VISCOSITY, SURFACE TENSION, AND ATOMIZATION OF WATER-METHANOL AND DIESEL EMULSIONS

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This article is the result of experimental studies of the rheology, viscosities, surface tensions, and atomization of water-methanol and diesel emulsions. The Span 80 and Tween 60 are employed to make three emulsifying agents, Y01, Y02, and Y03, with viscosity of 1.32–1.5 Pa s and HLB values of 5.36, 4.83, and 4.51, respectively. In the water-in-oil emulsions, the aqueous phase is between 10% and 50%; the agent concentration added is 0.8–8.0%. The viscosity of the emulsions is 0.003–0.02 Pa s, and the surface tension is 0.04–0.1 N/m. The types and concentrations of agents significantly influence the viscosity of the emulsions, and the higher concentration of the aqueous phase (< 50%) increases the viscosities of the emulsions, especially for higher agent concentration. Interfacial membrane and HLB values of the agents can explain all these phenomena. Higher aqueous phase concentration and agent viscosity results in larger Sauter mean diameter.

INTRODUCTION

The emulsified fuel, composed of methanol and diesel fuel, is a kind of clean fuel, with especially lower soot and NOx emissions. Recently, applications of such emulsified fuels were the focus of considerable researchers. In most conditions, water is needed in order to prepare the emulsions.

The group microexplosion (or lump-fashioned microexplosion) of water-diesel emulsion sprays was created when the emulsion fuel was injected into a high-pressure, high-temperature combustion bomb [1–4]. This phenomenon is called "secondary atomization," and can improve the mixing process at the macro- and microscales. The combustion process can be improved, and the flame temperature can be reduced for better NOx emission [4], due to the high latent heat of the added water and methanol. It is well known that the combustion process depends significantly upon the atomization and spray characteristics of the liquid fuels in many applications, and the atomization and spray also depend upon the viscosities and surface tension in many cases. The emulsion preparation, the property and the quantity of emulsifying agent, and the concentration of the aqueous phase in the emulsion may have significant influence on the viscosity and surface tension of the emulsions. Up to now, a lot of studies about emulsions have been reported on combustion characteristics, NO_x emission, and soot forma-

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tion [5–13]. According to our investigation, the results of the research are insufficient to indicate the physical properties of an emulsion, such as viscosity and surface tension of water-methanol and diesel emulsions.

This article answers some of the questions mentioned above through experimentation. The question of how the microexplosion takes place in water-methanol and diesel emulsion sprays will be answered by high-speed CCD shadow photography in other serial papers.

EXPERIMENTAL FACILITY AND METHOD

The emulsion mainly studied here is a kind of water-in-oil emulsion created by the aqueous phase (internal phase or dispersed phase) with the oil phase (matrix phase or continuous phase—diesel fuel). The "aqueous phase" here means water and methanol since the two components are miscible. The aqueous phase and oil phase are immiscible, so the additives (surfactants) were employed as emulsifying agents to obtain stable emulsions. Three compound emulsifying agents, Y01, Y02, and Y03, are prepared by mixing Span 80 and Tween 60; Table 1 shows the fraction of the mixing agent and its hydrophile-lipophile balance (HLB). The HLB value can describe the property of the agents; an agent with lower HLB value (3–6) easily forms a water-in-oil emulsion, and an agent with higher HLB value (8–18) forms an oil-in-water emulsion easily, if the aqueous phase fraction in the emulsion is in the range of 20–80%. The HLB values of Span 80 and Tween 60 are 4.3 and 14.9, respectively. The HLB value of the emulsifying agents is simply estimated by the equation $(4.3 \times X_{S80} + 14.9 \times X_{T60})$, where X_{S80} and X_{T60} are the fraction of Span 80 and Tween 60 in the emulsifying agent, respectively. The emulsions made by the agents can be kept for more than three months at room temperature without deformation and breakup, since the agents used create a strong interfacial membrane between the two phases. An ultrasonic facility was employed to make the emulsions.

The rheological experiments were performed using the NXS-11 Rotary Viscometer, manufactured by the Cheng-Du Instrument Factory in China. The range of measurement is 0.0028–17800 Pa s; the shear stress is 27.67–21970 Pa; the shear rate is 1.23–996/s; the revolution speed is 5.6–360 rpm; the environmental temperature is 5–35°C; and the material temperature is from room temperature to 95°C, if a thermostat is employed.

