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NEGATIVE PRESSURES OF DETERGENTS IN THE METAL BERTHELOT TUBE

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Abstract

Liquids can withstand negative pressures unless cavitation occurs. When any objects covered with dirt are in liquids under negative pressures, the objects are stretched by the surrounding liquids. Therefore, the dirt may be removed from the objects. Thus, a final goal of this study is to investigate cleaning effects of negative pressures, and, in this paper, as the first step to the goal, negative pressures of some kinds of commercial liquid detergents are measured by the Berthelot method using a metal tube. The method generates static negative pressures, which increases with a *repetition of a cycle through a quasi-isochoric process of a system composed of a metal tube, a sample liquid, and a sealing plug. Negative pressures for a domestic detergent recommended for removal of oils on metal surfaces, attained to ca. -20 MPa, the highest of the method, within only ca. 230 cycles. Furthermore, the pressure was attained without any de-gassing treatments to the tube recommended for high negative pressures. On a basis of composition of the detergent, industrial detergents were tested. Detergents including non-ionic surfactants generated similar high negative pressures, while that of an anion surfactant never attained.*

Keywords

Negative Pressure of Liquid, Berthelot Method, Detergent

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1. Introduction

Liquids can be stretched iso-tropically, and then, pressures of the liquids can be negative. The reason is that as average intermolecular distances of liquid states in equilibrium are longer than those of solid states and are shorter than those of vapor states, intermolecular potentials of liquids have not only repulsive parts but also attractive ones.

Negative pressures of liquids are important and interesting in science and technology (Imre, Maris, & Williams, 2002). For example, in order to elucidate anomalies of water, maximum densities of water under negative pressures have been investigated (Zheng, Durben, Wolf & Angell, 1991). Another example is phase diagrams of liquid crystals including negative pressure regions which will contribute to improvement of performance of liquid crystal displays (Hiro & Wada, 2011).

In spite of such importance and interest, there have been few experimental reports on negative pressures in liquids. The reason is that liquids under negative pressures are in a thermodynamically meta-stable state, similar to superheated liquids or supercooled ones. Before negative pressures become high in magnitude, tiny bubbles appear in the liquids suddenly, and the liquids translate in liquid-vapor co-existing states. The phenomenon of the bubble appearances is called cavitation. There have been few experimental methods of generating negative pressures of liquids.

Of the methods, the Berthelot method is orthodox because it can generate negative pressures relatively easily. When a solid container filled with a sample liquid is heated and then cooled in a temperature range, the liquid pressure changes from positive to negative through zero because of (i) difference of thermal expansion coefficients between the liquid and the container and (ii) their adhesion. As the material of the container, metal, glass, or mineral have been used.

Metal has three merits of (1) mechanical sealing without the use of a flame in a case of glass ones, (2) measurements of negative pressures by over-tightening the cap of the tube and then changing the densities of the liquids, and (3) their high strengths as pressure vessels. On the other hand, the metal has a demerit that negative pressures are lower in magnitude that those by others (Hiro, Ohde, & Tanzawa 2003). There have been elaborate studies on the Berthelot method using metal tubes in order to generate high negative pressures (Ohde, Komori, Nakamura, Tanzawa, Nishino, & Hiro 2001), by which authors can imagine experiments other than measurements of liquids' properties under negative pressures now.

Any objects in liquids under negative pressures can be stretched. If surfaces on the objects are covered with dust, the dust is expected to be separated from the surfaces by tensions equivalent to negative pressures. In other words, negative pressures might have cleaning effects in proportional to their magnitudes.

Thus, our research issue is finally to investigate cleaning effects of negative pressures of liquids, and, in this paper, as the first step to address the issue, negative pressures of some kinds of liquid detergents are measured by the Berthelot method using a metal tube. According to a previous study of negative pressure, limits of negative pressures depend on liquids' properties (Fisher, 1948). Therefore, it is important to measure negative pressures of liquid detergents because higher negative pressures in magnitude are expected to have higher cleaning effects.

