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The Viscosity of Dimethyl Silicone Oil and the Concentration of Absorbed Air

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We studied the viscosity behavior of 500 cSt dimethyl silicone oil with considerable concentration of absorbed air. For this purpose, a Couette rheometer with a transparent rotating outer cylinder and a fixed inner cylinder was established, in which the ambient pressure is controlled by a piston–cylinder apparatus. Careful torque calibration and equilibrium examination for the air–silicone–oil mixture were carried out. In the range of ambient pressure from 1 to 5 atm, corresponding to the air molar fraction from 11 to 35%, it was found that viscosity of the silicone oil decreases monotonically as the air concentration increases. The viscosity variation can be explained by the Eyring's model in which the free energy of activation is modified to account for the nonideality of the air–silicone–oil mixture. The excess free energy used to fit the viscosity variation is approximately equal to that used in the Krichevsky–Ilinskaya equation, which accounts for the nonideal solubility of the air–silicone–oil solution. The activation energy in the Arrhenius equation for viscosity–temperature relationship is identified as the activation enthalpy. © 2011 American Institute of Chemical Engineers *AIChE J,* 57: 3299–3304, 2011

Keywords: Couette rheometer, viscosity of dimethyl silicone oil, air absorption, the free energy of activation

Introduction

It is well known that dimethyl silicone oils can absorb considerable amount of air.[1,2] In the previous study,[3] we established a novel piston–cylinder apparatus to measure the solubility of air in dimethyl silicone oils and hydraulic oils. If the air concentration is expressed by the Bunsen solubility (defined below), linear relationship with the ambient air pressure is always obeyed in the pressure range of 0–350 kPa and temperature range of 293–353 K. In terms of the molar fraction, the concentration is well expressed by the Krichevsky–Ilinskaya equation.[4] The results for two dimethyl silicone oils with quite different molecular weight (480 and 15,840 g mol^{-1}) indicate that the air solubility mainly depends on the interaction with the monomers rather than with the relatively large molecules of dimethyl silicone oils.

The background of this work is to study the shear-induced cavitation. This type of cavitation is caused by shear stress. It may occur, e.g., in hydraulic oil, lubricant, and printing ink, where the absorbed light gases come out of the liquid in the form of bubbles at sufficiently high shear stress. As a result, the liquid fractures and the working process are seriously affected.[5,6] On the other hand, in hydrodynamics cavitations of major concern are caused by large pressure drops making the liquid itself vaporize into bubbles. The relatively simple composition, changeable molecular weight, and safety of dimethyl silicone oils with absorbed air provide a model fluid for studying the mechanism of shear-induced cavitation. We established a concentric-cylinder Couette rheometer with a transparent and rotating outer cylinder and a fixed inner cylinder. The ambient pressure is controlled by a piston–cylinder apparatus. The major difficulty of the measurement is that the temperature can not be controlled because of viscous

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heating.[7] Our experiments on dimethyl silicone oils show that the shear-induced cavitation occurred with both the super saturation and under saturation of air concentration at the shear stresses much less than the ambient pressure.[8] This is in sharp contrast with the experiment of Kottke et al.[5] on the polybutene (a Newtonian fluid), in which the shear cavitation occurred at the shear stress approximately equal to the ambient pressure. This indicates that the principal stress criterion for cavitation inception proposed by Bair and coworkers[5] and by Joseph[9] is not directly applicable to the liquids with absorbed light gases.

In our experiments on dimethyl silicone oils, the occurrences of cavitation were always accompanied by sudden drops of the shear stress and temperature.[8] It seems that the shear cavitation is caused by a mechanism in which the liquid tries to reduce its viscosity meanwhile keeping the apparent shear rate (that is, to reduce the rate of energy dissipation). At this stage, this mechanism is still rather ambiguous and we need to know what happens just before the cavitation. It is well known that cavitation is very sensitive to the presence of nucleus of bubbles. So, it is necessary to first investigate variation of the viscosity of dimethyl silicone oils with the concentration of absorbed air and with the temperature before the occurrence of cavitation. In this article, careful measurements of the viscosity of a dimethyl silicone oil done by our research group are presented and Eyring's rate theory based on the free energy of activation is used to explain the variation of viscosity with the concentration of absorbed air. For many practical applications, it is important to obtain reliable data of the viscosity of dimethyl silicone oils (e.g., see Barry[10]). In rheological measurement, it is a common practice to use silicone oil as a standard fluid to calibrate rheometer.[11] However, very few have noticed that the viscosity of silicone oils may considerably be affected by the absorbed gas, that is, by the equilibrium ambient pressure.