The rheological properties and viscosities of three agents are shown in Fig. 1. Y03 has the highest viscosity and it is a Newtonian fluid, but Y01 and Y02 are approximately Newtonian fluids. The viscosity of Y03 is 1.5 Pa s, about 1500, 1200, and 870 times that of water, methanol, and diesel fuel, which are 0.001, 0.00123, and 0.00172 Pa s, respec-

Table 1　Fractions and HLB of the Mixing Emulsifying Agents

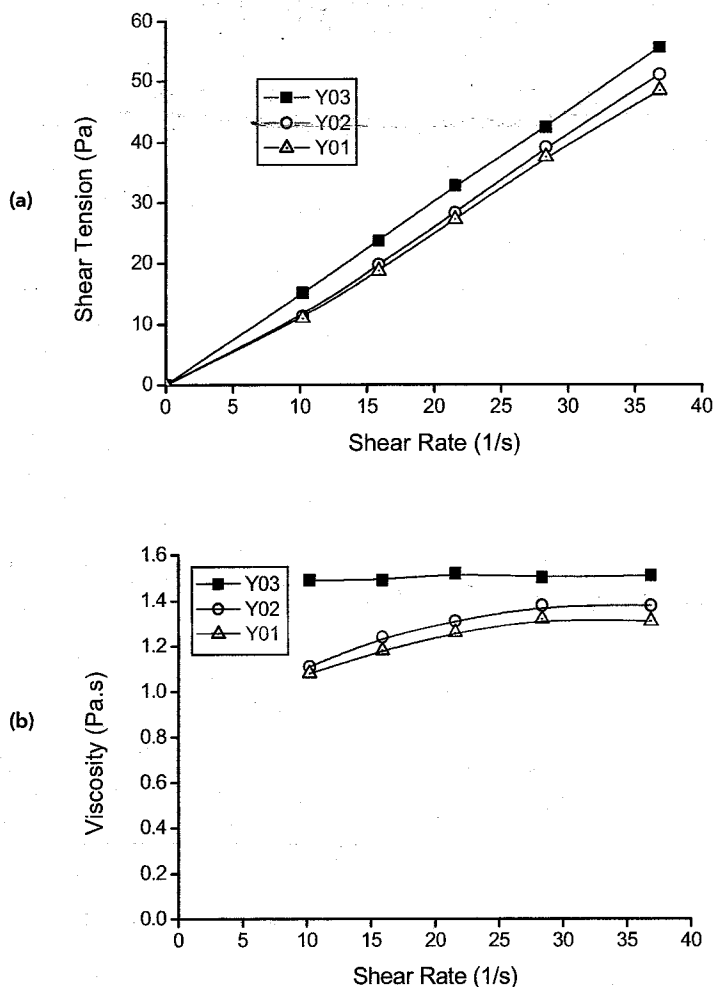| Agent	Y01	Y02	Y03
Span 80 (%)	90	95	98
Tween 60 (%)	10	5	2
HLB	5.36	4.83	4.51

(a)

(b)

Fig. 1 Rheological properties and viscosities of three agents: (a) rheological properties of agents; (b) viscosities of agents.

tively. The viscosities of Y01 and Y02 are 1.32 and 1.38 Pa s, and 88% and 92% of Y03, when the shear rate is fast enough.

A pressure injector with four holes of 0.35 mm diameter was employed to form the spray, and the injection pressure was in the range of 22–31 MPa. Pure diesel fuel was also tested for comparison. The Malvern Particle Analyzer SERIES 2600 made by the Malvern Company in England [14], based on the Fraunhofer diffract theory [15], was employed to measure the droplet size distribution of emulsions under room temperature and atmospheric pressure. The measurement laser is located 150 mm from the beginning of injection. The range of droplets measured by the Malvern Particle Analyzer is 1.9–88 µm. The average diameter of sprays is described by the Sauter mean diameter (SMD), meaning the ratio of the droplets' volume to their total surface area.

RESULTS AND DISCUSSION

Rheological Property of Emulsions and Discussions

Three compound emulsifying agents in Table 1 were employed to prepare the emulsions, and five different percentages of each of the three agents were applied as following: 0.8, 2.0, 4.0, 4.8, and 8.0%. The percentage of the aqueous phase (water and methanol) is in the range of 10–50%; the diesel fuel, water, and methanol concentrations in the emulsions are listed in Table 2. The D, W, and M, and the following digits, represent the percentage points in weight of diesel fuel, water, and methanol in the emulsions. For example, D80W10M10 means 80% of diesel fuel, 10% of water, and 10% of methanol in the emulsion. Because the diesel and water-methanol are combined first and the agents are added later, the concentration of agent has not been defined in this naming system.