2. Experiment

The Berthelot method using a metal tube has an ability to generate negative pressures repeatedly (Hiro & Wada, 2011). Fig. 1 shows a pressure-temperature diagram of the method. When a sample liquid sealed in the tube was heated, the liquid pressure increased with temperature to the point A in the figure. Next, as the liquid was cooled, the pressure decreased to B, and negative pressure built up. If cavitation occurred at C, the pressure jumped sharply to D where the liquid co-exists with its vapor. Next, the liquid was heated again, the pressure increased gradually to B along the liquid-vapor co-existing line, and attained steeply to the initial A. This cycle, ABCDBA, was called temperature cycle.

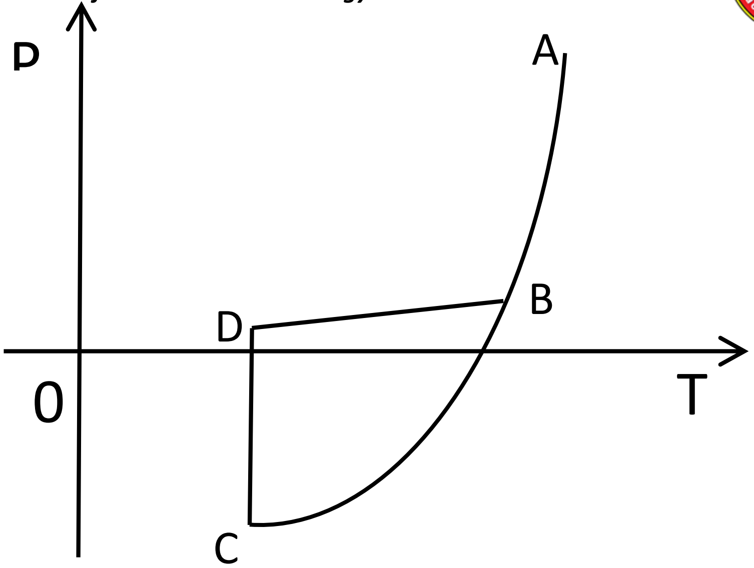

Figure 1: *The Berthelot Method*

An experimental tube used in this study is shown in Fig. 2. The tube consisted of a metal screw cap, a metal ball, and a pressure transducer. A top part of the transducer was used as a specimen chamber of ca. $40*10^{-6}$ m^3.

Sealing of a sample liquid to the chamber was carried out by putting the ball on the top part, fastening the cap so as to compress the ball to the edge, and giving the ball an amount of plastic distortion. In this study, no de-gassing treatments to the ball and the liquid, such as filtering, boiling or irradiation of ultrasonic waves to them, were performed. The treatments had been believed to be effective to remove cavitation nuclei, namely gas molecules dissolved in the liquid, very tiny bubbles in the liquid, gases trapped in crevices on the chamber wall or on dirt suspended in the liquid.

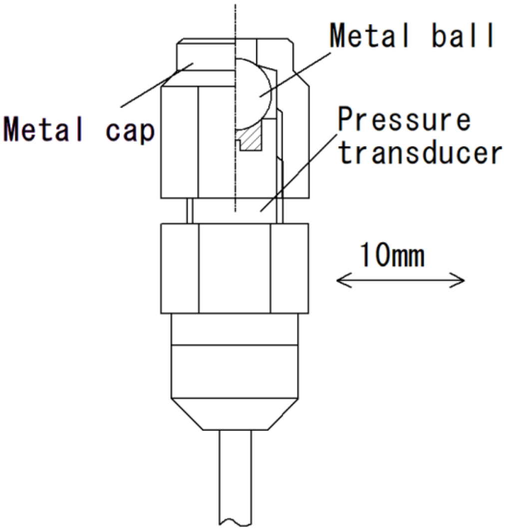

Figure 2: *The Berthelot Tube*

In order to repeat temperature cycles, authors used an apparatus as shown in Fig.3. The apparatus carried out the repetition of the cycle automatically. When the tube was in the hot bath, the liquid pressure was positive. After a period of time, the tube was moved from the bath and was left in air. The pressure decreased gradually, became negative. When cavitation occurred suddenly, a pressure signal from the pressure transducer jumped up. The PLC detected the signal change and commanded the motor so that the tube was returned in the hot bath. Thus, temperature cycles were repeated automatically.