Experimental Setup and Material

As shown in Figure 1, the established Couette rheometer consists of a set of electric motor, torque transducer and processor, a pair of concentric cylinders with the rotating outer one made of transparent epoxy and the fixed inner one made of black nylon, a piston–cylinder apparatus equipped with a pressure transducer to control the ambient pressure between the concentric cylinders, a temperature transducer mounted at the middle of the inner cylinder wall, and a computer to communicate and process the data. The adoption of rotational outer cylinder and fixed inner one guarantees that the flow in the working section remains simple shearing, i.e., the so called Couette flow, even at high Reynolds numbers. In the Couette flow, shearing is driven by the relative displacement of walls, rather than by pressure gradient, so the pressure is uniform and equal to the ambient pressure.[2] The inner diameter of the outer cylinder is 139 mm and the gap between the cylinders is 0.3 mm or 0.5 mm in the working section. The relatively large radii of the cylinders and small gap make high shear rates realizable provided the fluid's viscosity is sufficiently low. By axially moving the piston in the pressure control apparatus using the hand wheel (Figure 1), the ambient pressure can be changed from 0.1 to 6 atm. The temperature transducer has the step-response time of 0.2 s and monitors in situ the temperature variation of the fluid in the working section. The scheme of rotational outer cylinder and static inner cylinder demands much of the dynamic sealing of the rheometer, technical details of the procedures that realize a perfect sealing of the Couette rheometer were reported by Guo et al.[7]

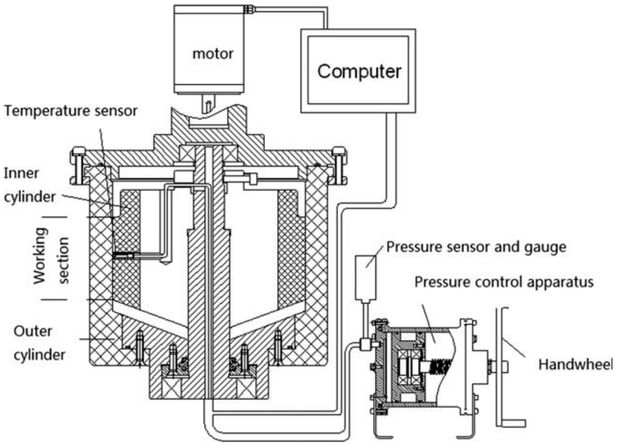

Figure 1. Schematic representation of the established Couette rheometer.

The dimethyl silicone oil studied in this work is named by 500 cSt silicone oil; its density is 970 kg m^{-3}. Based on its brand kinematical viscosity (500 cSt), the molecular weight of 15,840 g mol^{-1} is estimated by using Barry's formulas,[10] from which the molar volume is 1.6 L mol^{-1}.

Torque calibration

When rotating, the torque produced by the working section of the Couette rheometer is as given:

$$M_{\mathrm{w}} = \frac{\eta n (\pi d)^2 L d}{2\delta} \tag{1}$$

where n denotes the rotation speed, d is the inner diameter of the outer cylinder, L is the axial length of the working section, and δ is the gap of the working section between the inner and outer cylinders. Given the torque of the working section, M_{w}, the viscosity, η, can be calculated by Eq. 1. The silicone oil in the parameter range of this study (the ambient pressure from 1 to 6 atm and the temperature from 15 to 50°C) is an incompressible Newtonian fluid. Thus, the viscosity is independent of the shear rate and the pressure (Figure 2b). In this study, the rotational speed of the outer cylinder was fixed to 250 r min^{-1} corresponding to the shear rate of 3660 s^{-1}.

