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Non-Newtonian Flow of Water-in-Oil Emulsions[*1]

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In order to obtain information on the dispersion state of W/O type emulsions, the steady-flow viscosity in a wide shear range has been studied using a capillary type viscometer. Emulsions prepared by using Arlacel 83 or Arlacel 60, are classified according to the kind of hydrocarbon used as the suspending fluid, *i.e.*, benzene, cyclohexane, liquid paraffin, isopropyl myristate, and squalane systems, respectively. Although all systems show the so-called shear thinning flow, shear dependence of the viscosity is not only influenced by the disperse phase concentration and emulsifier concentration, but is also much effected by the kind of suspending fluid. Such non-Newtonian behavior is observed markedly in benzene systems. It may thus be assumed that the water droplets in benzene have a tendency to form a large aggregate not easily redispersed under shear. The formation of aggregate may be facilitated by the disturbance of the orientation of the adsorbed emulsifier molecules at the interface due to the mutual interaction between the π-electron in benzene molecule and the emulsifier molecule.

The study of rheological properties of W/O type emulsion is of utmost importance for the quality control in the fields of pharmaceutics, foods and cosmetics. However, only few reports have been presented on this subject, compared with those on O/W type.

According to Albers *et al.*[1–3] water-in-benzene emulsions, in which energy barriers between the water droplets can be calculated theoretically, are not stable against aggregation by an adsorbed layer of emulsifier and show non-Newtonian flow.

Furthermore, the relative viscosity of W/O type emulsion is found to be influenced by the species of suspending fluids, although the result was obtained by the so-called one-point method under steady shearing stress.[4] Thixotropy in the W/O type emulsion reported by Vól'fenzon[5] could not be accepted as a general phenomenon, because the sample used was a mixture of seed oil, bees wax, spermaceti and lanolin as the oil phase.

In order to observe the relationship between the rheological properties of W/O type emulsions and their components, the authors tried adjusting the W/O emulsion of different components by making various combinations of emulsifiers and oil components. The emulsions which were relatively stable were chosen to observe how their viscosity changes with the rate of shear, and how the dispersion state changes with oil composition.

Experimental

Sample. Table 1 shows emulsifiers and suspending fluids of emulsions used. In order to prevent the so-called creaming of the emulsion due to density difference between the disperse phase and continuous phase, the density of the oil phase was adjusted to that of water by addition of carbon tetrachloride. No emulsifier listed in the table, however, produced a well stabilized emulsion which has higher alcohol or cast or oil as its suspending fluid. Likewise emulsions prepared with other oil components in which emulsifiers other than sorbitan fatty acid ester were used, could not be used as a sample for viscosity measurement, because of excessive rate of coalescence of suspending droplets. Thus systems of hydrocarbon as their suspending fluid and sorbitan fatty acid ester as their emulsifier were employed for the viscosity measurements. Details of the preparation of the sample are as follows. A given quantity of oil containing the emulsifier was mixed with the specified amount of water (from 0.1 to 0.6 in its volume fraction) and then stirred at a rotational speed of 9000 rpm for 5 min by an homogenizer (manufactured by Tokushu Kika Kogyo).

Droplet size and size distribution of the system were

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1) W. Albers and J. Th. G. Overbeek, *J. Colloid Sci.*, **14**, 501 (1959).

2) W. Albers and Th. G. Overbeek, *ibid.*, **14**, 510 (1959).

3) W. Albers and J. Th. G. Overbeek, *ibid.*, **15**, 489 (1960).

4) S. Matsumoto, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect).*, **86**, 324 (1965).

5) I. I. Vól'fenzon, *Kolloid Zhur.*, **27**, 8 (1965).

TABLE 1. EMULSIFIERS AND SUSPENDING FLUIDS OF EMULSION USED FOR THEIR PREPARATION

Emulsifier	
Sorbitan monostearate (Arlacel 60)*	
Sorbitan sesquioleate (Arlacel 83)*	
Glyceryl monostearate (Atmul 84)*	
Polyoxyethylene (5.5 mol) cetyl ether (Nikkol BC 5.5)**	
Polyoxyethylene (2 mol) monostearate (Nikkol MYS 2)**	
Polyoxyethylene (2 mol) monooleate (Nikkol MYO 2)**	
Trioleyl phosphate (Hostaphate KO 300)***	
Cu-laurate	
Mg-laurate	
Suspending fluid	
Cyclohexane	Castol oil
Benzene	Hexadecanol (Branched chain C_{16} fatty alcohol)
Liquid paraffin	
Squalan	Cyclohexanol
Isopropyl myristate	1-Octanol

* Kao-Atlas Co., Ltd., Japan.
** Nikko Chemicals Co., Ltd., Japan.
*** Hoechst AG., Germany.

obtained by means of microscopy.

