

The Influence of Viscosity and Surface Tension on Atomization of Water/Methanol and Diesel Emulsions

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Abstract

This paper shows the result of experimental studies of the influence of viscosities, surface tensions on atomization characteristics of water/methanol and diesel emulsions. 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 was produced by Span 80 and Tween 60. In the W/O 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 and the aqueous phase (< 50%) significantly influence the viscosity of the emulsions and the Sauter Mean Diameter, measured by Malvern Particle Analyzer SERIES 2600.

Keywords: Emulsion, Rheology, Viscosity, Surface Tension

Introduction

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

The group micro-explosion (or lump- fashioned micro-explosion), of water-diesel emulsion sprays, was found clearly by Ruby Laser Holographic High Speed Camera in 1988, when the emulsion fuel was injected into a high pressure, high temperature combustion bomb^[1-3] This phenomenon is called "secondary atomization", and can improve the mixing process in macro- and micro-scales. The combustion process can be improved, and the flame temperature can be reduced for better NO_x emission, due to the high latent heat of added water and methanol. At the same time, a No-Water Layer at boundary of emulsion droplet was observed by Holography^[2].

Many questions concerning with the strength of micro-explosion and the criteria of micro-explosion are interesting and still unsolved. How much aqueous phase is still there when micro-explosion takes place? What is the roll of aqueous phase residues to influence the occurrence and the strength of micro-explosions? Maybe the no-water layer plays an important roll in micro-explosions, and it is formed by Hill Vortex induced by shear force of surrounding gas when the speed difference between the emulsion droplet and surrounding gas is big enough. Now there is no proper

explanation for such complex phenomena, the guess is that the heating history and transportation of water dots in the emulsion droplets play very important rolls, under different ambient temperature and pressure conditions. So the viscosity of emulsion has very significant influence on heat and mass transportation process, and also on the mean diameters and diameter distribution of emulsion droplets, which were observed by experiments.

Since the detailed experimental studies for micro-explosions are rather difficult for such small, such fast process in a dense emulsion spray, especially for the variations of many parameters in a high pressure, high temperature vessel by high speed laser holography, detailed numerical simulation was proposed. However, when we started to study this phenomenon from very beginning, we found we can hardly found many useful basic physical and chemical properties of emulsions, and even physical knowledge for this problem. This is why we study the rheological properties, surface tension and spray characteristics of emulsions, which are parts of a series of mechanism study for micro-explosion of emulsions.

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 aqueous phase in the emulsion may have significant influence on the viscosity and surface tension of emulsions.

According to our investigation, the results of the research are insufficient to indicate the physical properties of emulsion, such as viscosity and surface tension of water/methanol and diesel emulsions.

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

The Preparation of Emulsifying Agents and the Test Facility

The emulsion mainly studied here is a kind of water-in-oil (W/O) 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. The HLB (hydrophile-lipophile balance) value can describe the property of the agents; a lower HLB value (3~6) easily forms a W/O emulsion, and a higher HLB value (8~18) forms an O/W emulsion easily. Three compound emulsifying agents Y01, Y02 and Y03 with HLB values of 5.36, 4.83 and 4.51 respectively, were prepared for the experiments, by mixing commercial surfactants Span 80 (HLB=4.3) and Tween 60 (HLB=14.9), in ratios of 90:10, 95:5 and 98:2 respectively. These 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.

The rheological experiments were performed using the NXS-11 Rotary Viscometer manufactured by the Cheng-Du Instrument Factory in Sichuan Province, 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 r/min; the environmental temperature is 5~35°C; 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 Figure 1. The 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 of that of water, methanol and diesel fuel, which are 0.001 Pa·s, 0.00123 Pa·s and 0.00172 Pa·s, respectively. The viscosities of Y01 and Y02 are 1.32, 1.38 Pa·s, and 88 % and 92 % of Y03, when the shear rate is fast enough.

The Rheological Property of Emulsions

Three compound emulsifying agents, mentioned above, were employed to prepare the emulsions, five

different percentages of each of three agents were applied as following: 0.8%, 2.0%, 4.0%, 4.8%, 8.0 %; the percentage of the aqueous phase (water and methanol) is in the range of 10% and 50%; the diesel fuel, water and methanol concentrations in the emulsions are listed in table 1. The capital letters D, W, M, and the following digits, represents 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 at first, and the agents are added later, the concentration of the agents cannot be defined in this naming system. An ultrasonic facility was employed to make the emulsions.