The rheological characteristics of the DWM and DW emulsions are measured, and the results show that both emulsions appear as Newtonian fluids [16], but not the pseudoplastic fluids. This point of view differs from previous studies [17, 18]. Figure 1 shows that three emulsifying agents are approximately Newtonian fluids, and this may explain that the emulsions in our work have the property of Newtonian fluids. The detailed figures for rheological properties are shown in Ref. [16].

Figures 2–4 indicate the viscosities of DWM emulsions with added Y01, Y02, and Y03, respectively. Each data point shown in the figures represents the average of five measurement data for five different shear rates. The viscosity for the emulsion D50W25M25 significantly increases with increasing agent addition and the viscosities for the other emulsions increase smoothly. The viscosity of all emulsions greatly increases with increasing the aqueous phase concentration.

The viscosities of the emulsions are in the range of 0.003–0.02 Pa s. When the emulsion contains little emulsifying agent and aqueous phase, the viscosities of the emulsions are slightly higher than that of diesel fuel; but when the aqueous phase concentration is near 50% and the agent concentration is more than 4.8%, the viscosities of the emulsions are about 12 times that of diesel fuel and 20 times that of water. In this case, the

Table 2   Percents of Diesel Fuel, Water, and Methanol in Emulsions

Emulsion	Diesel fuel	Water	Methanol	Aqueous phase*
D90W5M5	90	5	5	10
D90W10	90	10	—	10
D80W10M10	80	10	10	10
D80W20	80	20	—	10
D75W25	75	25	—	25
D70W15M15	70	15	15	30
D70W20M10	70	20	10	30
D70W30	70	30	—	30
D60W20M20	60	20	20	40
D60W40	60	40	—	40
D50W25M25	50	25	25	50
D50W30M20	50	30	20	50

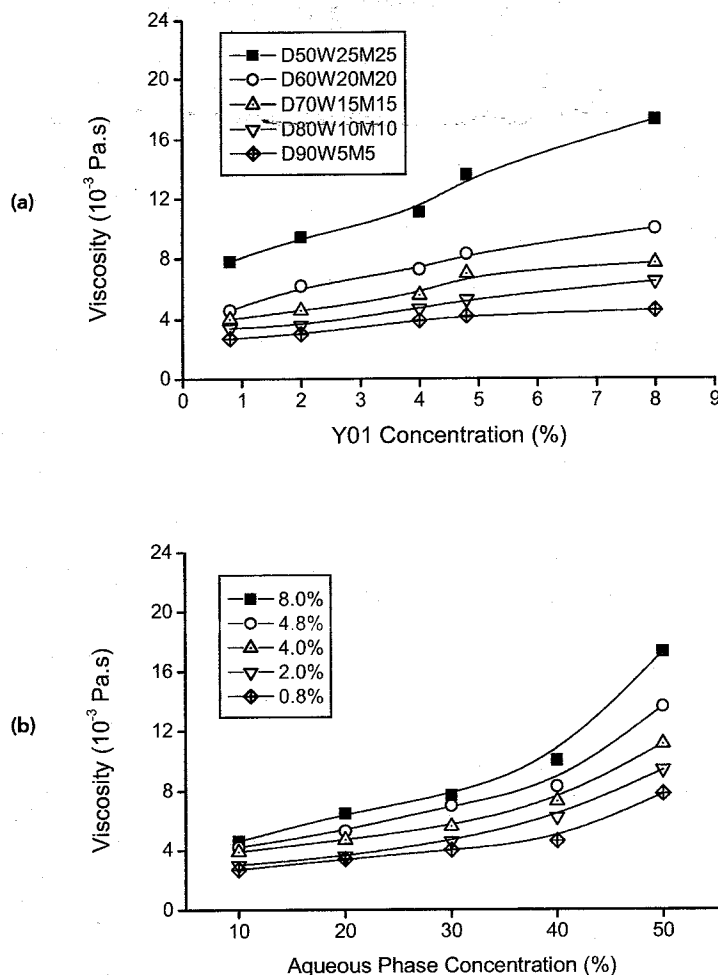* The aqueous phase includes water and methanol.

Fig. 2 Viscosities of DWM emulsions with Y01 addition: (a) viscosity with Y01 concentration; (b) viscosity with aqueous phase concentration.

atomization and mixing process of the emulsions will differ from the diesel fuel, which will be mentioned later.

