation, such decrease in population width can be noticed for a toluene emulsion assisted by SDS-n-hexa-decane⁶⁾. Therefore, visible oil droplets are expected to have some favorite sizes at this stage.

3.3 Specific conductivity

Ionic surfactants are expected to serve as an indicator of microscopic surface area of hydrophobic particles as shown in **Fig. 8**.

When oil droplets are small enough to give a large surface area, dodecylsulfate anions will adsorb on the area quite sparsely. This leads to low ionic repulsion between the anions and their weak association with Na^+ ion. With growth of the droplets, the surface area becomes smaller, and hence, anion adsorption should be denser, accompanying recombination of Na^+ to reduce the electrostatic repulsion between the anions. These processes can be detected with conductivity measurement depending mostly on Na^+ 's mobility. Therefore, SDS is thought to act as a conductive probe.

Fig. 9 shows the conductivity of sonicated benzene solution, to which SDS molecules were added as the conductive probe.

At both 5.0 and 1.0 mM/L SDS concentrations, the specific conductivity was initially higher than oil-free SDS solutions and then decreased with time. It became lower than that of

Fig. 8 Proposed model for the behavior of conductive probe. After dispersion of oil in water, anionic surfactant will sparsely adsorb on small class droplets (A), leaving the counter ion in the bulk phase. This will raise the conductivity due to the mobile Na^+ ion. With droplet growth to the middle-(B) and the visible class (C) ones, the density of adsorbed surfactant molecules on the droplet surface increases, leading to recombination of the counter ions to the surfactant molecules. This will result in a decrease in the conductivity from the initial level.

Fig. 9 Temporal behavior of the specific conductivity of SDS-added 40 mM/L benzene-in-water dispersed solution. Broken line indicates the conductivity level of oil-free SDS solution. Measurement was done using an immersed type cell. (a) 1 mM/L SDS concentration and (b) 5 mM/L SDS concentration.

SDS solution in 5~10 min. The initial high conductivity may be due to the sonication effect on the water structures which decrease the mobility of hydrophobic dodecylsulfate ions, or the dissociation effect on Na^+ from dodecylsulfate ions deposited on the nanometer-sized oil droplets. The latter scheme is already proposed as mentioned above. The low conductivity around ~15 min seems to indicate formation of larger droplets, because SDS acts as the emulsifier as well as the conductive probe. Coarsely emulsified droplets are understood as being highly unstable, for the SDS concentrations used are not high enough to prepare a large number of small emulsified droplets. The initial conductivity decrease with time is comparable with that for the earlier droplet evolution in Fig. 9, and hence, the decrease may be attributed to the ionic recombination of Na^+ with dodecylsulfate ions adsorbed on the growing oil droplets, which are possibly of the fine or middle classes. Conductivity change was also recorded with the flow cell system combined with the homogenizer (Fig. 10).

While the conductivity decreased as in the batch type measurements, transient temperature rise was more furious. Therefore, further test is undergoing for the flow-type system.

4 Conclusion

In conclusion, metastable oil droplets were observed in the nanometer-submicron range

Fig. 10 Time course of the specific conductivity of 40 mM/L benzene-in-water mixture during and after high-speed stirring dispersion. Sample was subjected to dispersion at 1.73×10^4 rpm for 20 min. Horizontal broken lines "SDS" and "Start" indicate the conductivity level of oil-free, aqueous 5 mM SDS solution and that of the same solution after gentle mixing with benzene prior to 20 min-dispersion, respectively.

when the oils were dispersed in water in the surfactant-free condition with either sonication or a high-shear rate homogenization. Their size distribution was found to be discrete over the three classes of diameters. This discrete nature seems to be characteristic of surfactant-free droplets and indicative of their evolution/growth process. Although the droplet sizes obtained from dynamic light scattering data need to be checked further, we feel that the droplets really exist in the nanometer-submicron range. The physical and interfacial properties of the oil-in-water dispersed solutions are now under investigation together with further checking of the droplet sizes.