The rheological characteristics of the DWM and DW emulsions are measured, and the results show that both emulsions appear as Newtonian fluids, but not the pseudo-plastic fluids. This point of view differs from previous studies^[4,5]. The reasonable explanation is that the emulsifying agents used are approximately Newtonian fluid. The detailed figures for rheological properties are shown in reference [6].

Each data point shown in the following figures represent the average of five measurements for five different shear rates. All the relative error distribution of five measurements for the same data point is random deviation and less than $\pm 0.0\%$, and the most of the errors are less than $\pm 0.0\%$. This phenomenon means that the emulsions can be considered as Newtonian fluids.

The figure of each measurement was averaged from three readings, the reading errors is less than 0.1% of full scale of the Viscometer, and the error deviation of three readings for the same measurement is less than $\pm 0.3\%$ of full scale of the Viscometer. So, for each measurement, the error can be neglected.

From the figures, the following is evident:

The viscosities of the emulsions are in the range of 0.003 and 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 emulsions are about twelve times that of diesel fuel, and twenty times that of water. In this case, the 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 through the concentration of the agent is very little. Increasing the concentration of the agent will greatly increase the viscosity of emulsion if 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 emulsion.

The viscosity of the agent Y03 is only 14% higher than that of Y01, but the viscosity of emulsion with 8% of Y03 is 40% more than with 8% of Y01, when 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 in 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 as DWM emulsions.

Figure 6 shows that the influence of the ratio of water-to-methanol on the viscosities of DWM emulsions is complicated for different aqueous phase concentrations in the emulsions; more work should be done in order to understand the reason for this. In general, when the ratio of water-to-methanol is higher, the viscosity of the emulsions will increase rapidly, especially under the condition of higher agent concentrations.

Discussion on Viscosity Property of Emulsions

Traditional research recognizes that the viscosity of emulsion is based on the concentration of the dispersed phase, such as Einstein's formula and modified Hatschek's formula^[7]. The influence of the size of the internal phase and the emulsifying agents on the viscosity of emulsions was recognized, but was 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 very strong interfacial membrane. The sizes of the dispersed phase (water/methanol), here are in the range of 1~5 μ m, and the emulsions can be kept for some time.

In the emulsion, 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, so 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. When the aqueous phase concentration is high, the viscosity will increase slightly since the internal phase will become larger; the local shear rate gradient will not increase very much if the agent concentration is not high enough, and the viscosity will increase greatly, since the internal phase will not become larger, and the thickness of the matrix phase in the gap becomes much thinner if the agent concentration is high enough to form a much larger interfacial area.

Among the three agents, Y03 has lowest HLB value, and may adsorb most 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 and 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 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 upon interface conditions between the dispersed phase and the matrix phase, which is different from that described in Hatschek's formula.

The Measurement of Surface Tension of Emulsions

Under higher shear force and higher bulb generating rate conditions, the dynamic surface tension is much higher than static surface tension in the multi-phase 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 7 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 fuel are 0.07 N/m, 0.02 N/m and 0.02 N/m respectively. The dynamic surface tensions of the emulsions studied are between 0.04 N/m and 0.1 N/m, slightly higher than diesel fuel. Why is the surface tension of 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 are not well dissolved in the diesel fuel, and the strong interfacial membrane prevents the deformation of emulsion, so the dynamic surface tension is higher than diesel fuel, and it is higher when the stretch rate is higher.

Atomization Characteristics of Emulsion Spays

The Malvern Particle Analyzer SERIES 2600, based on the Fraunhofer Diffraction Theory, was employed to measure the droplet size distribution of emulsions under room temperature and atmospheric pressure, the Independent Model was applied to get the Sauter Mean Diameter SMD. A pressure injector, with four holes of 0.35 mm in diameter, was employed to form spray, and the injection pressure is in the range of 22 MPa to 31 MPa. Pure diesel fuel was also tested for comparison.