What the computer collects directly is the output torque of the motor, M_{m}, which contains the contributions from the flow resistance in the working section, M_{w}, from the flow resistance in the upper and lower sections, M_1, and the mechanical friction torque, M_f. The friction torque was obtained by making the rheometer work without liquid in it and was found to increase linearly with the ambient pressure,

$$M_f = 0.00083p + 0.172 \tag{2}$$

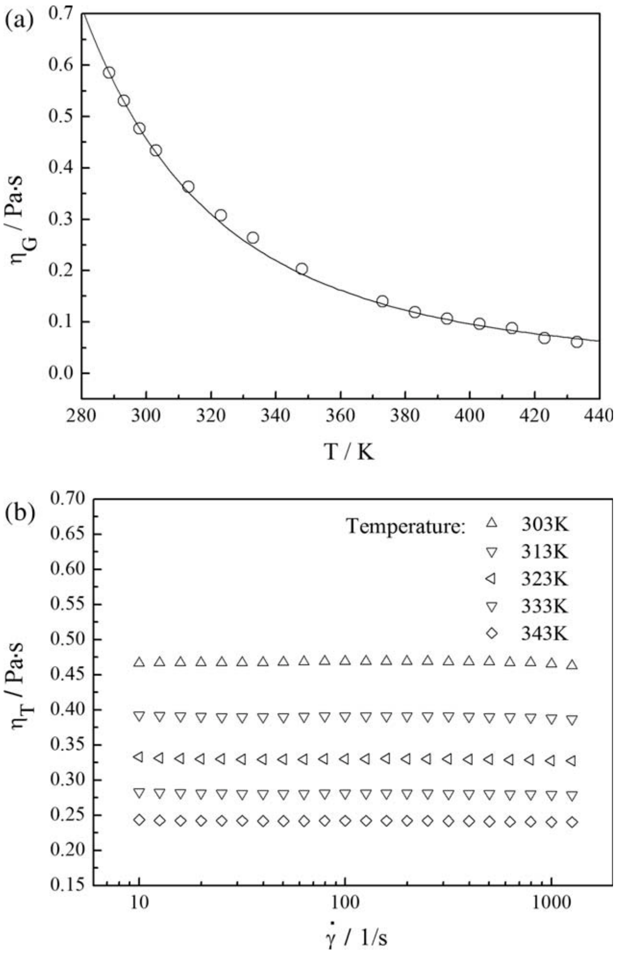

Figure 2. (a) Viscosity of 500 cSt dimethyl silicone oil vs. the temperature, measured by Gemini-200 rheometer at the atmospheric pressure; (b) viscosity of the silicone oil vs. the shear rate, measured by AR-GII rheometer at the atmospheric pressure.

in which M_f is in N·m, and p is in kPa. The maximum error of Eq. 2 is about 2%.

We measured the viscosities of the 500 cSt silicone oil at the pressure of 1 atm by using the commercial rheometer Gemini-200 (Bohlin) with the cone–plate fixture for the shear rates from 1 to 50 s^{-1} and the temperatures from 285 to 433 K, and using the commercial rheometer AR-GII (TA) with the concentric-cylinders fixture for the shear rates from 10 to 1200 s^{-1} and the temperatures from 303 to 343 K. It should be emphasized that the Gemini or AR-GII rheometer has accurate temperature control (±0.1 K) and torque measurement but no pressure control, so they are not appropriate for studying the variation of viscosity because of absorbed air. The viscosities measured by the two rheometers have a systematic difference of 0.02 Pa s. As shown in Figure 2, the silicone oil's viscosity is confirmed to be independent of the shear rate but strongly dependent on the temperature. The viscosity–temperature relationship can be well fitted by the Arrhenius equation:

$$\eta_G = Ae^{E/RT},\ \ A = 0.0009\,\text{Pa s},\ \ E = 15530\,\text{J mol}^{-1} \qquad (3)$$

where η_G denotes the steady viscosity measured by the Gemini rheometer at the atmospheric pressure, T is the absolute temperature, R the gas constant, and E is usually called as the activation energy.

