



Assessing Validity of Diffusion Controlled Model in Acid Neutralization of Lubricant Oil

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Abstract: Engine corrosion has been a long prevalent problem which is further aggravated by acids produced during combustion of fuels. Sulphur containing fuels produce sulphuric acid which must be neutralized in order to prevent corrosion at the engine cylinder lining and piston rings. In order to prevent this corrosion, lubrication oil used in combustion engines contains basic additives like CaCO_3 -based reverse micelles for neutralizing the acid produced. The mechanism and rate limiting step in the reaction between acid droplets and basic reverse micelles has long been a subject of study. Literature on sulphuric acid droplets neutralization speculates that diffusion of micelles towards the acid droplet is the rate limiting step. However, through this research, we have proved that a diffusion-controlled mechanism alone is not applicable. This has been done by studying various capillary video microscopy experiments on sulphuric, nitric and acetic acid. To prove the invalidity of a diffusion-controlled mechanism, we have assessed the diffusion coefficient and the viscosity at different temperature. Models for finding the diffusion coefficient & viscosity are based on Fick's law and Stokes Einstein equation respectively. The obtained viscosity from assuming a diffusion-controlled model is compared to observed viscosity (actual viscosity) in lubricant oil to measure deviation of diffusion-controlled model from actual neutralization kinetics. Finally, we have hypothesized alternative reaction mechanisms to explain the considerable deviation found in viscosity values.

Keywords: Acid Droplet Neutralization, Diffusion-Controlled Kinetics, Acid Droplet Neutralization, Lubricant Oil, Maritime Diesel Engines

1. Introduction

Maritime diesel engines use Sulphur containing fuels which on combustion produce Sulphuric acid. The acid produced must be neutralized in order to prevent corrosion at the engine cylinder lining and piston rings [10]. On similar lines, ethanol containing gasoline produces acetic acid on combustion which must be neutralized in order to prevent corrosion [1]. Hence, lubrication oil for combustion engines contains basic additives like CaCO_3 -based reverse micelles to neutralize the acids produced during combustion. The mechanism of interfacial reaction between the acid droplets (micrometer scale radius) and alkaline reverse micelles (nanometer scale radius) can be broken down into following four steps:

Step 1: Collision of the acid droplet and reverse micelle due to diffusion

Step 2: After a successful collision, the reverse micelles

adsorb to the acid interface

Step 3: After adsorption, a channel forms and acid & CaCO_3 react by the transferring of the acid into the reverse micelles.

Step 4: The acid products (placed in the reverse micelle) desorb from the droplet interface

In addition to interfacial reaction, in the case of acetic acid, it has been proved that the acid molecules escape the droplet and additional neutralization takes place in the bulk of the lubricant oil. However, this phenomenon is absent in the case of sulphuric acid.

For recording the acid droplet radius dependence on time, a capillary video microscopy system is used. On the basis of these experiments, several models have been proposed to represent the kinetics of acid and lube oil mixtures which assume different steps to be rate

determining. For sulphuric acid neutralization, it was proposed that diffusion is the rate limiting step and the role of other steps in kinetics was neglected [7]. Another supporting argument for diffusion-controlled mechanism is inferred from results obtained from sulphuric acid neutralisation by Jianzhong Fu, Yunfeng Lu, Curt B. Campbell, Kyriakos D. Papadopoulos [6]. The droplet radius values obtained if plotted as R^2 vs t at 25°C , gives a straight-line curve which is in coherence with diffusion-controlled model.

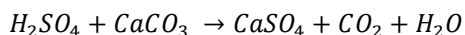
In this report, the main aim is to check the validity of a diffusion-controlled model in which diffusion (step 1) is the rate determining step (i.e. one can assume that all other steps happen instantaneously). For this, we have calculated the diffusion coefficient by assuming the neutralization for different acid and lube mixtures to be diffusion controlled. Further, the viscosity is calculated from the diffusion coefficients at different temperature using Stokes Einstein equation. This obtained viscosity is compared to observed viscosity (actual viscosity) in lubricant oil to measure deviation of diffusion-controlled model from actual neutralization kinetics.