The laser beam center was focused on an area 150 mm from the nozzle. And the injection duration is about one second, the SMD was obtained by averaging the droplet size for whole duration at the giving area.

Figure 8 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 to 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 higher emulsion viscosity and much larger SMD, with a higher aqueous phase concentration. For diesel fuel, injection pressure of 22 MPa can produce very fine SMD (15 micros), but for an emulsion of 50% aqueous phase and Y03, 22 MPa produces a less desired SMD of 26 micros, and 31 MPa is better.

The result shows 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 emulsion is much higher than diesel fuel, due to 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, the agent Y03 is Newtonian fluid. The viscosity of Y03 is 1.5 Pa·s, the viscosities of Y01 and Y02 are 1.32 Pa·s, 1.38 Pa·s, and 88 % and 92 % of that of Y03, when the shear rate is faster.

The emulsions are composed of aqueous phase (water and methanol) with oil phase (diesel fuel). All the emulsions are Newtonian fluid, in which the percentage of the aqueous phase (water and methanol) is in the range of 10% and 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 with that of diesel fuel 0.00172 Pa·s.

The experiment shows following points of view:

a) 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, if other conditions are fixed.

b) Different concentrations of emulsifying agents significantly influence the viscosities of the emulsions, especially for the aqueous phase with a concentration higher than 40%, if other conditions are fixed.

c) 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.

d) All the phenomenon mentioned above can be explained applying the interfacial phenomena between aqueous phase and oil phase in emulsions and HLB values of the agents.

e) 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.

f) The surface tensions of water/methanol and diesel emulsions, increase when the stretch rate is increased, and are in the range of 0.04 N/m and 0.1 N/m, slightly higher than that of diesel fuel.

g) The higher the aqueous phase concentration is, the larger is the Sauter Mean Diameter – SMD, especially for an aqueous phase of more than 30~40%, and the slightly higher viscosity of Y03 results in much larger

SMD. Viscosity of emulsion may play very important role on SMD.

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Table 1: The diesel fuel, water and methanol concentrations in the emulsions