In the Couette rheometer, flow in the working section is a simple shearing, so the viscosity is calculated by using Eq. 3 and the torque produced by the working section, M_w, can be obtained by using Eq. 1. Then the torque produced by the upper and lower sections, M_1, is got by deducting the friction torque and the working section torque from the motor output torque, M_m. By starting 250 r min^{-1} rotation of the outer cylinder, the temperature of silicone oil in the working section rose quickly because of viscous heating and poor heat conductivity of the inner and outer cylinder walls. However, the working section has a narrow gap and large aspect ratio, so the temperatures of silicone oil in the upper and lower sections, hence their viscosities, should keep their original values provided the viscosity measurement did not take very long time. Actually, measurements at the initial room temperature of 296 K (the equilibrium temperature) and the ambient pressure of 1 atm showed that M_1 changed from 0.21 to 0.23 N m as the fluid temperature in the working section increased from 296 to 323 K. Taking the mean value of 0.22 N m for M_1, the relative error with respect to M_w is <1%. At the ambient pressure other than 1 atm, the incompressibility implies that the flow field does not change due to any changes of the boundary pressure. So, we took $M_1 = 0.22$ N m in the measurement by fixing the equilibrium temperature $T_e = 296$ K and the rotational speed $n = 250$ r min^{-1}, and write

$$M_w(T, x_2(p, T_e)) = M_m(T, x_2(p, T_e)) - M_1 - M_f(p) \qquad (4)$$

where T is the fluid temperature in the working section, p is the ambient pressure, x_2 is the molar fraction of air absorbed in the silicone oil. The expression $x_2(p,Te)$ emphasizes that the molar fraction of absorbed air is determined by the equilibrium temperature and ambient pressure, and the ambient pressure has no direct effect on the torque of the working section. The equilibrium temperature T_e is different from the fluid temperature T in the working section, which is rising during the viscosity measurement.

Equilibrium air absorption of the silicone oil

We have measured the volume variations because of a step change of the ambient pressure and after the equilibrium of air absorption in the Couette rheometer. It was filled with 500 cSt silicone oil up to the middle of the working section; taking the advantage of narrow gap between the concentric cylinder-pair (0.5 mm), the location of liquid's free surface was very sensitive to small changes of the liquid's volume. In the range of ambient pressure from 1 to 5 atm, it was found that the relative volume changes caused by a step change of the ambient pressure or by the later air absorption were both less than 0.0027. So, the variations of the oil's volume could be neglected and the incompressibility approximation is valid.

In our previous work,[3] the relationship between the ambient pressure, the temperature, and the equilibrium concentration of air absorbed in the 500 cSt silicone oil was studied by using a piston–cylinder apparatus. The apparatus was

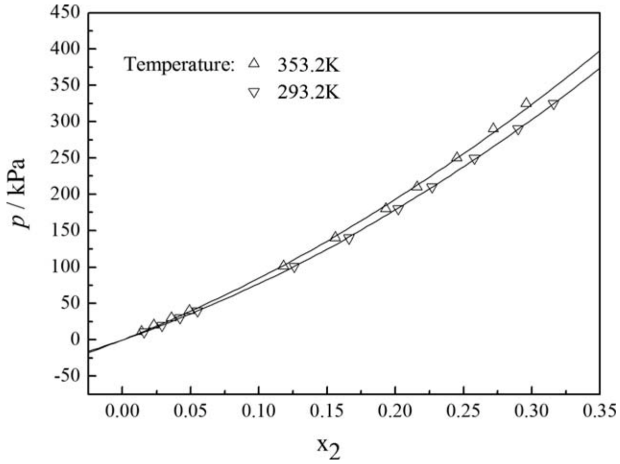

Figure 3. Ambient pressure vs. the equilibrium molar fraction, x_2, of air in the 500 cst silicone oil at two temperatures.