2. Experiment

In order to observe the acid neutralization with time and temperature, a capillary video microcopy system is setup. A single acid droplet is injected into an oil filled channel using a specially prepared micropipette. The neutralization starts immediately on contact and the entire process is filmed [11]. Thus, dependence of acid droplet radius with time can be plotted using this experimental setup at different temperatures. In this report, radius versus time plots from capillary video microscopy experiments have been used for three different acids- sulphuric acid, acetic acid and nitric acid in order to model the neutralization mechanisms [4]. The corresponding lubricant oil in the experiments is defined on the basis of its base number (BN). Base number, also called total base number, is defined as the amount of milligram of KOH equivalent to the base content in 1 gram of an oil sample [14]. In all experiments, the density of lubricant oil is taken as 0.93 g/cm^3 .

2.1. Sulphuric Acid Neutralization

The reaction of Sulphuric acid neutralization by CaCO_3 reverse micelles is as follows:



The Sulphuric acid used in the experiments was 50% in volume (9.33 mol/l) while the lubricant oil used was 70 BN (0.581 mol/l). The capillary experiment was performed 4 times with different initial radius at 25° , 100° , 130° and 170° . At 25° , the acid droplet with $R_0=71.44 \mu\text{m}$ took about 2 hours to neutralize. At 100° , the acid droplet with $R_0=76.45 \mu\text{m}$ took about 1 minute to neutralize. At 130° , the acid droplet with $R_0=58.30 \mu\text{m}$ took about 20 seconds to

neutralize. At 170° , the acid droplet with $R_0=43.55 \mu\text{m}$ took about 4 seconds to neutralize [6]. Here R_0 is the initial radius of the acid droplet (i.e. at $t=0$).

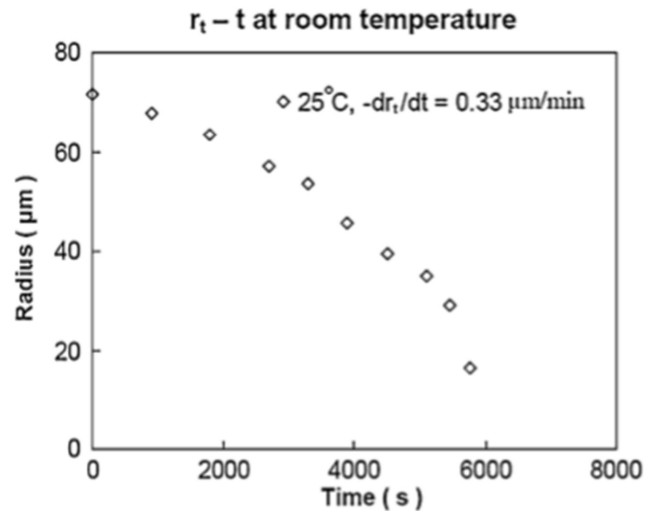


Figure 1. Sulphuric acid (9.3mol/l) droplet radius with time at 25°C in 70 BN lube oil [6].

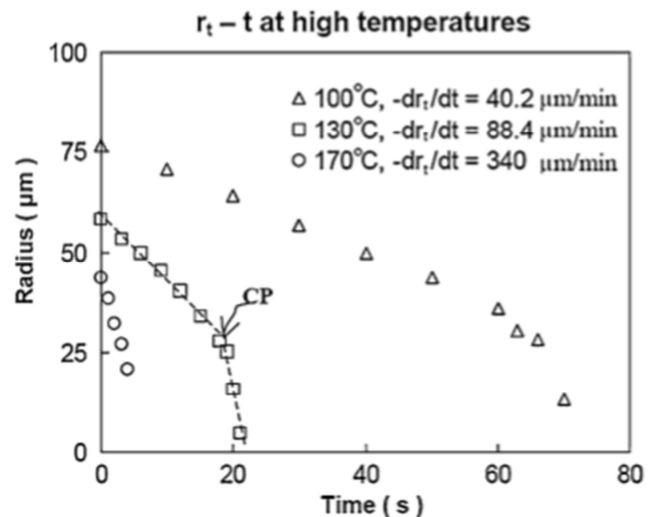
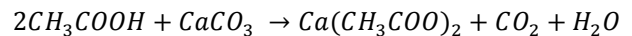