D90W5M5	D80W10M10		D70W15M15	D60W20M20	D50W25M25
			D70W20M10		D50W30M20
D90W10	D80W20	D75W25	D70W30	D60W40	

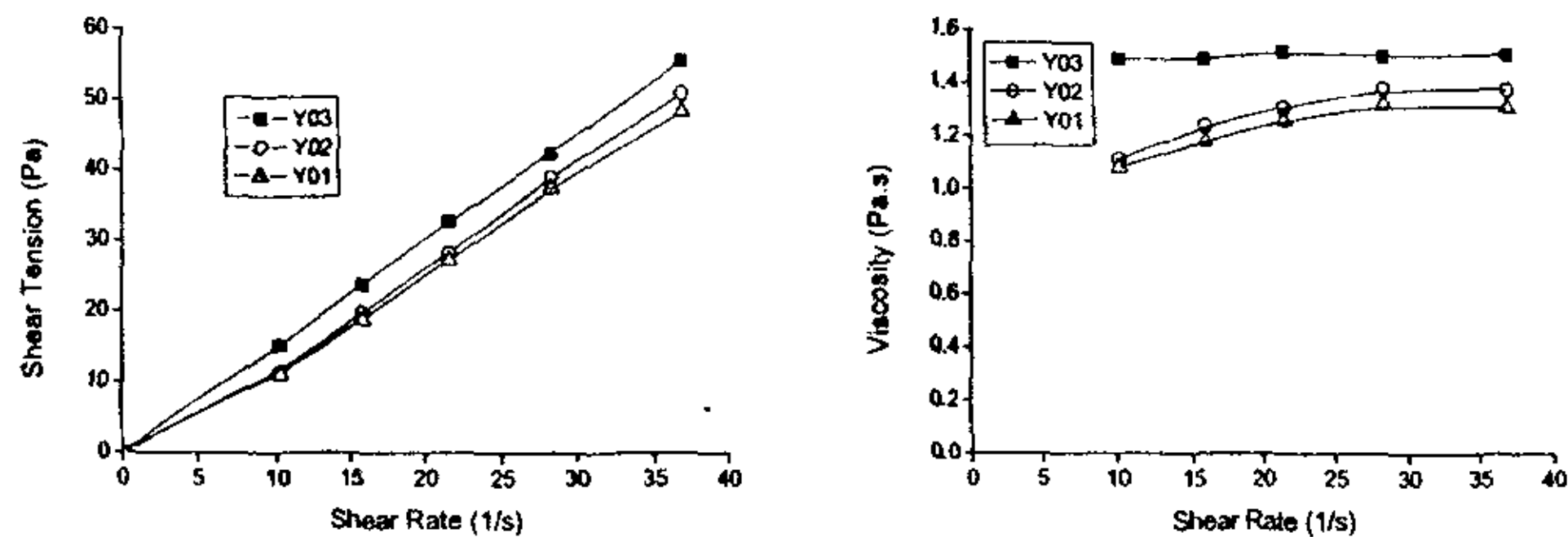


Fig.1: Rheological property and