The viscosity of the emulsifying agent with different HLB values significantly influences the viscosity of the emulsion, even though the concentration of the agent is very low. Increasing the concentration of the agent will greatly increase the viscosity of the emulsion if the aqueous phase concentration is more than 40%. If the aqueous phase concentration is less than 30%, there is no significant influence on the viscosity of the emulsion.

The viscosity of the agent Y03 is only 14% higher than that of Y01, but the viscosity of the emulsion with 8% of Y03 is 40% more than with 8% of Y01, when the aqueous phase concentration is more than 40%. It is true that if the aqueous phase is as great in volume as the oil phase, the agent plays a more important role for the viscosity of emulsions.

By adjusting the ratio of water-to-methanol and the agent concentration, the viscosities of emulsions increase with increased aqueous phase concentration. If the aqueous phase concentration is higher than 40%, the trends in viscosities of emulsions with less than 2% of the agents differ from that for viscosities of emulsions with more than 4% of the agents. In this case, viscosity increases slowly with increasing aqueous phase concentration, if the agent concentration is lower; viscosity increases rapidly by increasing the aqueous phase concentration, if the agent concentration is higher. It is shown that the emulsifying agents play a very important role in changing the viscosity of emulsions—especially for higher aqueous phase concentration.

Figure 5 shows that DW emulsions have similar features to DWM emulsions, but the curves are not as sharply changed as those in Figs. 2–4.
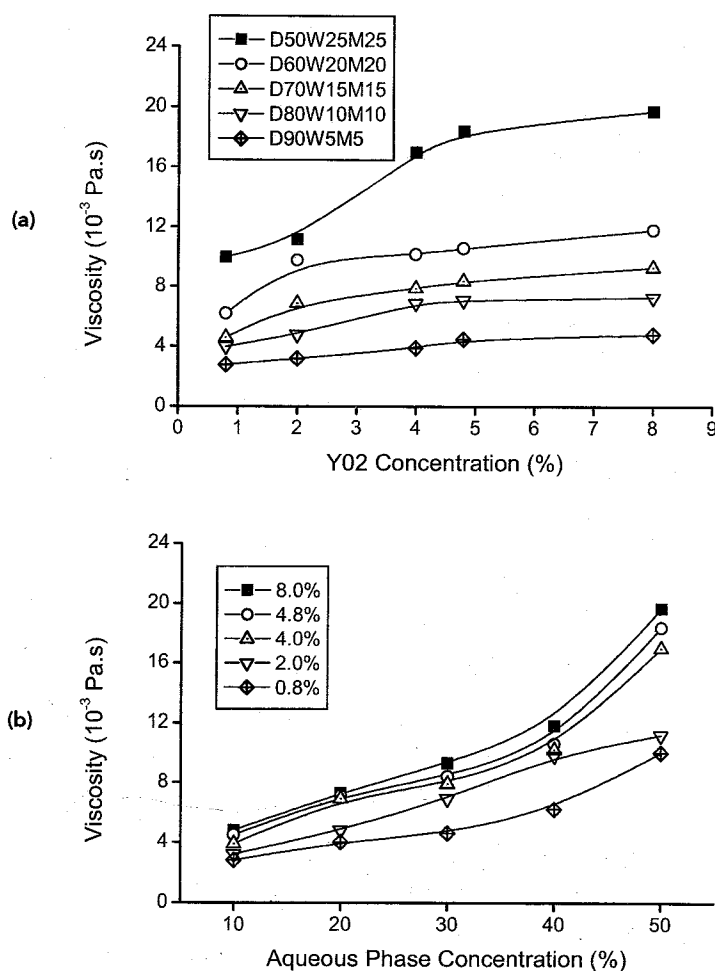