Figure 2. Sulphuric acid droplet (9.3mol/l) radius with time at 100, 130 and 170°C [6] in 7.

2.2. Acetic Acid Neutralization

The reaction of acetic acid neutralization by CaCO_3 reverse micelles is as follows:



The pure acetic acid used in the experiments had molarity 17.5 mol/l while the lubricant oil used was 13.1 BN (0.1087 mol/l). The capillary experiment was performed 3 times with same initial radius of $40 \mu\text{m}$ at 25°C , 50°C and 70°C . At 25° , the observed initial droplet shrinking rate (dR/dt) is $-0.35 \mu\text{m/s}$. At 50°C , the observed initial droplet shrinking rate (dR/dt) is $-0.69 \mu\text{m/s}$. At 70°C , the observed initial droplet shrinking rate (dR/dt) is $-1.49 \mu\text{m/s}$ [2].

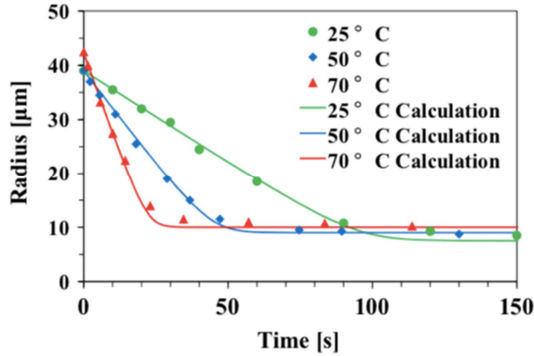


Figure 3. Acetic acid (17.5 mol/l) droplet radius with time at 25, 50 and 70°C in 13.1 BN lube oil [2].

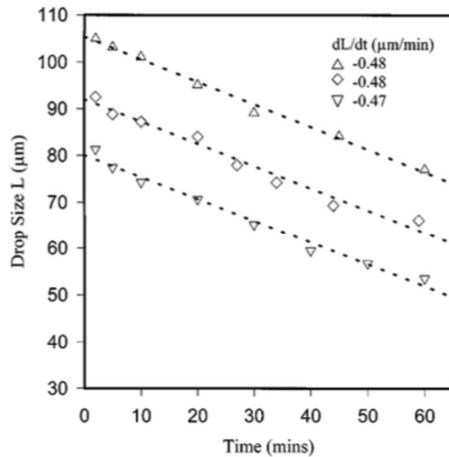
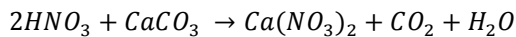


Figure 4. Nitric acid (15.6 mol/l) droplet radius with time at ambient temperature [3] in 70 BN lube oil.

2.3. Nitric Acid Neutralization

The reaction of nitric acid neutralization by CaCO_3 reverse micelles is as follows:



The nitric acid used in the experiments had molarity 15.6 mol/l while the lubricant oil used was 70 BN (0.581 mol/l). In this experiment, the acid droplet was not a perfect sphere, but instead it deformed to become an ellipsoid. Hence, the largest axial dimension (l) was recorded with time rather than the radius (like in 2.1 and 2.2). The capillary experiment was performed 3 times with different initial largest axial dimension of 105, 90 and 80 μm at the ambient temperature. In all the three experiment, the initial droplet shrinking rate (dl/dt) was same and equal to 0.48 $\mu\text{m}/\text{min}$ [3].