viscosity of three emulsifying agents

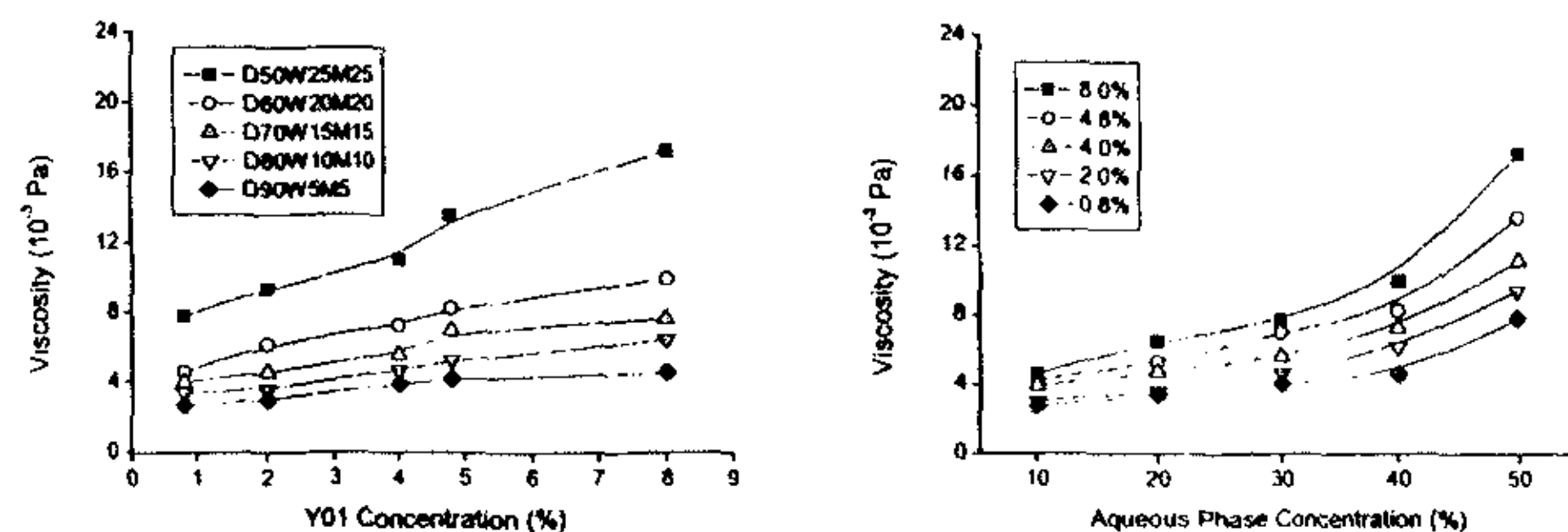


Fig.2: The viscosities of DWM emulsions with Y01

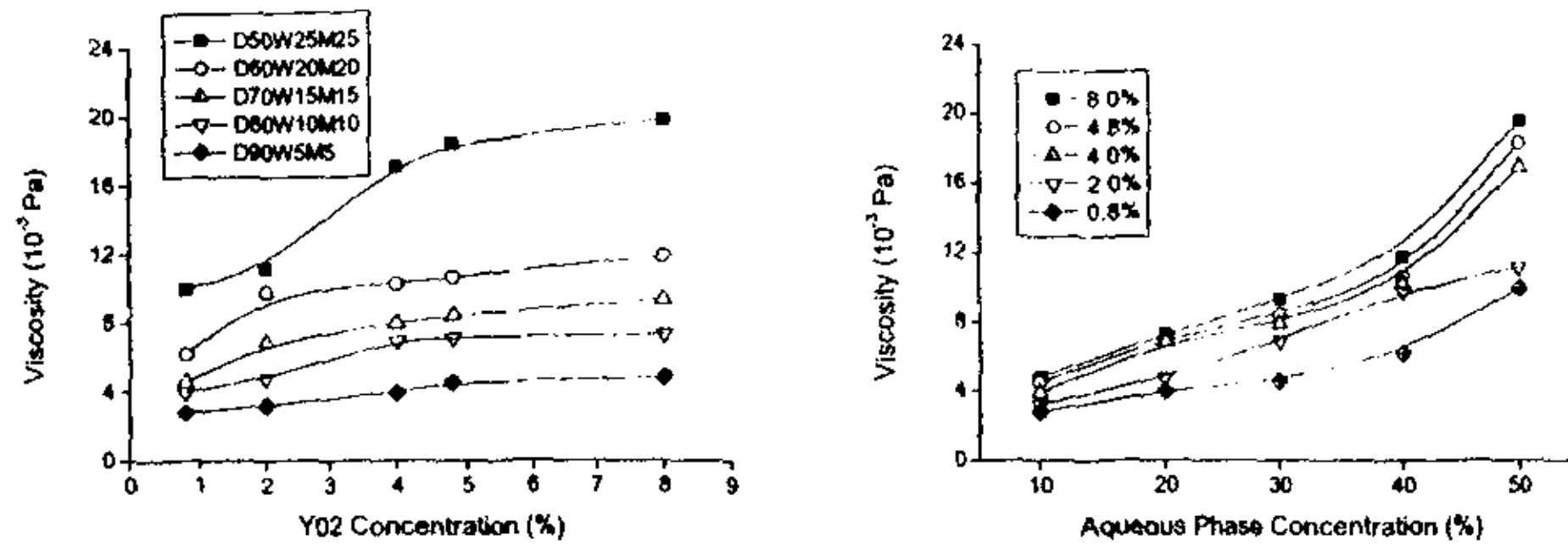


