A Research on Air in Oils*

by Hiroshi KATAKURA**, Shigeru TSUJI***,

Ryuichiro YAMANE**** and Hirotaka FUJITA*****

In this report, air solubility of petroleum-based oil and change in diameter of a stationary bubble in the oil are investigated. The air solubility may be evaluated by the theory on regular solutions. For the petroleum-based oil of five different types measured air solubility was approximately same as that calculated by assuming that the solubility parameter is $1.4 \times 10^4 \sqrt{\text{J/m}^2}$ for paraffin-based oil, or $1.6 \times 10^4 \sqrt{\text{J/m}^2}$ for naphthene-based oil. No considerable difference in the diffusivity of dissolved air was observed among measured values in the oil of five different types. A bubble, which had once changed in diameter under low or high pressure, took a long period of time to recover the original size in stationary oil such as in swirling oil. And these phenomena appeared after such pressure change was repeated multiple times.

Key Words: Cavitation, Fluid Power Systems, Mass Transfer, Aeration, Solubility, Air, Oil, Solubility Parameter, Diffusivity, Bubble.

1. Introduction

There are a lot of research on phenomena of mass transfer through boundary between liquid phase and gas phase. On mass transfer of air through surface of a bubble in such an oil as hydraulic fluid or lubricant, however there are only a few studies including ours[1][2] and quite a few unsolved problems still remain. Especially, knowledges of air solubility of the oil and diffusivity of dissolved air in the oil, which are essential in solving the problems, are quite insufficient.

This report is mainly concerned with the air solubility of petroleum-based oil obtained from theoretical and experimental studies, and also with the diffusivity of dissolved air obtained from experimental studies on the change in diameter of a stationary bubble in the oil are mainly presented.

2. Symbols

- C : Concentration of dissolved air in oil expressed in volume molarity.
 C_s : Solubility of air in oil expressed in volume molarity.
 D : Diameter of a bubble.

- f : Fugacity in considered state.
 f^o : Fugacity in state of pure liquid.
 M : Molecular weight, average molecular weight or molar mass.
 P : Absolute pressure.
 R : Universal gas constant.
 T : Absolute temperature.
 t : Time.
 V : Molar volume.
 X : Solubility of substance in oil expressed in mole fraction.
 δ : Solubility parameter.
 χ : Diffusivity of dissolved air.
 ρ : Density.
 σ : Surface tension.
 ϕ : Volume fraction.

Subscripts

- a : Expressing the value of air.
 c : Expressing the value of critical state.
 i : Expressing the value of initial condition.
 j : $j=1$ or $j=2$.
 o : Expressing the value of oil.
 1 : Expressing the value of oxygen.
 2 : Expressing the value of nitrogen.

3. Oil Used in Experimental Studies

Following five different types of petroleum-based oil were used in our experimental studies. Fluid A and Fluid B are commercial hydraulic fluids whose from different manufacturers. Fluid C is a commercial wear-resistant hydraulic fluid, and Fluid D and Fluid E are commercial pure petroleum whose ingredients are different from each other. Fluids A-D are paraffin-based oil and Fluid E are a naphthene-based oil. Viscosity of Fluid A is VG38 and that of the others is VG56. Table 1 shows the physical values of the oil, such as, the density, ρ_o , number average of molecular weight, M_n , and

* Received 1st February, 1983.

** Research Associate, Tokyo Institute of Technology (Tokyo Kogyo Daigaku), Ookayama 2-12-1, Meguro-ku, Tokyo, Japan.

*** Professor Emeritus, Tokyo Institute of Technology.

**** Associate Professor, Tokyo Institute of Technology.

***** Engineer, Mitsubishi Heavy Industry Ltd..

weight average of the molecular weight, M_w , which was measured by means of high-speed liquid chromatography. The distribution of molecular weights of ingredients was almost similar to that shown in Figure 1, in which Fluid A is illustrated, though the small differences in their average molecular weights were ignored.

In this report, the number average of molecular weight, M_n , is used as the average molecular weight of the oil, M_o , in the following sections.

4. Air Solubility of Oil

4.1 Calculation of air solubility

As the oil may usually be regarded as a dilute solution of air, the following relation holds between the air solubility expressed in volume molarity, C_s , and that expressed in mole fraction, X_a ;

$$C_s = (\rho_o/M_o)X_a \quad (1)$$

M_o : Molar mass of oil

ρ_o : Density of oil.