3. Method

3.1. Diffusion Coefficient

The main objective of this publication is to check the applicability of a diffusion-controlled model which assumes all steps other than diffusion to happen instantaneously. For this diffusion-controlled model, we have calculated the diffusion coefficients using Pilling and Seakins as reference [9].

3.1.1. Deriving Diffusion Coefficient Using Fick's Law

Assume a single cell X at the center in an environment of cell Y and the solvent. On this setup, the flux (mol/s) of Y is given by [15]:

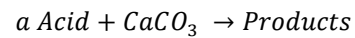
$$J = 4\pi r[Y]D \quad (1)$$

Where [Y] is the bulk concentration of Y

r is the sum of radius of X and Y (=radius of X if $r_X \gg r_Y$)

D is the diffusion coefficient

Therefore, during the neutralization of acid droplet by reverse micelles containing lubricant oil, the flux of CaCO_3 is given by (1). The concentration of CaCO_3 (defined as [B]) is derived from the base number of the lubricant oil. The reaction for "a" molecules of acid neutralization by CaCO_3 is given as under. Note that in the case of sulphuric acid, "a" is 1 whereas it is 2 for acetic and nitric acid.



Further, by considering instantaneous reaction and adsorption, we equate the flux of CaCO_3 to the rate of consumption of acid which is given as follows. Here n_{acid} represents the number of moles of acid in the droplet.

$$\frac{1}{a} \frac{dn_{\text{acid}}}{dt} = 4\pi r[B]D$$

n_{acid} can also be obtained by the product of molarity (defined as [A]) and volume of acid droplet. Therefore,

$$\frac{1}{a} \frac{dn_{\text{acid}}}{dt} = \frac{1}{a} 4\pi r^2 \frac{dr}{dt} [A] = 4\pi r[B]D$$

$$\Rightarrow \frac{r \frac{dr}{dt} [A]}{a[B]} = D \quad (2)$$

3.1.2. Diffusion Coefficient Calculation from Capillary Experiment Observations

From (2), we can conclude that the product of acid droplet radius (r) and droplet shrinking rate (dr/dt) must remain constant in a diffusion-controlled mechanism (given that $\Delta[B] \sim 0$). From the capillary experiments, we can get the value of r and dr/dt at different times. However, the value of [B] is known only at the initial condition (through BN of lube oil). Thus, the diffusion coefficient has been calculated at time t=0 for all capillary experiments.

3.2. Viscosity

The diffusion coefficients obtained through (2) have been used to calculate the corresponding lubricant oil viscosity using the Stokes Einstein relation for Brownian motion. Comparing the calculated viscosity with actual viscosity gives us a measure of the deviation of actual neutralization rate from that obtained by assuming diffusion-controlled mechanism [8].

3.2.1. Stokes-Einstein Equation for Viscosity

The viscosity of lubricant oil at different temperatures from the diffusion coefficient can be calculated using (3) [12].

$$D = \frac{k_B T}{6\pi\eta(T)R_L} \quad (3)$$

Where k_B is the boltzman constant

T is the absolute temperature

$\eta(T)$ is the viscosity of lubricant oil at temperature T

R_L is the radius of calcium carbonate reverse micelle

The radius of calcium carbonate reverse micelle is reported between 1.5 and 10 nm. For our calculations of viscosity, we have assumed the radius as 5 nm.

3.2.2. Uncertainty in Viscosity Calculated Using Stokes Einstein Equation

Since viscosity is calculated using (3), error may arise from deviation in value of diffusion coefficient D and radius of reverse micelles R_L (assuming thermal equilibrium). In D, which is calculated using (2), the variable which may cause substantial error is bulk concentration of limestone, [B]. The general assumption is that lubricant oil has limestone in excess (compared to sulphuric acid) and its concentration is assumed to be constant with time. However, since we are calculating diffusion coefficient at time $t=0$, the above assumption is not required for the calculation and hence error due to [B] will not be reflected in our model.