Fig.3: The viscosities of DWM emulsions with Y02

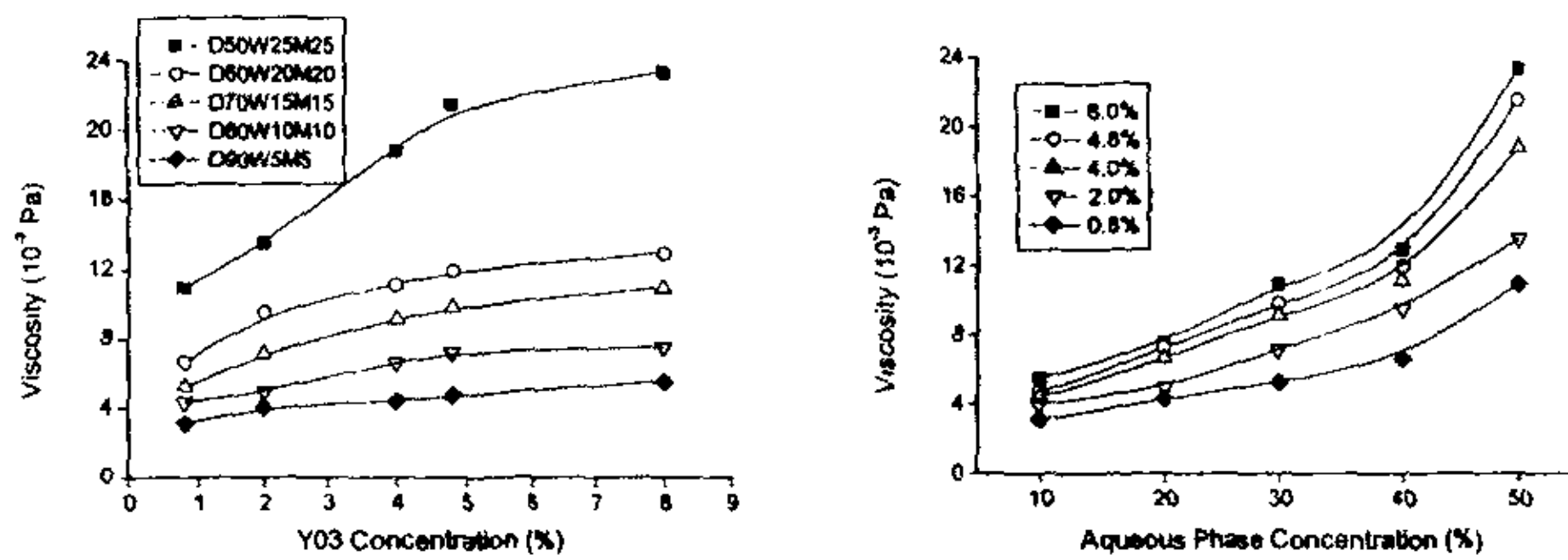


Fig.4: The viscosities of DWM emulsions with Y03

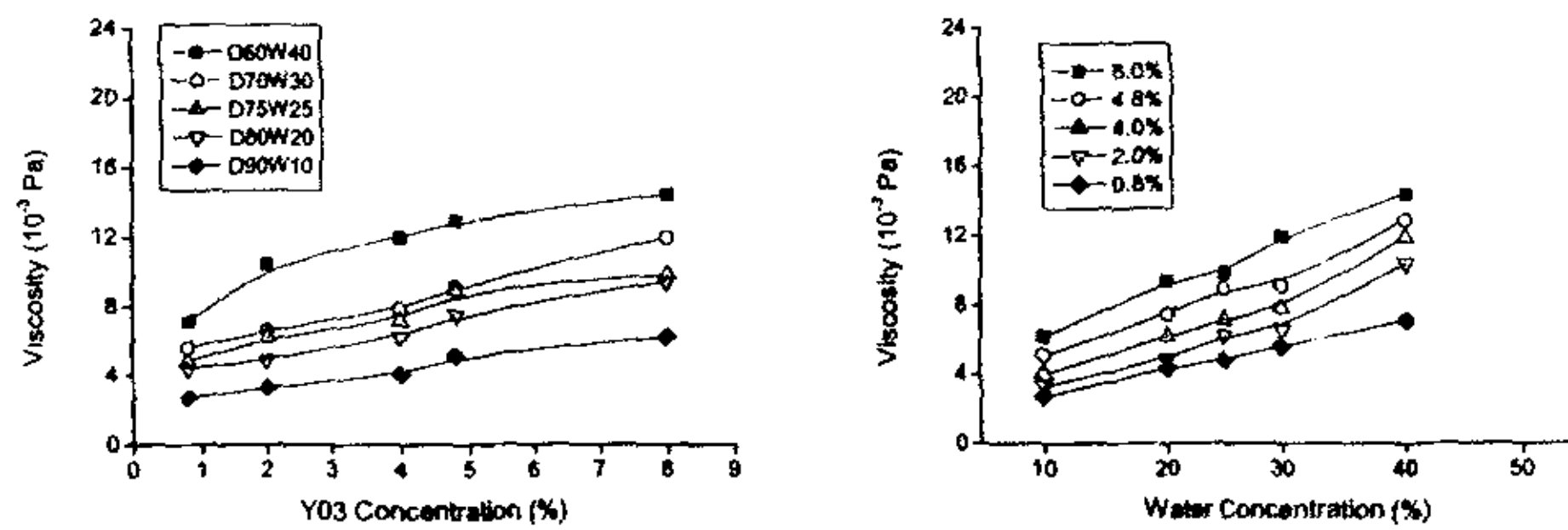