immersed in a heat bath; the cylinder was partially filled by the silicone oil and partially by air; the piston's position was adjusted constantly for a preset pressure. When a new equilibrium of air absorption was reached for the assigned pressure and temperature, the change of the gas's volume was determined by the initial and final positions of the piston. Using the equation of state for ideal gas (for air $p < 600$ kPa and $T > 273$ K), the amount of air absorbed in the silicone oil was determined. The Bunsen solubility is defined as follows:

$$\delta = V_a / V_T \tag{5}$$

where V_a is the volume of gas dissolved in liquid, reduced to the standard state ($p = 101.3$ kPa and $T = 273$ K), and V_T is the volume of the liquid at the temperature of measurement. Our measurements indicate that the Bunsen solubility of air in the 500 cSt silicone oil is proportional to the equilibrium ambient pressure, and it decreases as the temperature increases, and can be expressed by the following equation:

$$\delta = 0.084 e^{250.8/T} p / p_1 \tag{6}$$

where p_1 is equal to 101.3 kPa and T is the absolute temperature. The molar fraction of air with the mean molecular weight of 29 g mol^{-1} is related to the Bunsen solubility by the following equation:

$$x_2 = \frac{\delta \times V_T / V_{\mathrm{air}}}{V_T / V_{\mathrm{sil}} + \delta \times V_T / V_{\mathrm{air}}} = \frac{\delta}{1.371 + \delta} \tag{7}$$

where V_{air} and V_{sil} denote the molar volume of air and silicone oil, respectively, at the standard state, separately. In terms of the molar fraction of air, the solubility can be well fitted by the Krichevsky–Ilinskaya equation,[4] as shown in Figure 3,

$$\ln \frac{p}{x_2} = \ln H_{2,1}^{(p_1^s)} + \frac{A}{RT}(x_1^2 - 1) + \frac{v_2^{-\infty}(p - p_1^s)}{RT} \tag{8}$$

where x_1 and x_2 are the molar fraction of the solvent and solute, respectively; $H_{2,1}^{(p_1^s)}$ is the Henry's constant at the vapor pressure p_1^s; A is an empirical energy constant and depends weakly on the temperature (-2000 J mol^{-1} at 293.2 K and -2200 J mol^{-1} at 353.2 K, according to the fitting of experimental data); $A(x_1^2 - 1)/RT$ is the nonideality correction to the Henry's law, that is, the variation of the activity coefficient of solute; $v_2^{-\infty}$ is the partial molar volume of solute at infinite dilution. As volume change of the solution because of the air absorption is negligible, the term $v_2^{-\infty}(p - p_1^s)/RT$ can be neglected.

In our experiment, to judge whether the air absorption reached equilibrium, the ambient pressure was checked and adjusted frequently to keep it assigned value. This method took very long time to reach equilibrium in the Couette rheometer because of the low diffusivity of air in silicone oils (approxiamtely 5×10^{-5} cm^2 s^{-1} at 303 K as measured by using a cylinder–piston apparatus); e.g., for a step change of the ambient pressure from 1 to 2 atm, the equilibrium process required 4 days. However, given a target pressure, from the known Bunsen solubility of air in silicone oil (Eqs. 5 and 6), the amount of air that need to be absorbed to reach to a new equilibrium in the Couette rheometer can be calculated before the viscosity measurement. To accelerate the air dissolution, we first adjusted and kept the ambient pressure to a pressure considerably higher than the target pressure and slowly rotated the outer cylinder, and monitored the air absorption. When the required amount of air absorption was reached, the ambient pressure was quickly reduced to the target one. In this way, the dissolution time for the change of ambient pressure from 1 to 2 atm was reduced to about 2 days.

Experimental Results and Modeling

When an equilibrium state of air absorption of the 500 cSt silicone oil was reached in the Couette rheometer, we started viscosity measurement by using rotational speed of 250 r min^{-1} of the outer cylinder (the shear rate $\dot{\gamma} = 3660$ s^{-1}). The temperature of silicone oil in the working section increased with the time because of viscous dissipation and low heat conductivity of the outer and inner cylinder walls. The temperatures of silicone oil and the output torques were collected synchronously by the computer. After implementing torque correction, the variation of viscosity of silicone oil with the increasing temperature at an ambient pressure corresponding to a certain air molar fraction was obtained. Experiments of 500 cSt silicone oil at six ambient pressures (1, 1.5, 2, 2.5, 3, and 4 atm) were carried out and the data were interpolated for five temperatures from 303 to 323 K, the results are shown in Figure 4. One can see that, at a certain temperature, the viscosity of silicone oil decreases monotonically as the air molar fraction increases from 11 to 35%, and the decreasing of viscosity is uniform with respect to different temperatures. The maximum reduction of viscosity is about 15%.