Since the air, whose main ingredients are oxygen and nitrogen, as gas phase and the oil as liquid phase are in equilibrium, the absolute pressure of the air in the considered state, P_a , is expressed as

$$P_a = P_1 + P_2 \quad (2)$$

using partial pressure of oxygen in the state, P_1 , and that of nitrogen in the state, P_2 . The air solubility of oil, X_a , is expressed as

$$X_a = X_1 + X_2 \quad (3)$$

using the oxygen solubility expressed in mole fraction X_1 in case that pure oxygen in gaseous state and the oil are in equilibrium at the pressure P_1 , and the nitrogen solubility X_2 in case that pure nitrogen in gaseous state and the oil are in equilibrium at the pressure P_2 .

Assuming that air-dissolved oil is a regular solution, the solubility of oxygen or nitrogen, X_j ($j=1$ or 2), is expressed as

$$X_j = \frac{f_j}{f_j^0} \exp \left[-\frac{V_j \phi_o^2 (\delta_o - \delta_j)^2}{RT} \right] \quad (4)$$

using the fugacity of j -ingredient in state of pure liquid, f_j^0 ; the fugacity of

the j -ingredient in the considered state, f_j ; the molecular volume of the j -ingredient, V_j ; the volume fraction of the oil as solvent, ϕ_o ; the solubility parameter of the oil, δ_o ; the solubility parameter of the j -ingredient, δ_j ; the universal gas constant R and the absolute temperature in the considered state, T [3]. In this research $\phi_o=1$ and

$$f_j = P_j \exp \left[\frac{9 T_{cj} P_j}{128 T P_{cj}} \left(1 - \frac{T_{cj}^2}{T^2} \right) \right] \quad (5)$$

T_{cj} : Critical temperature of j -ingredient

P_{cj} : Critical pressure of j -ingredient

may be approximately valid, so that the solubility of j -ingredient of the oil, X_j , is expressed as

$$X_j = \frac{P_j}{f_j^0} \exp \left[\frac{9 T_{cj} P_j}{128 T P_{cj}} - \frac{27 T_{cj}^2 P_j}{64 T^3 P_{cj}} - \frac{V_j (\delta_o - \delta_j)^2}{RT} \right] \quad (6)$$

The absolute value of the third term is usually much greater than those of the others in the bracket of Eq. (6), so Eq. (6) may be simplified into

$$X_j = \frac{P_j}{f_j^0} \exp \left[-\frac{V_j (\delta_o - \delta_j)^2}{RT} \right] \quad (7)$$

Data may be available for fugacities of oxygen and nitrogen in the state of pure liquid, f_j^0 ($j=1$ or 2), and for the molar volumes of them, V_j ($j=1$ or 2). Also data may be available for the solubility parameters δ_j ($j=1$ or 2) if the temperature dependencies are assumed to be very small [3]. And also the relations may be available

$$\left. \begin{aligned} P_1 &= 0.2 P_a \\ P_2 &= 0.8 P_a \end{aligned} \right\} \quad (8)$$

which are approximately valid for usual air.

The solubility parameter, δ_o , of which authors could not find any existing data, is thought to be

$$\delta_o = (1 \sim 2) \times 10^4 \sqrt{J/m^3} \quad (9)$$

Table 1 Density and average molar weight of oil.

Fluid	ρ_o ($\times 10^3$ kg/m ³)	M_n	M_w
A	0.867	408	498
B	0.876	391	488
C	0.878	420	508
D	0.880	367	451
E	0.895	271	354

$T = 288$ K

Fig. 1 Typical distribution of molar weights of ingredients in oil.

by assuming that the parameter is similar to those of pure hydrocarbons in state of liquid as measured in some past studies.

Figure 2 indicates the results of air solubility thus obtained. And also percentage of the oxygen in the oil, in which the dissolved air is saturated, may be calculated by the above method as shown in Figure 3.

4.2 Measurement of the air solubility

The air solubility was measured as follows. The test oil was made at the considered temperature and atmospheric pressure by aerating the oil in a constant-temperature water bath for many hours after the oil had been degassed once in vacuum and then oversaturated in high-pressure dry air. The air concentration of the oil, whose measurement method has been described in our paper[2], was considered the value of the air solubility in the considered state.