Viscosity Measurement. Capillary viscometer of Maron-Belner type[6] was used for all viscosity measurements. By this viscometer the viscosity of a fluid in the range from a relatively high shear stress to a low stress can be obtained continuously by a single measurement. The principle and procedure of the measurement and the dimensions of the viscometer are given in a report[7] on polyvinylpyrrolidone solution.

All measurements were made at 32°C ± 0.01°C in a constant temperature bath.

The relative viscosity (η_{rel}) was calculated as the ratio between the viscosities of emulsion and suspending fluid (containing no emulsifier).

Results and Discussion

The relative viscosity of both cyclohexane and benzene systems stabilized by Arlacel 60 and Arlacel 83 is shown in Figs. 1 and 2. Non-Newtonian flow of each sample is observed throughout the range measured. It can be mentioned from the results that the dependence of viscosity on the rate of shear of the samples is noticeable in the benzene system. It is also noted that the dispersed droplets in the system form large aggregates in the low rate of shear. This fact may be responsible for the generation of a viscosity curve as represented diagramatically in broken line due to a heterogeneity of the disperse phase concentration in the capillary of viscometer. Such a tendency appears markedly in the system using Arlacel 60 as its emulsifier, where the value of maximum shear stress at which dispersed droplets form large aggregates, not entering in the capillary tube, *i.e.*, yield value, increases with increasing diperse phase concentration as indicated in Table 2.

In the emulsion using hydrocarbon other than benzene, as the suspending fluid, no large aggregates of droplets were observed, although aggregates consisting of a small amount of dispersed droplets can be detected by means of microscopy. Dependence of viscosity of the system on the rate of shear is similar to that of the cyclohexane system shown in Figs. 1 and 2. From this it may be sug-

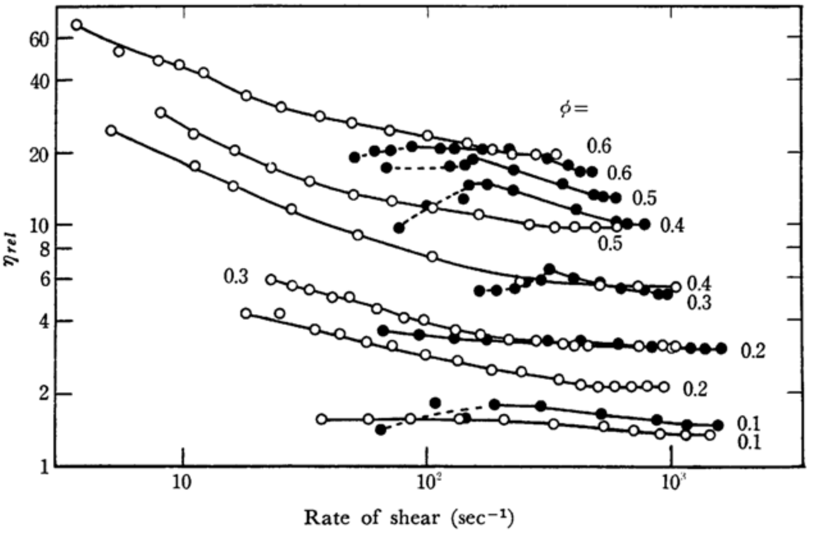

Fig. 1. Plots of relative viscosity *vs.* rate of shear for water in cyclohexane (+CCl_4) and water in benzene (+CCl_4) emulsions (ϕ=0.1—0.6) stabilized by 20 mM Arlacel 60 at 32.0°C.
○, Cyclohexane ●, Benzene

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[6] S. H. Maron and R. J. Belner, *J. Appl. Phys.*, **26**, 1457 (1955).

[7] T. Mineshita, T. Watanabe and S. Ono, This Bulletin, **40**, 2217 (1967).