Fig. 3   Viscosities of DWM emulsions with Y02 addition: (a) viscosity with Y02 concentration; (b) viscosity with aqueous phase concentration.
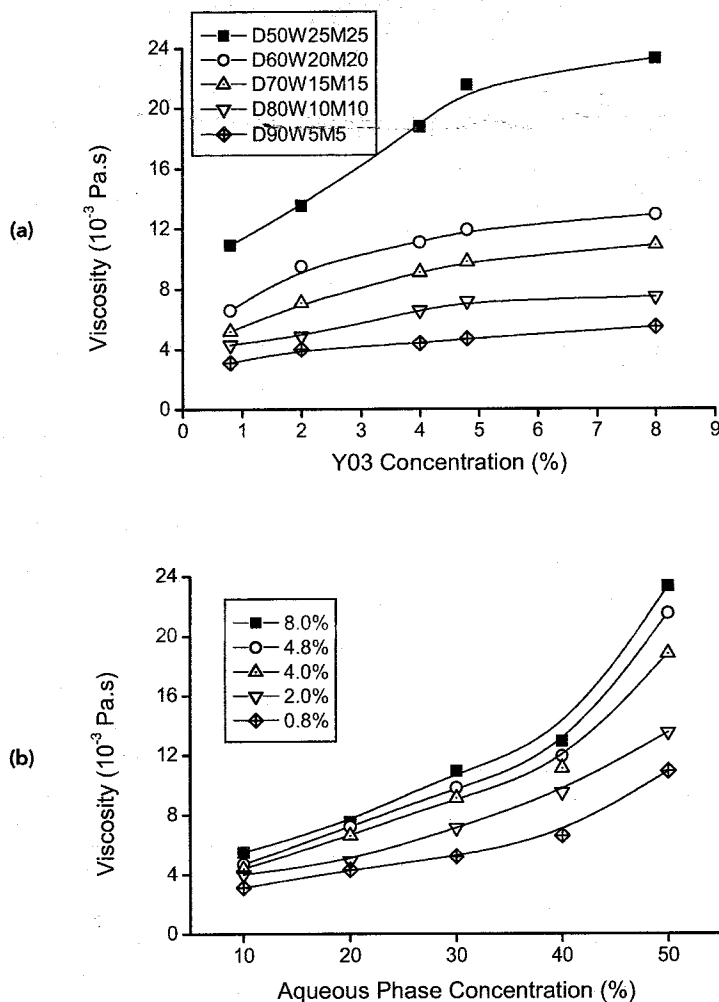
Fig. 4 Viscosities of DWM emulsions with Y03 addition: (a) viscosity with Y03 concentration; (b) viscosity with aqueous phase concentration.

Traditional research recognizes that the viscosity of an emulsion is based on the concentration of the dispersed phase, such as Einstein's formula and the modified Hatschek's formula [19]. In those works, the influence of the size of the internal phase and the emulsifying agents on the viscosity of emulsions was recognized, but not studied very well.

The emulsifying agents used in our experiments have shown very good effects in reducing the surface/interface tensions and in forming a very strong interfacial membrane. The sizes of the dispersed phase (water-methanol) here are in the range of 1–5 μm (see Fig. 6), and the emulsions can be kept for longer time.

Figure 7 indicates the mechanism of the behavior of agents in emulsions. In emulsions, the agents are adsorbed outside the dispersed phase—aqueous phase (water and methanol)—and some oil phase molecules are also adsorbed outside the agents' molecules

to form deformable dots, which are larger than the aqueous phase dots; so the thickness of the matrix phase in the gap, which is located between the water-agent-oil dots and where the matrix phase (diesel fuel) distorts freely, becomes much thinner, especially when the aqueous phase concentration is very high. In a shear flow field, the water-agent-oil dots can hardly be distorted since the interfacial membrane is very strong, and the continuous phase will have much higher local shear rate gradients microscopically than single-phase fluid; thus, the apparent viscosity of emulsions will be much higher than that of single-phase fluids—either the dispersed phase (water-methanol) or continuous phase (diesel fuel).