In this experiment, firstly, five kinds of commercial domestic detergents were tested as sample liquids. Suppliers recommended that the detergents were used to wash dishes (Cucute, Kao Co., Tokyo, Japan), to clean one's teeth (Clearclean, Kao Co., Tokyo, Japan), to breach something (Haiter, Kao Co., Tokyo, Japan), to launder cloths (Attack, Kao Co., Tokyo, Japan), and to remove oils on metal surfaces (Magiclean, Kao Co., Tokyo, Japan), respectively. Then, two kinds of surfactants, namely alkyl-amine-oxide and alkyl-glycoside, were selected on the basis of product catalog of the detergent whose negative pressure was the highest in them. The former included a kind of cationic surfactant while the latter did nonionic surfactant. Three kinds of industrial detergents, which included the surfactants, were examined. Their commercial names were "AMPHITOL 20N", "MYDOL 10", and "MYDOL 12" made by Kao. Co.. Hereafter, five domestic detergents are abbreviated as A, B, C, D, and E, while three industrial detergents are done as 1, 2, and 3. Tables 1 and 2 show five kinds of domestic detergents and three kinds of industrial detergents, respectively.

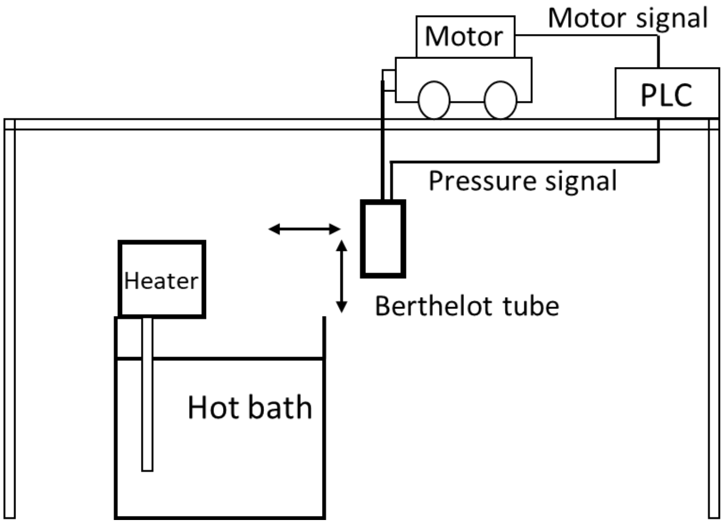

Figure 3: *Automatic Temperature Repeater*

Table 1: *Components of Five Kinds of Domestic Detergents*

Detergents	Remarks Recommended by Suppliers
A	to wash dishes
B	to clean one’s teeth
C	to breach something
D	to launder cloths
E	to remove oils on metal surfaces

Table 2: *Components of Three Kinds of Industrial Detergents*

Detergents	Components	Rates(wt%)
1	Dimethyl lauryl amine oxide Water	65 35
2	Decyl glycoside Ethanol Sodium carbonate Water	40 2.5 0.3 57.2
3	Lauryl glycoside Ethanol Sodium carbonate Water	40 2.5 0.3 57.2

3. Results and Discussion

3.1 Negative Pressures for Five Kinds of Domestic Detergents

Relations between negative pressures for detergents A and E and temperature cycles are shown in Fig. 4. Negative pressures for both detergents increased with temperature cycles with scatters, though the formers were much higher than the latters. The increasing trends were observed for other detergents, too and were similar to those reported before (Hiro, Ohde, & Tanzawa, 2003).

The detergent D withstood ca. -20 MPa of negative pressure, while that of A did only ca. -6 MPa. In particular, ca. -20 MPa, which has been the highest ever reported in the metal tube, were attained within only ca. 230 cycles in spite of no treatments for de-gassing both the ball and the liquid.