Generally speaking, the air concentration in initially undersaturated test oil that with aeration using dry air at constant pressure, C_{under} , may be $C_{\text{under}} \leq C_s$ at the pressure, while the concentration in the initially oversaturated oil that with aeration, C_{over} , may be $C_{\text{over}} \geq C_s$. Thus the difference between, C_{under} and C_{over} , by which range of measurement error may be estimated, should be considered when the air solubility is measured. In this research, therefore, not only either C_{under} or C_{over} but also both of them were measured in some cases.

Air solubility measurements of Fluid A in atmospheric pressure, X_a , are shown in Fig. 4. The measurements in both cases that the test oil was initially oversaturated (white points) and undersaturated (black points) are plotted there. The slant lines are theoretical results calculated for several solubility parameters, δ_o . From this figure, the air solubility

Fig. 2 Calculated air solubility.

Fig. 3 Calculated percentage of the oxygen in dissolved air.

of Fluid A in atmospheric pressure, X_a , is found to be approximately $X_a = 0.19\%$, which is almost the same as the calculated results based on the assumption of $\delta_o = 1.4 \times 10^4 \sqrt{\text{J/m}^3}$. In this way we found the measurement error range of about 10% at the lower temperature, at which the diffusion of dissolved air is slower and the oil viscosity is higher, and also a much smaller range of errors at higher temperatures.

Air solubilities measurements of Fluids B-E at atmospheric pressure are illustrated in Fig. 5. The solid lines are calculated results for various solubility parameters δ_o . The air solubilities of Fluids B-D, X_a , are found to be approximately $X_a = 0.18\% \sim 0.2\%$ which is almost the same as the calculated result by assuming $\delta_o = 1.4 \times 10^4 \sqrt{\text{J/m}^3}$. But the air solubility of Fluid E, X_a , is only found to be approximately $X_a = 0.11\% \sim 0.12\%$ which is almost the same as the calculated result based on the assumption of $\delta_o = 1.6 \times 10^4 \sqrt{\text{J/m}^3}$.

From the above results and the fact that Fluids A-D were paraffin-based oils and Fluid E was a naphthene-based oil, it may be concluded that the air solubility of paraffin-based oil is approximately the same as the value calculated by assuming $\delta_o = 1.4 \times 10^4 \sqrt{\text{J/m}^3}$, and the air solubility of naphthene-based oil is approximately the same as the value calculated by assuming $\delta_o = 1.6 \times 10^4 \sqrt{\text{J/m}^3}$.

4.3 A discussion on solubility parameter of oil

From past research on solution, it

Fig. 4 Measured air solubility of Fluid A in atmospheric pressure.

Fig. 5 Measured air solubility of Fluids B-E at atmospheric pressure.

has been confirmed empirically that

$$\delta = 2.2 \times 10^4 \times (\sigma/V^{1/3})^{0.43} \quad (10)$$

σ : Surface tension N/m
 V : Molar volume m^3/mol
 δ : Solubility parameter $\sqrt{\text{J}/\text{m}^3}$

at temperature $T=298\text{K}$ in a liquid composed only of molecules which have not any radicals. Then, molar volume V may be assumed to be

$$V = M/\rho \quad (11)$$

M : Average molar mass of liquid
 ρ : Density of liquid,

and the solubility parameter, δ_0 , at temperature $T=298\text{K}$ may be calculated using the surface tension σ_0 ; the density ρ_0 ; and the average molecular weight M_0 ; around the temperature.

From Eqs. (10), (11) and the surface tension $\sigma_0=3.3\text{cN/m}$ of Fluid A, which had been measured at temperature $T=296\text{K}$, we obtain

$$\delta_0 = 1.6 \times 10^4 \sqrt{\text{J}/\text{m}^3} \quad (12)$$

This value is roughly 10% larger than the result obtained in Section 4.2. The presence of a difference between them, however, is thought to be reasonable, because the surface tension σ is significantly affected even by a very small amount of contaminations in the oil. That is to say, this method to calculate the solubility parameter of the oil, δ_0 , may be judged to be useful when this much of error may be tolerated.