The radius of the reverse micelles was chosen as 5 nm, however, radii between 1.5 and 10 nm are reported. When the radius of the reverse micelles gets lower, the corresponding viscosity, may increase by a factor of as high as 3 (1.5 nm versus the 5 nm used for the calculations given here).

3.2.3. Uncertainty in Viscosity Calculated by Sautermeister and Priest at High Temperatures

As mentioned above, the actual viscosities used for comparison (section 5.1) are from the work of Sautermeister

and Priest [8] who calculated the viscosities as a function of temperature for paraffinic base oil (HVI160B) [13]. Viscosities were measured using a Malvern “Kinexus” Rheometer with cone on plate arrangement. In their publication, they have reported a potential error (through error bars) of about $\pm 30\%$ for HVI160B base oil at 150°C .

4. Results

4.1. Diffusion Coefficient

Section 3.1 explains the methodology to calculate diffusion coefficients using capillary experiments (section 2). The molarity and experimental values for different acid and lubricant mixtures is stated in section 2 of this report. In the following tables 1-3, we have shown the results for calculated diffusion coefficients at the initial condition ($t=0$) for different temperatures. Figure 5 presents the results of section 4.1.1-4.1.3 graphically wherein diffusion coefficients are plotted on the y axis (logarithmic) with temperature on the x axis (linear).

4.2. Viscosity

Section 3.2 explains the methodology to calculate viscosity using capillary experiments (section 2). In the following sections tables 1-3, we have also shown the results for calculated viscosity at the initial condition ($t=0$) for different temperatures by using the diffusion coefficients obtained in section 4.1. Figure 6 presents the results of table 1-3 graphically wherein viscosities are plotted on the y axis (logarithmic) with temperature on the x axis (linear).