To explore the mechanism of viscosity reduction caused by air absorption, we consider the classical Eyring's rate theory for liquids,[2,12] in which the work done by the shear stress is consumed to change the energy barrier for molecules to "jump" from equilibrium positions to "holes." In this, model liquid's viscosity is closely related to the free energy of activation,

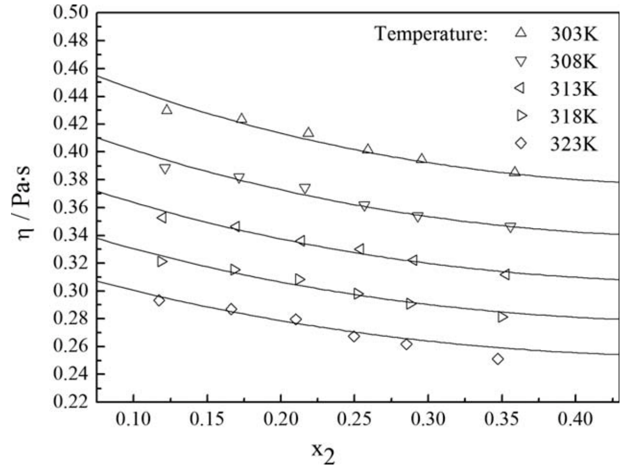

Figure 4. Viscosity of 500 cSt silicone oil vs. the air molar fraction x_2; the solid lines are the fitting by using Eq. 12.

$$\eta = \frac{Nh}{V} e^{\Delta F_0^{\ddagger}/RT} \tag{9}$$

where N denotes the Avogadro number, h the Planck constant, V is the molar volume of liquid, R the gas constant, and T is absolute temperature; $\Delta F_0^{\ddagger}$ is the Gibbs free energy of activation of the liquid. Here $\Delta F_0^{\ddagger}$ is not equivalent to the activation energy E appeared in Eq. 3, the difference lies in the entropy of activation. As the variation of molar volume of the 500 cSt silicone oil because of air absorption is negligible, we can take $V = 16.3$ L mol^{-1} from its density and molecular weight. The viscosity of gaseous air is about three orders of magnitude smaller than that of 500 cSt silicone oil. If the mixture of air–silicone–oil is ideal, the mixture rules, such as proposed in Ref. [12], cannot produce considerable changes of the viscosity found in our experiment. Thus, we have to consider the nonideality of the air–silicone–oil mixture, which is characterized by the excess Gibbs free energy (e.g., see Prausnitz et al.[4]). The simplest model of excess Gibbs free energy g^{E} is given by the following equation:

$$g^E = Ax_1x_2 \tag{10}$$

where x_1 and x_2 are the molar fraction of solvent and solute, respectively, and A is a empirical energy constant and weakly dependent on the temperature. Thus, we can modify the Erying's model as follows:

$$\eta = \frac{Nh}{V} e^{\frac{\Delta F_0^{\ddagger} + Ax_1x_2}{RT}} = \frac{Nh}{V} e^{\frac{\Delta F_0^{\ddagger} + A(1-x_2)x_2}{RT}} \tag{11}$$

Table 1. Fitting Parameters for the Viscosity Vs. the Molar Fraction of Air by Using Eq. 12

T (K)	303	308	313	318	323
A (J mol^{-1})	−2600	−2700	−2800	−2850	−2900
B	−0.715	−0.817	−0.915	−1.01	−1.115

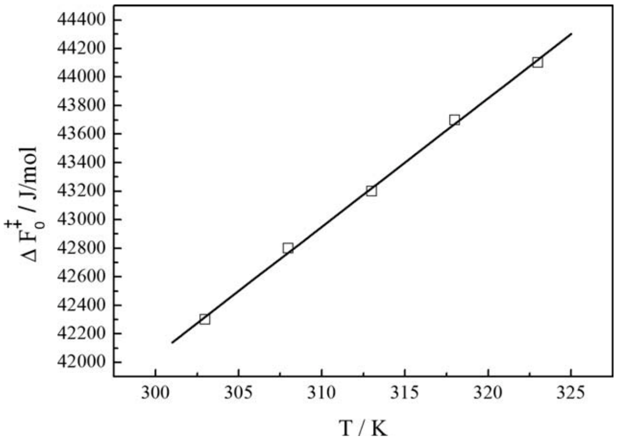

Figure 5. Linear relationship between the free energy of activation and the temperature.