5. Change in Bubble Diameter and Diffusivity of Dissolved Air

Figure 6 is a sketch of our experimental apparatus. A transparent closed vessel A, in which the pressure was controlled by a compressor C and a vacuum pump D, was set in a constant-temperature water bath B. A glass dish E was in the vessel. A single stationary bubble was in stationary oil in the dish. The oil temperature was measured by a thermometer F. The bubble diameter was measured photographically using a stroboscope G and a

Fig. 6 Experimental apparatus used in this study.

camera H.

Every experiment was done as follows. The glass dish was filled with the test oil whose concentration C was made equal to the air solubility in initial state, C_0 . The bubble diameter in the oil was confirmed to remain in the initial state, and then the pressure in the vessel was changed.

Figure 7 is an example of experimental results on the change in bubble diameter in case that the pressure in the vessel A was changed at $t=0$ as a step function. P_i in the figure is a pressure in the vessel at the time before the pressure was changed, and P is one at the time after the pressure was changed. The solid lines are the closest results calculated by the theory of Epstein-Plesset, when the initial bubble diameter D_i may be calculated by Boyle's Law, the diffusivity of dissolved air κ is regarded as the unknown constant in the theory and effects of surrounding solid are ignored. In this research the measured values thus obtained, κ , were regarded as measured values of the diffusivity of the dissolved air.

Figure 8 is an example of experimental results of the diffusivity of the dissolved air, κ . It may be confirmed that no significant difference is indicated in diffusivities in cases that the bubble was growing up (white points) and when contracting (black points). Figure 9 shows the measured diffusivity κ in Fluids B-E which is the mean value obtained in the above two cases.

Therefore, the diffusivity of the dissolved air thus obtained is found to be $1 \times 10^{-10} \text{m}^2/\text{s} < \kappa < 5 \times 10^{-10} \text{m}^2/\text{s}$ around the room temperature, to increase with the temperature T and to be $7 \times 10^{-10} \text{m}^2/\text{s} < \kappa < 11 \times 10^{-10} \text{m}^2/\text{s}$

Fig. 7 Typical change in bubble diameter (1).

Fig. 8 Measured diffusivity of the dissolved air in Fluid A.

around $T=330\text{ K}$, and also the differences among the measured values of diffusivity in the five kinds of oils were not large in the comparison considering the accuracy of measurements.

Figure 10 shows examples of changes in bubble diameter in the oil measured in case that the pressure in the vessel A, P , changes several times as shown above. It is found that the bubble which has changed in diameter under low or high pressure takes a long period of time to recover the original size in stationary oil such as the bubble once grown under a low pressure in swirling oil[1], and also that this phenomenon appears after such pressure changes are repeated several times.

6. Conclusions

In this paper, the authors present the theoretical and the experimental results about the air solubility of petroleum-based oil, and also the experimental results about the diffusivity of dissolved air in oils of 5 different types which may affect the bubble diameter in stationary oil. The results can be summarized as follows:

(1) Air solubility of paraffin-based oil is approximately the same as the value calculated by the theory on regular solutions by assuming $\delta_0=1.4\times 10^4\sqrt{J/m^3}$, and it is almost independent of its additives and so on. The air solubility of naphthene-

based oil is approximately the same as the value calculated by the theory by assuming $\delta_0=1.6\times 10^4\sqrt{J/m^3}$.

(2) The measured diffusivity of dissolved air x is $(1\sim 5)\times 10^{-10}\text{ m}^2/\text{s}$ around the room temperature, and no considerable differences are observed among the measured values of the diffusivity of the oil of the different types.

(3) The bubble which has changed in diameter under low or high pressure takes a long period of time to recover the original size in stationary oil such as in swirling oil, and these phenomena appear after such pressure changes are repeated several times.

Acknowledgment

The authors would like to express their thanks to Mr. S. Imai, Mr. K. Akaba, Mr. N. Haijima and Mr. T. Maruyama for their kind cooperation in the construction of the apparatus and in the execution of experiments.

References

- [1] Tsuji, S. and Katakura, H., Bull.JSME, Vol.19, No.138(1976), P.1497.
- [2] Tsuji, S. and Katakura, H., Bull.JSME, Vol.21, No.156(1978), P.1015.
- [3] For example: Shinoda, K., Yoeki to Yokaido (in Japanese), 1980, P.109, Maruzen.

Fig. 9 Measured diffusivity of the dissolved air in Fluids B-E.

Fig. 10 Typical change in bubble diameter (2).