If the aqueous phase concentration is increased, the thickness of the matrix phase in the gap will become much thinner; the local shear rate gradient becomes much greater and the apparent viscosity becomes much higher. If the aqueous phase concentration is high, but the agent concentration is not high enough, the viscosity of emulsions will increase
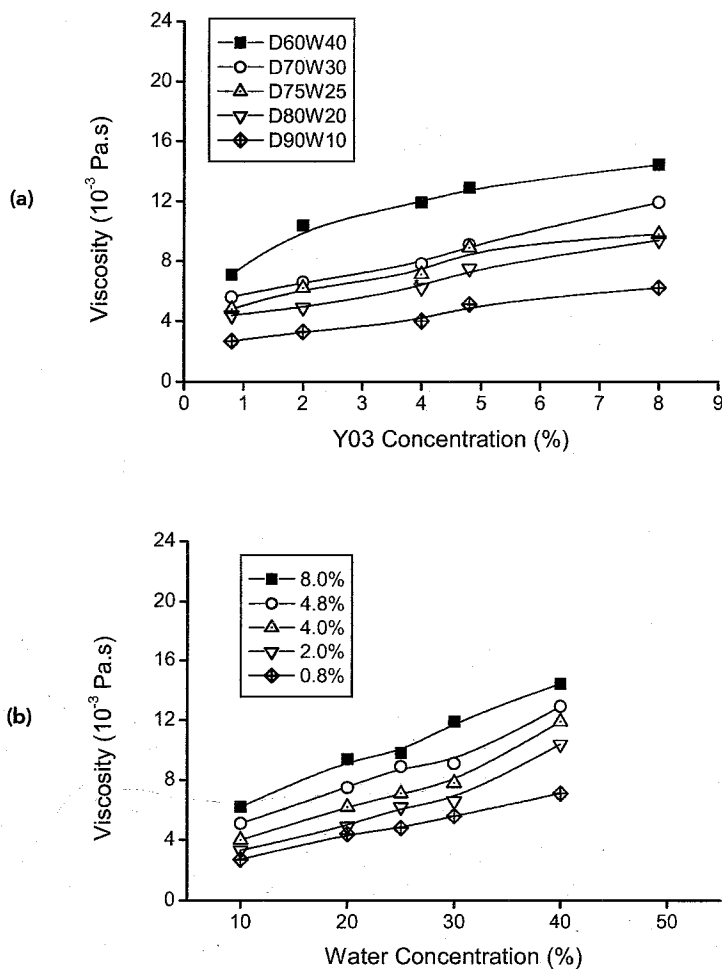

Fig. 5 Viscosities of DW emulsions with Y03 addition: (a) viscosity with Y03 concentration; (b) viscosity with water concentration.
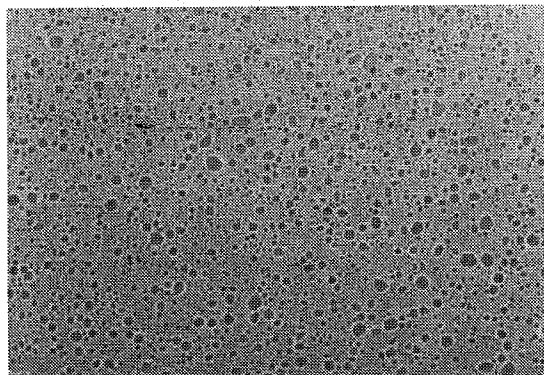
Fig. 6 Micrograph of emulsion (D90W10) by TEM.

slightly because the internal phase will become larger and the local shear rate gradient will not increase very much. If the aqueous phase concentration is high, and the agent concentration is also high enough to form a much larger interfacial area, the viscosity of emulsions will increase greatly because the internal phase will not become larger and the thickness of the matrix phase in the gap becomes much thinner.

Among the three agents, Y03 has the lowest HLB value and may adsorb most of the oil molecules outside the agent membrane to form the largest water-agent-oil dots. In this case, the apparent viscosity of the emulsion with Y03 is much higher than emulsions with Y01 or Y02, if other conditions are fixed—even if Y03 has slightly higher viscosity than Y01 and Y02. If more emulsifying agent is added, part of the agent will dissolve into the oil phase because of the relatively low HLB, and will greatly increase the viscosity of the
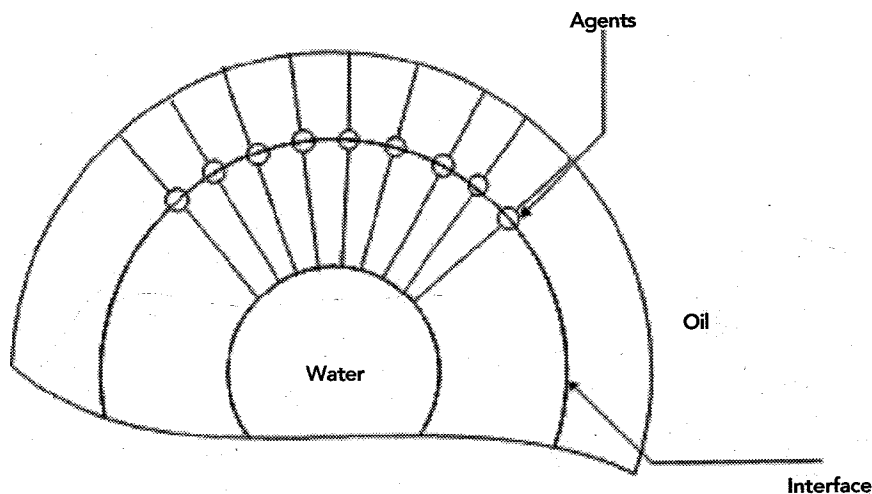

Fig. 7 Mechanism of the behaviors of agents in emulsions.

continuous phase. It is clear that HLB and the viscosity of the agent have a very important influence on the viscosities of emulsions.