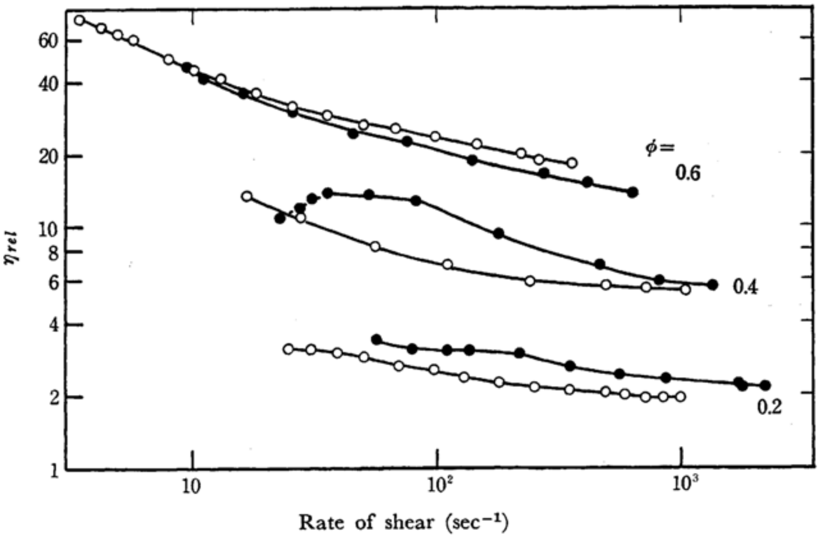

Fig. 2. Plots of relative viscosity *vs.* rate of shear for water-in-cyclohexane (+CCl_4) and water-in-benzene (+CCl_4) emulsions ($\phi=0.1-0.6$) stabilized by 20 mM Arlacel 83 at 32.0°C.
○, Cyclohexane ●, Benzene

TABLE 2. CONCENTRATION DEPENDENCE OF YIELD VALUE OF BENZENE-IN-WATER EMULSION STABILIZED BY 20 mM ARLACEL 60

Disperse phase concentration (ϕ)	0.1	0.2	0.3	0.4	0.5	0.6
Shear stress (dyne/cm^2)	1.08	1.43	12.3	15.2	17.2	20.4

gested that the non-Newtonian flow shown by these W/O type emulsions is due to the variation in the number of droplets forming the aggregates of respective flow units with the rate of shear.

At a fixed disperse phase concentration, the values of relative viscosity of various samples are different as shown in Fig. 3.

The relationships between the relative viscosity and the rate of shear at different concentrations of the emulsifier, at a constant disperse phase concentration, are shown in Figs. 4 and 5 for the cyclohexane and benzene systems, respectively. In both cases, emulsifier concentration has no effect upon the dependence of relative viscosity on the rate of shear, although the value of relative viscosity in a whole range of rate of shear increases with increasing emulsifier concentration. This increase may be due to the increase of viscosity in the suspend-

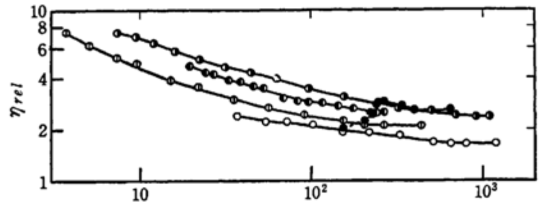

Fig. 3. Plots of relative viscosity *vs.* rate of shear for water-in-oil emulsions ($\phi=0.15$) of various suspending fluid stabilized by 27 mM Arlacel 60 at 32.0°C.

◓ Isopropylmyristate system
◑ Liquid paraffin system
○ Squalan system
◐ Benzene system
● Cyclohexane system

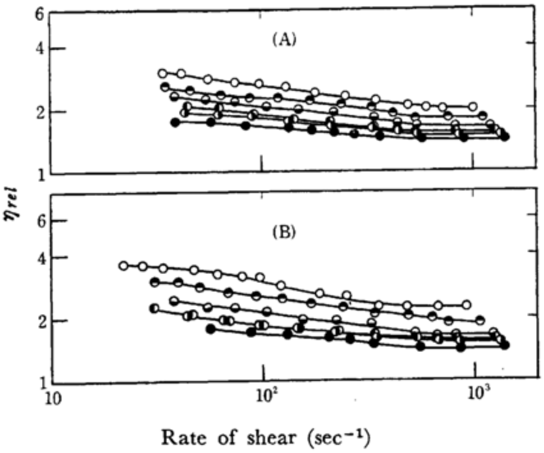

Fig. 4. Plots of relative viscosity *vs.* rate of shear for water-in-cyclohexane (+CCl_4) emulsions ($\phi=0.15$) stabilized by Arlacel 60 and Arlacel 83 respectively at 32.0°C.
(A) Arlacel 60 concentration are ●, 3mM; ◑, 8 mM; ◐, 14 mM; ◒, 27 mM; ◓, 55 mM; ○, 82 mM.
(B) Arlacel 83 concentration are ●, 2 mM; ◑, 6 mM; ◐, 10 mM; ◒, 21 mM; ◓, 42 mM; ○, 63 mM.