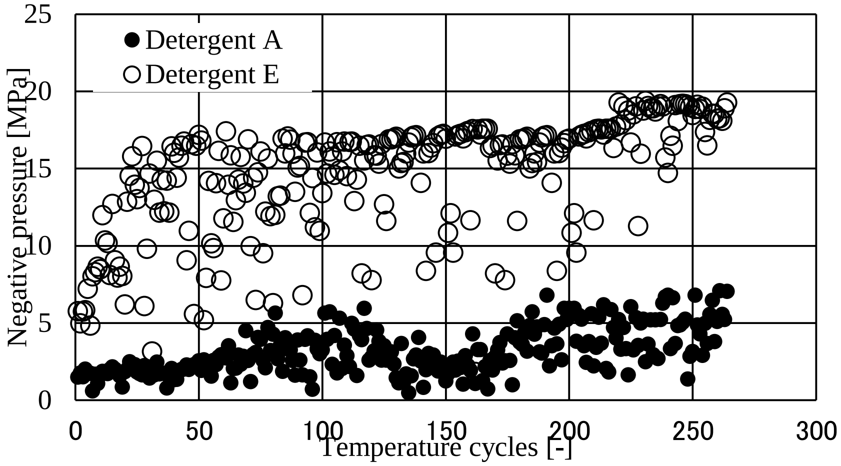

Figure 4: *Relations between Negative Pressures and Temperature Cycles*

Histograms of negative pressures, -P, for five kinds of liquid detergents are shown in Fig. 5. Only the histogram of the detergent E has a bar belonging to a negative pressure range of 16 MPa < |-P| <= 20 MPa.

The detergent E did not undergo any treatments for de-gassing it. Nevertheless, ca. -20MPa was obtained within initial 230 cycles. This implies that cavitation nuclei were not gases or not bubbles, which existed in the detergent itself, but those existed in the ball – the detergent interface.

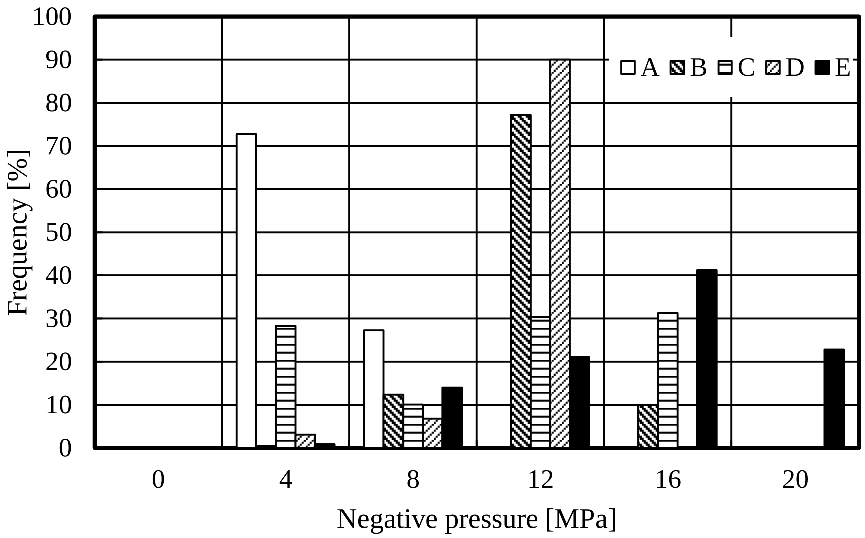

Figure 5: *Histograms of Negative Pressures for Detergents*

The increasing trend of negative pressures and the existence of gases in the interface nuclei led authors to an idea that relevant nuclei were considered to be gases trapped within crevices on the metal surfaces as reported before (Ohde, Watanabe, Hiro, Motoshita and Tanzawa, 1993).

Suppliers have recommended that the detergent E is used to remove oils adhering on metal surfaces or dirt originating from the oils. It is well-known that any dirt on the metal surfaces makes wettabilities for any liquids to the surfaces low. Low wettabilities should have caused large amounts of gases in crevices on the metal surfaces; the detergent E improved the wettabilities of the surfaces contacting with it, removing amounts of gases in crevices and high negative pressures around ca. -20 MPa.

3.2 Negative Pressures for Two Kinds of Industrial Detergents

Histograms of negative pressures for three kinds of components are shown in Fig. 6.