Fig.5: The viscosities of DW emulsions with Y03

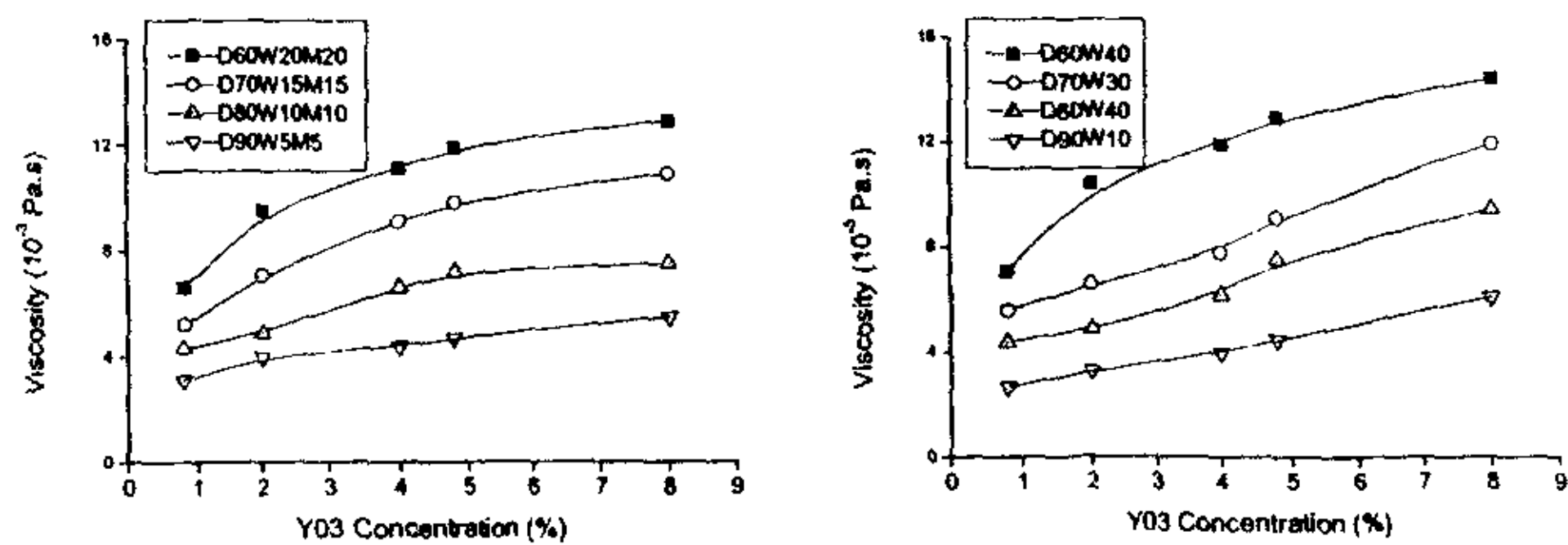


Fig.6: The viscosities of emulsions with different ratio of water to methanol

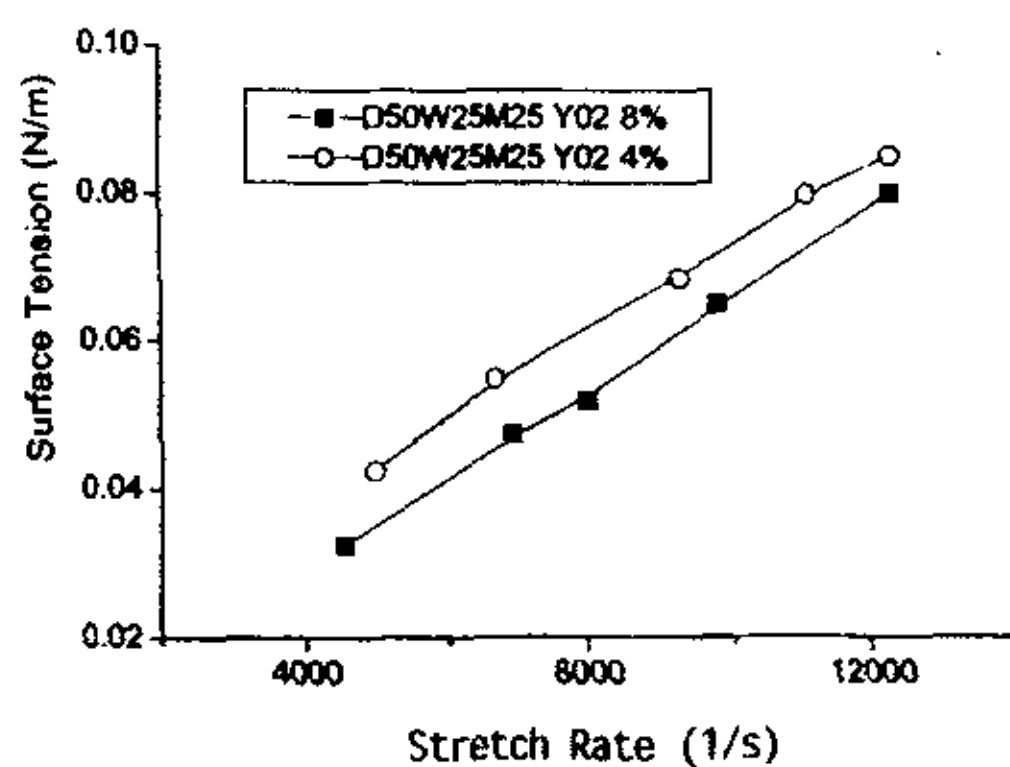