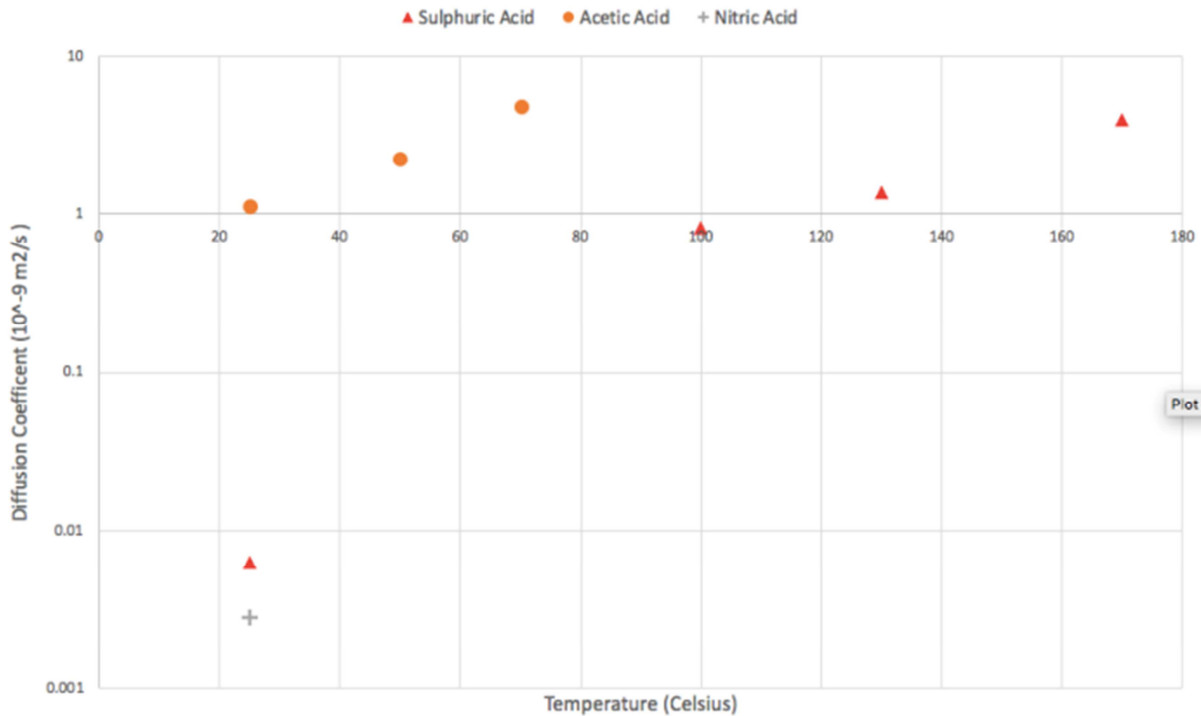


Figure 5. Diffusion coefficients with temperature calculated for different acid/lube oil mixtures using capillary experiments at $t=0$.

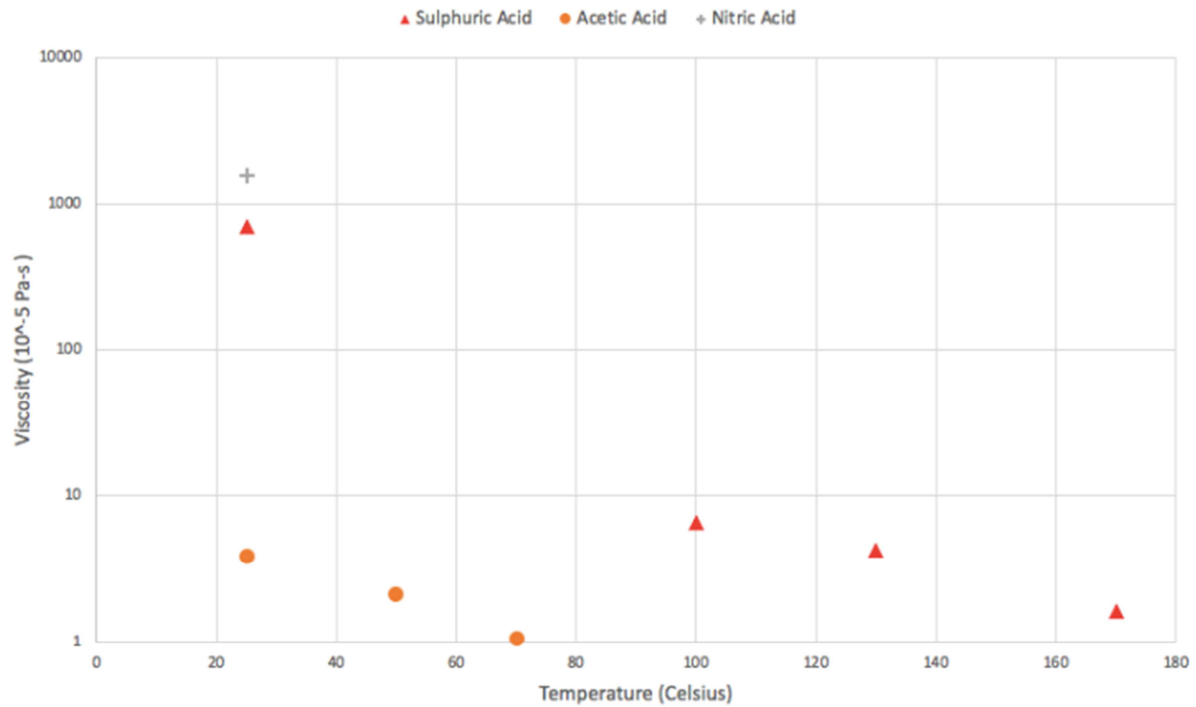


Figure 6. Viscosity of lubricant oil with temperature calculated using capillary experiments at $t=0$.

Table 1. Sulphuric Acid {Refer to section 2.1 for experiment}.

Temperature T (°C)	25	100	130	170
Diffusion Coefficient D (10^{-9} m ² /s)	0.0063	0.820	1.379	3.962
Viscosity (10^{-5} Pa-s)	693.25	6.643	4.283	1.638

Diffusion coefficient of CaCO₃ reverse micelle & Viscosity of lubricant oil (at $t=0$) calculated using capillary experiment [6]

Table 2. Acetic Acid {Refer to section 2.2 for experiment}.