According to this model, the logarithm of viscosity has a quadratic dependence on the molar fraction of solute:

$$\ln \eta = B + C(x_2 + x_2^2) \tag{12}$$

where $B = \ln(Nh/V) + \Delta F_0^{\ddagger} / RT$, $C = A/RT$. For each temperature, we fitted the experiment data of lnη vs. x_2, the results are shown in Figure 4 and the parameters are listed in Table 1; average error of the fitting is ~2.3%. The energy constant A determined by viscosity variation is from −2600 J mol^{-1} at 303 K to −2900 J mol^{-1} at 323 K, which are approximate to the energy constant determined by the air solubility using the Krichevsky–Ilinskaya equation, where $A =$ −2000 J mol^{-1} at 293.2 K and −2200 J mol^{-1} at 353.2 K. The negative values of the energy constant indicate that the interaction between the air and silicone oil molecules is attractive.

The Gibbs free energy of activation consists of the activation enthalpy $\Delta H^{\ddagger}$ and the activation entropy $\Delta S^{\ddagger}$:

$$\Delta F_0^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \tag{13}$$

From the values of B listed in Table 1, the free energy of activation $\Delta F_0^{\ddagger}$ was calculated. As shown in Figure 5, $\Delta F_0^{\ddagger}$ vs. T is linear in our experimental temperature range, thus it can be deduced that the activation entropy $\Delta S^{\ddagger} = -90$ J mol^{-1} K^{-1} and the activation enthalpy $\Delta H^{\ddagger} = 15{,}050$ J mol^{-1} are constant in this temperature range. When compared with Eq. 3, where the Arrhenius expression for the viscosity–temperature relationship of 500 cSt silicone oil at 1 atm is obtained by Gemini-200 rheometer, the activation energy $E = 15{,}530$ J mol^{-1} that should be identified as the activation enthalpy.

Conclusions and Discussion

The viscosity of 500 cSt dimethyl silicone oil with considerable air absorption has been measured by using a specially established, carefully calibrated Couette rheometer, in which the concentration of absorbed air was determined by controlling the ambient temperature and pressure for long enough time. The viscosity does not depend on the shear rate but depends strongly on the temperature and also considerably on the concentration of absorbed air. In the range of our measurement, the viscosity decreases as the concentration of absorbed air increases. The viscosity behavior can be explained by Eyring's rate-process theory in which the free energy of activation is modified to account for the nonideality of the air–silicone–oil solution. The excess Gibbs free energy used to predict the viscosity variation is the same as that used in the Krichevsky–Ilinskaya equation, which account for the nonideal solubility of the air–silicone–oil solution. The activation energy in the Arrhenius equation for viscosity–temperature relationship is identified as the activation enthalpy.

The cavitation theory proposed by Bair and coworkers[5] and by Joseph[9] states that when the shear stress of Newtonian fluids approximates the ambient pressure, one of the principal stresses switches from negative to positive (from compression to extension), and because there are always defects in the liquid, such as contaminants, gas nuclei etc., the liquid cannot stand the extension and cavitation will occur. Under the experimental conditions of this article, no cavitation was observed. However, by applying higher rotational speed, say $n = 500$ r min^{-1}, visual cavitation was easily observed but at the shear stress much less than the ambient pressure. This implies that Bair/Joseph's cavitation criterion should be modified to take into account the air solubility at dynamic conditions. At this stage, we are carrying out relevant experiments on the silicone oil and exploring any peculiar behavior of the viscosity and the activation free energy just before the inception of cavitation.

Acknowledgments

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