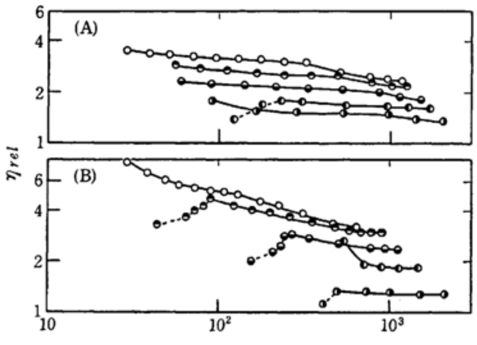

Fig. 5. Plots of relative viscosity *vs.* rate of shear for water-in-benzene (+CCl_4) emulsions (ϕ= 0.15) stabilized by Arlacel 60 and Arlacel 83 respectively at 32.0°C.
(A) Arlacel 60 concentration are ◑, 8 mM; ◐, 14 mM; ◒, 27 mM; ◓, 55 mM; ○, 82 mM.
(B) Arlacel 83 concentration are ◑, 6 mM; ◐, 10 mM; ◒, 21 mM; ◓, 42 mM; ○, 63 mM.

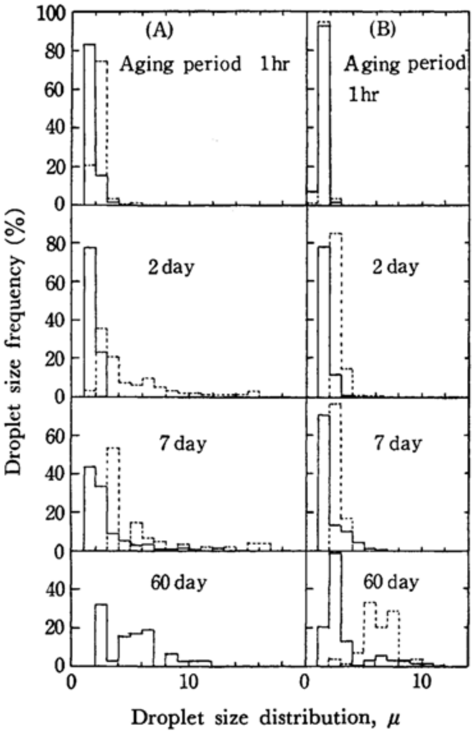

Fig. 6. Changes of droplet size distribution on aging. In the case of W/O emulsions (ϕ=0.15) stabilized by Arlacel 83.
—— Cyclohexane system
---- Benzene system
Emulsifier concentration: (A) 6 mM; (B) 21 mM

ing fluid. In the case of the benzene system stabilized by Arlacel 60, the yield value tends to become smaller with increasing emulsifier concentration as shown in Table 3. This may be brought about by the increase in the amount of the adsorbed emulsifier on the surface of the dispersed droplets with the increase of the amount of the emulsifier used. In the benzene system stabilized by Arlacel 83, the tendency to form large aggregate of droplets seems to be smaller compared with that in the system using Arlacel 60 as an emulsifier. The surface of water droplets of emulsion stabilized by Arlacel 83, containing sesquioleate chains per sorbitan molecule, is more densely covered with oleophilic chains than in the case of emulsion stabilized by Arlacel 60 containing one stearic chain per sorbitan molecule. Thus, the size of aggregate of the former emulsion could be smaller than in the case of the latter emulsion owing to the steric effect of the oleophilic group.

All viscosity measurements were made with two-day old samples. Further aging tests of sample revealed no effect upon the dependence of viscosity on the rate of shear, although a slight decrease in viscosity by aging was noted in all samples. This tendency seems more noticeable in the benzene system. This may be caused by the change in the droplet size distribution resulting from the coalescence of dispersed droplets. Microscopic examination of the size distribution of the dispersed droplets reveals the transition from mono disperse to poly disperse immediately after preparation (refer to Fig. 6 for sample with Arlacel 83 as emulsifier and Fig. 7 for sample with Arlacel 60 as emulsifier). Such transition is slightly faster in the case of the benzene system. Therefore, as a result of coalescence of the droplets, the number of droplets in an aggregate changes with time. Since any change in the dependence of the viscosity on the rate of shear could not be observed, the decrease in viscosity by aging would be brought about by the broadening of the droplet size distribution.