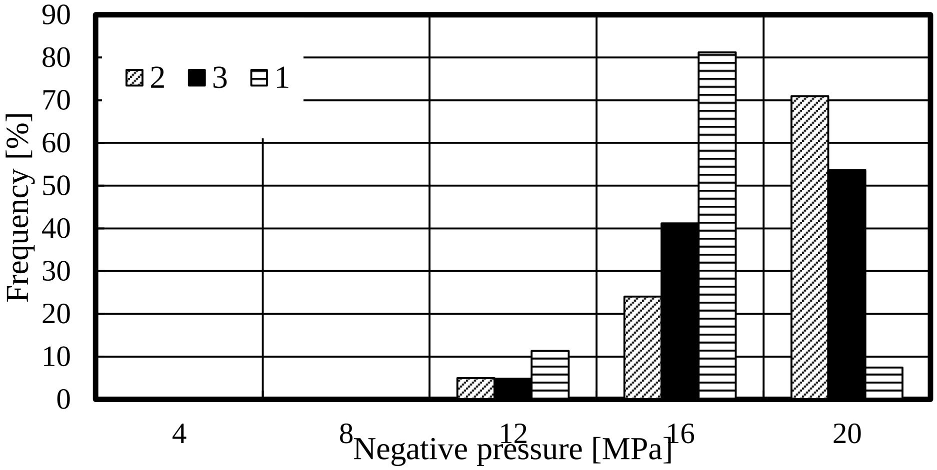

Figure 6: *Histograms of Negative Pressures for Components*

As compared with the histogram of the detergent 1, those of the components 2 and 3 had higher frequencies of higher negative pressure ranges; frequencies for a range of 16 MPa < |-P| <= 20 MPa were ca. 8% for 1, ca. 70% for 2, and ca. 55% for 3.

The surfactants of 2 and 3 were non-ionic, while that of 1 was cationic. Non-ionic surfactants had abilities to generate high negative pressures. In order to check difference of viscosity, another detergent 2 which had different concentration was tested. Figure 7 shows the histograms. The histogram of 25% detergent indicated a similar trend to that of 100% detergent.

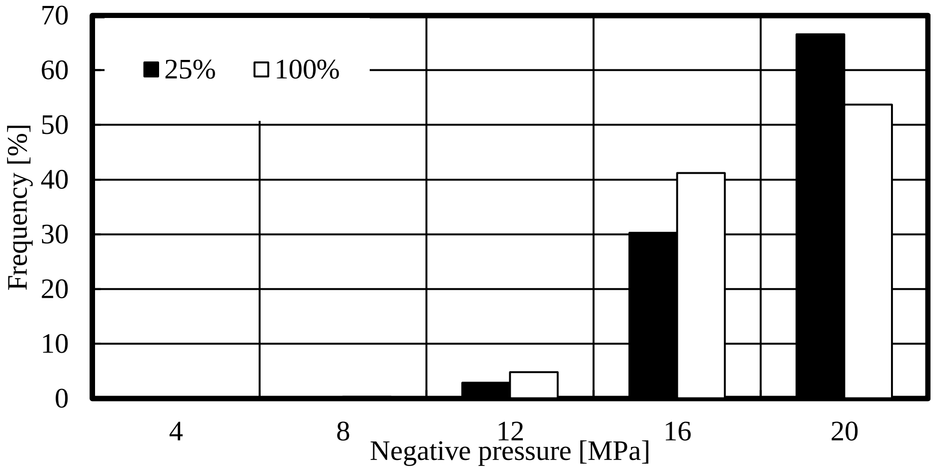

Figure 7: *Histograms of Negative Pressures for Two Components C Different in Concentration*

4. Conclusion

As the first step to investigate cleaning effects of negative pressures of liquids, negative pressures of some kinds of commercial liquid detergents were measured by the Berthelot method using a metal tube. On domestic detergents, negative pressures for a detergent recommended for removal of oils on metal surfaces attained to ca. -20 MPa. On industrial detergents, negative pressures for detergents including nonionic surfactants of alkyl glycoside attained to ca. -20 MPa. The negative pressures of ca. -20 MPa were the highest in magnitude in the method.

In near future, effects of negative pressures on detergency of materials such as cloths or fine mechanical parts by using the two liquid detergents will be studied.

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