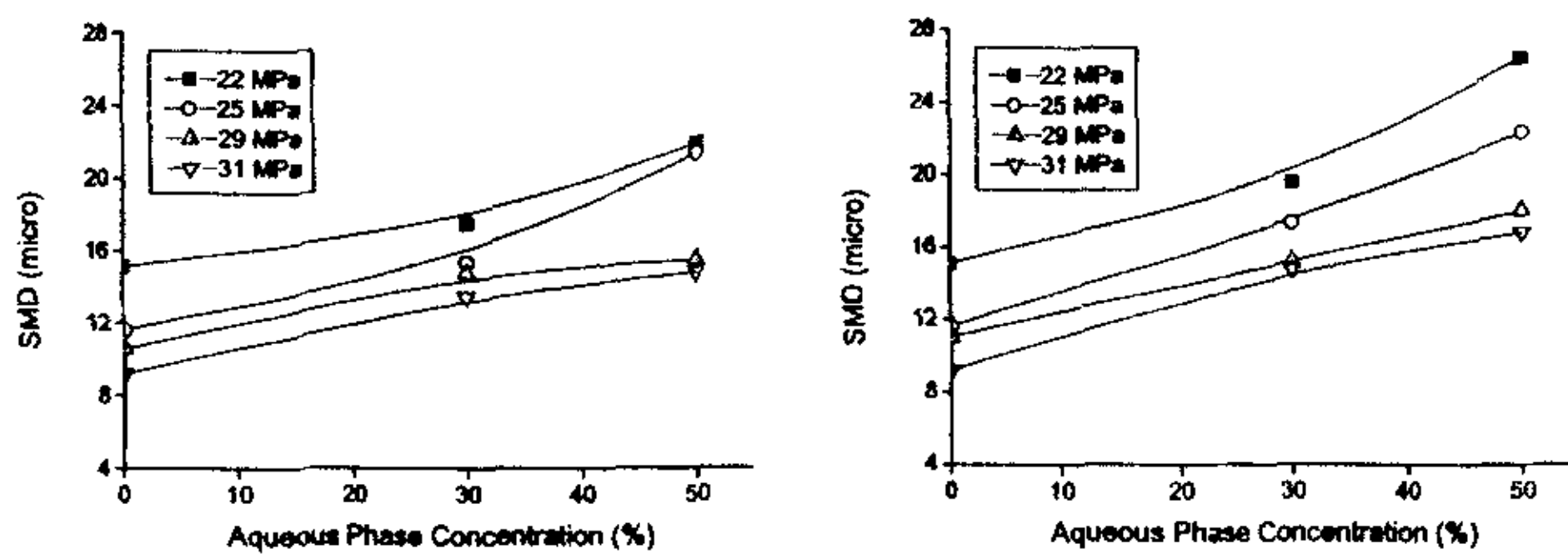


Fig.7: Dynamic surface tension of D50M25W25 emulsion with Y02



Y01 (1.2 %)

Y03 (1.2 %)

Fig.8: The Sauter mean diameters of emulsions