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References

- 1) M.-P. Pileni, *Adv. Colloid Interface Sci.* **46**, 139 (1993).
- 2) P.G. Bowers, C. Hofstetter, C.R. Letter and R.T. Toomey, *J. Phys. Chem.* **99**, 9632 (1995).
- 3) K. Everth and J. Merry, *Int. J. Pharm.* **14**, 349 (1983).
- 4) K. Schaschek, J. Popp and W. Kiefer, *J. Raman Spectrosc.* **24**, 69 (1993).
- 5) K. Nakatani, T. Uchida, H. Misawa, N. Kitamura and H. Masuhara, *J. Phys. Chem.* **97**, 5197 (1993).
- 6) C.M. Miller, J. Venkatesan, C.A. Silbe, E.D. Sudol and M.S. El-Aasser, *J. Colloid Interface Sci.*, **162**, 11 (1994).
- 7) D.J. McClements and S.R. Dungan, *Colloids and Surface*, **104**, 127 (1995).
- 8) S.G. Oh and D.O. Shar, *J. Phys. Chem.* **97**, 284 (1993).
- 9) T.P.M. Beelen, W.H. Dokter, H.F. Van Garderen and R.A. Van Santen, *Adv. Colloid Interface Sci.*, **50**, 23 (1994).
- 10) A. Erzan and N. Gungor, *J. Colloid. Interface Sci.* **176**, 301 (1995).
- 11) P. Taylor, *Colloids and Surface*, **99**, 175 (1995).

[報文] 水溶液中における準安定な油微粒子の生成と成長 —光散乱法, 伝導度プローブ法による検討—

加茂川恵司^{*1,*2}・酒井 俊郎^{*3}・桃澤 信幸^{*2,*3}・島崎 益男^{*3}

榎村 眞一^{*4}・酒井 秀樹^{*2,*3}・阿部 正彦^{*2,*3}

*1 文部省初等中等教育局 (〒100-0013 東京都千代田区霞ヶ関)

*2 東京理科大学界面科学研究所 (〒162-0825 東京都新宿区神楽坂 1-3)

*3 東京理科大学理工学部 (〒278-0022 千葉県野田市山崎 2641)

*4 エム・テック株式会社 (〒547-0002 大阪市平野区加美東 3-3-8)

ベンゼンなどの油性物質を水中に滴下して超音波または機械的分散処理を行うことにより, 界面活性剤を含まない準安定油滴分散溶液を調製した。種々の油滴濃度, 超音波照射時間, 分散方法で調製した油滴の大きさの経時変化を, 動的散乱および伝導度測定により調べた。その結果, 油滴のサイズは 10^{-1} , 10^{-2} , 10^{-3} nm オーダーにそれぞれピークを有する 3 つの離散的な分布を与えることがわかった。油滴サイズの分布の中心は処理後 10~50 分の間に増大したが, 3 個のピークを与える粒子径の値は変化しなかった。これらの結果から, 界面活性剤を含まない系においても, マイクロエマルジョン-エマルジョンサイズの微小な油滴が過渡的に調製できることが示唆された。

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[報文] 3-[(8 Z, 11 E, 13 Z)-8, 11, 13-pentadecatrienyl] catechol の合成および *Rhus vernicifera* 漆樹液中のトリエンウルシオール成分の分析

新村 典康・神谷 幸男・佐藤 崇弘・片野 一郎・宮腰 哲雄

明治大学理工学部工業化学科 (〒214-8571 川崎市多摩区東三田 1-1-1)

ウルシオールの主成分である 3-[(8 Z, 11 E, 13 Z)-8, 11, 13-pentadecatrienyl] catechol の合成について検討した。(3 E, 5 Z)-3, 5-heptadienyl-triphenylphosphonium iodide から得られた ylide と 3-(8-oxo-1-octyl) catechol diacetate との Wittig 反応および, カテコール水酸基の段階的な保護, 脱保護により目的化合物を高収率で合成することができた。更に, 合成トリエンウルシオールを標品として, 産地や収穫時期の異なる漆樹液中のトリエンウルシオール成分の定量分析を行った。塗料としての品質が高い漆樹液には多量のトリエンウルシオールが含まれている。従って, トリエンウルシオール成分の定量分析は, 漆樹液を評価する良い手法である。本研究によって, トリエンウルシオール成分の含有量は産地や収穫時期によって異なることが判明した。

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