Temperature T (°C)	25	50	70
Diffusion Coefficient D (10^{-9} m ² /s)	1.126	2.221	4.797
Viscosity (10^{-5} Pa-s)	3.878	2.134	1.047

Diffusion coefficient of CaCO₃ reverse micelle & Viscosity of lubricant oil (at $t=0$) calculated using acetic acid droplet capillary experiment [2]

Table 3. Nitric Acid {Refer to section 2.3 for experiment}.

Temperature T (°C)	Ambient Temperature (assumed 25°C)
Diffusion Coefficient D (10^{-9} m ² /s)	0.00279
Viscosity (10^{-5} Pa-s)	1562.6

Diffusion coefficient of CaCO₃ reverse micelle & viscosity of lubricant oil (at $t=0$) calculated using nitric acid droplet capillary experiment [3]. The ellipsoid has been considered to be a sphere with diameter equal to largest axial dimension. The below table gives the diffusion coefficient for the case where initial largest axial dimension is equal to 105 μ m.

Table 4. Far Deviated Viscosity Values Obtained.

Temperature T (°C)	25	100	130	17
η_{actual} (Pa-s)	0.195	0.014	0.0066	0.0028
η_{calc} (10^{-5} Pa-s)	693.25	6.643	4.283	1.638
$\frac{\eta_{calc}}{\eta_{actual}}$	0.0355	0.00474	0.00648	0.00585

5. Conclusion

5.1. Far Deviated Viscosity Values Obtained in Section 4.2

Comparing viscosities obtained in section 4.2.1 for sulphuric acid with actual viscosity values from work of Sautermeister and Priest [8], we can check the validity of our diffusion limited model. The following table 4 gives the actual viscosity values (η_{actual}) of lubricant oil at 25°C, 100°C, 130°C and 170°C. It also states the obtained viscosities for sulphuric acid in section 4.2.1 (η_{calc}) again. Further, the ratio $\eta_{calc}/\eta_{actual}$ has been calculated. This shows us that η_{calc} is just 3% of η_{actual} at 25°C and approximately 0.5% of η_{actual} at 100-170°C.

5.2. Assessing the Validity of a Diffusion-controlled Model

From section 3.2.2 and 3.2.3, the value of $\frac{\eta_{calc}}{\eta_{actual}}$ (taking into account uncertainty in calculation of η_{actual} and η_{calc}) should not vary by more than a factor of 5 than that calculated in section 5.1. Taking this uncertainty into consideration, the ratio is still far off from 1 and hence, we can say that a diffusion-controlled mechanism as such is not applicable.

In order to obtain $\frac{\eta_{calc}}{\eta_{actual}}$ equal to 1 (i.e. verifying a diffusion controlled model), the diffusion coefficient value D must be substantially lower than what we observed in section 4.2.1. This is possible if droplet shrinking in experiments is not only due to neutralization but also other physical or chemical processes. If this is the case then droplet shrinking rate (dr_1/dt) due to neutralization (and hence, diffusion) will be smaller than observed dr/dt in experiments and a smaller

value of diffusion coefficient D will be obtained. Below we have explored some possible additional processes which may cause the acid droplet to shrink in addition to the 4-step neutralization process in the introduction of this report:

It is possible that excess sulphuric acid may enter the reverse micelle (refer to step 3 in introduction of this report) and after the neutralisation, when the reverse micelle desorbs, this excess un-neutralized sulphuric acid may escape with the products inside the reverse micelle. This would result in observed dr/dt to be greater. Reference to this hypothesis is also made in past publications [5].

The formation of gaseous CO_2 can be observed in the neutralization of all three acid/lube oil mixtures. It may be possible that the gaseous CO_2 acts to promote release of sulfuric acid from the droplet and into the bulk of the lubricant oil.

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