According to the experiments, it is clear that the viscosity variation in the emulsions depends on interface conditions between the dispersed phase and the matrix phase, which is different from traditional theory.

Surface Tension of Emulsions

Under higher shear force and higher bulb-generating-rate conditions, dynamic surface tension is much higher than static surface tension in the multiphase system, which is different from the single-phase system. Since surface tension is very important for atomization and droplet diameter distribution in the atomization process, the dynamic surface tensions of the emulsions were measured by the maximum bulb pressure method. The significant influence of the emulsifying agent on the dynamic surface tension of emulsions was observed.

The experimental results show that the dynamic surface tension of emulsions will decrease when the concentration of emulsifying agents increases; and the dynamic surface tension increases when the stretch rate is increased, if other conditions are fixed. Figure 8 shows two typical curves for dynamic surface tension, which are for D50W25M25 emulsions containing 2 and 4% of emulsifying agent Y02.

The surface tensions of water, methanol, and diesel emulsion fuels are 0.07, 0.02, and 0.02 N/m, respectively. The dynamic surface tensions of the emulsions studied are between 0.04 and 0.1 N/m, slightly higher than diesel fuel. Why is the surface tension of an emulsion not much lower than that of diesel fuel since surfactants are added? The reason is very interesting. It is assumed that the surfactants are concentrated in the interface, but they are not well dissolved in the diesel fuel, and the strong interfacial membrane prevents the deformation of the emulsion; thus, the dynamic surface tension is higher than diesel fuel, and it is higher when the stretch rate is higher.
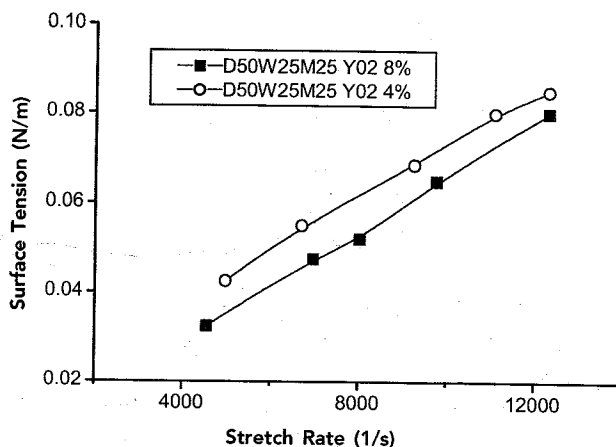

Fig. 8   Dynamic surface tension of D50M25W25 emulsion with Y02 addition.

Atomization Characteristics of Emulsion Spays

Figure 9 shows the SMD distribution of emulsions with different aqueous phase concentrations (D100, D70W20M10, D50W30M20) under different injection pressures. The agents used here are Y01 and Y03, and the concentration is fixed at 1.2%. From this figure, it can be seen that the higher the aqueous phase concentration, the larger the SMD, especially for the aqueous phase at more than 30–40%; and the slightly higher viscosity of Y03 results in a higher emulsion viscosity and larger SMD, with a higher aqueous phase concentration. For diesel fuel, an injection pressure of 22 MPa can produce a very fine SMD (15 μm), but for an emulsion of 50% aqueous phase and Y03, 22 MPa produces a less desired SMD of 26 μm, and 31 MPa is recommended for better emulsion spray formation.
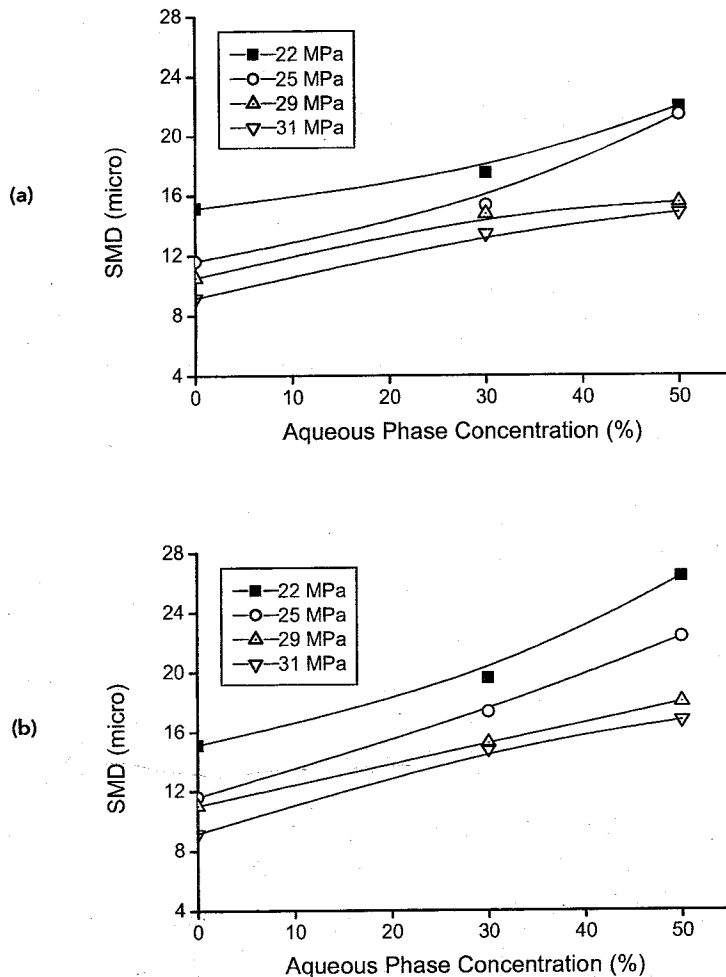
(a)