TABLE 3. DEPENDENCE ON THE EMULSIFIER CONCENTRATION OF YIELD VALUE OF BENZENE-IN-WATER EMULSION (ϕ=0.15) STABILIZED BY ARLACEL 60

Arlacel 60 concentration (mM)	8	14	27	55	82
Shear stress (dyne/cm^2)	5.82	8.52	4.69	2.53	1.31

Thus, it can be said that the benzene system shows an extraordinary characteristic in contrast to all other samples studied.

It is known that aromatic hydrocarbon indicates various affinity or peculiar solvating effects irrespective of its nonpolar character. It has been found in recent years that such an effect is due to π-electron possessed by the aromatic hydrocarbon reacting as proton acceptor of hydrogen bond, similar to lone electron-pair possessed by oxygen atom. Previously one of us (S.M.) proved that, in the case of O/W type emulsion, the dispersion state of aromatic hydrocarbon as the oil com-

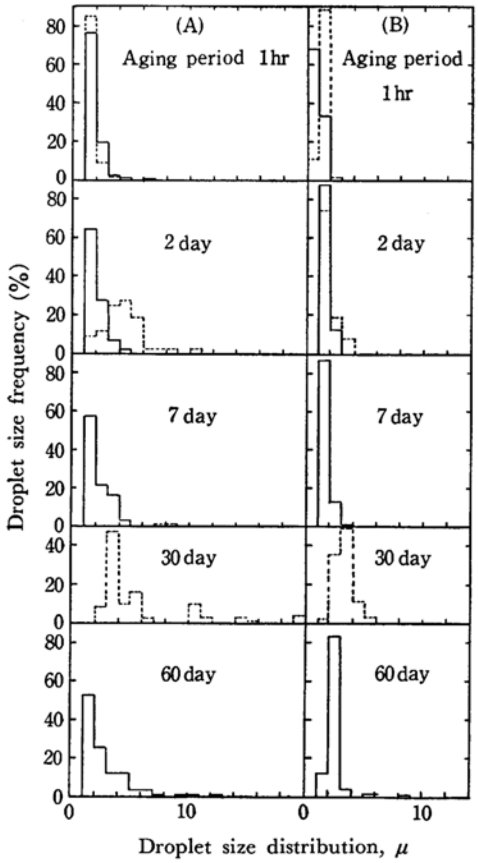

Fig. 7. Changes of droplet size distribution on aging. In the case of W/O emulsions ($\phi=0.15$) stabilized by Arlacel 60.
—— Cyclohexane system
---- Benzene system
Emulsifier concentration: (A) 8 mM; (B) 27 mM

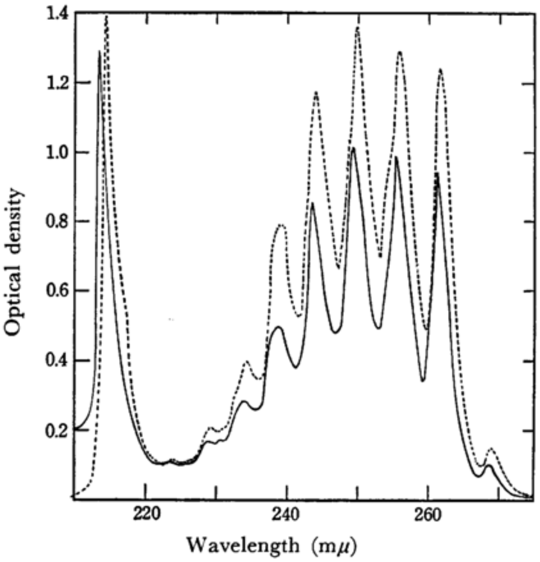

Fig. 8. UV absorption spectrum.
---- Cyclohexane : Benzene (=1000 : 1)
—— 0.5 mM Arlacel 60 in cyclohexane : Benzene (=1000 : 1)

ponent can be distinguished from that of other nonpolar oil components.[8] Although the results were obtained with O/W type emulsions, we can assume that the results thus obtained could be also applicable to W/O type emulsions. UV absorption spectrum of benzene shifts towards shorter wavelength by the addition of Arlacel 60 or Arlacel 83, as shown in Fig. 8. This fact suggests that there is an interaction between the hydrophilic group of the emulsifier molecules adsorbed on the surface of dispersed droplets and the π-electrons of benzene. It is probable that the orientation of emulsifier on the surface of the droplet is disturbed and the resistance to the occurence of aggregation or coalescence of the droplets in the emulsion is reduced. Thus emulsions having benzene as oil component are regarded as extraordinary.

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8) S. Matsumoto, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **85**, 741 (1964).