(b)

Fig. 9   SMD of emulsions with aqueous concentration: (a) 1.2% Y01 addition; (b) 1.2% Y03 addition.

The results show the influence of viscosity on the SMD and firmly supports the rheological studies mentioned above. Traditional atomization theory considers that surface tension plays a most important role on the mean droplet diameter, but not on the viscosity. However, for emulsions, the mechanism of droplet breakup may differ from uniform liquid, since the diameter of the internal phase is not much less than the diameter of the emulsion droplets. The interfacial membrane between the internal phase and the continuous phase is strong enough to prevent the consequent breaking up of droplets into very fine droplets; also, the viscosity of the emulsion is much higher than diesel fuel because of the effect of a strong membrane in this case, which is mentioned above.

CONCLUSIONS

The Span 80 and Tween 60 are employed to make three compound emulsifying agents, Y01, Y02, and Y03, with the Hydrophile-Lipophile Balance (HLB) values of 5.36, 4.83, and 4.51, respectively. The agents Y01 and Y02 are approximately Newtonian fluids, and the agent Y03 is a Newtonian fluid. The viscosity of Y03 is 1.5 Pa s, the viscosities of Y01 and Y02 are 1.32 and 1.38 Pa s, and 88 and 92% of that of Y03 when the shear rate is faster.

The emulsions are composed of an aqueous phase (water and methanol) with an oil phase (diesel fuel). All the emulsions are Newtonian fluids in which the percentage of the aqueous phase (water and methanol) is in the range of 10–50%, the percentage of emulsifying agents added is 0.8–8.0 %, and the viscosity of the emulsions is 0.003–0.02 Pa s, compared to that of diesel fuel, 0.00172 Pa s.

The experiment shows the following:

1. The different kinds of emulsifying agents, with different HLB values, have significant influence on the viscosity of the emulsions, even if the viscosities of the agents have only a slight difference, as long as all other conditions are fixed.
2. Different concentrations of emulsifying agents significantly influence the viscosities of the emulsions, especially for the aqueous phase with a concentration higher than 40%, as long as other conditions are fixed.
3. Increasing the aqueous phase concentration in the emulsions (not more than 50%), the viscosities of the emulsions will increase. The increasing tendencies are different for different agent concentrations when the aqueous phase is more than 40%; the gap for agent concentration is between 2% and 4%, if other conditions are fixed.
4. All the phenomena mentioned above can be explained by applying the interfacial phenomena between aqueous phase and oil phase in emulsions and HLB values of the agents.
5. When changing the ratio of methanol to water in the emulsion, the behavior of the emulsions is complicated; more studies must be done to understand the mechanism.
6. The surface tensions of water-methanol and diesel emulsions increase when the stretch rate is increased and are in the range of 0.04–0.1 N/m, slightly higher than that of diesel fuel.
7. The higher the aqueous phase concentration is, the larger the Sauter mean diameter (SMD) is, especially for an aqueous phase of more than 30–40%, and the slightly higher viscosity of Y03 results in a larger SMD. The viscosity of an emulsion may play a very important role on the SMD.

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