Neutralization of acetic acid by automobile motor oil

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ABSTRACT

The neutralization reaction of concentrated and diluted acetic-acid droplets in fully formulated lubricant oil was studied using capillary video-microscopy. Based on video analysis, an interface-reaction-rate-controlled kinetic mechanism is proposed to describe the neutralization process at different conditions. When glacial and diluted acetic acid droplets were neutralized in fully formulated lubricant oil, the experimentally measured shrinking radius agreed very well with the mathematical model. According to Arrhenius equation, the activation energy of neutralization reaction was determined to be constant and its range ($E_a > 21$ kJ/mol) further validated the assumption as interface-controlled reaction kinetics.

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1. Introduction

When automobile engines operate, a wide range of acids can be produced as a result of fuel combustion in the combustion chamber [1]. Depending on the fuel utilized, very strong acidic species can be generated. Their nature and characteristics are strictly related to fuel composition. Part of these acids pass through the combustion chamber and come into contact with other metallic parts of the engine, leading to corrosion phenomena and to subsequent rapid wear of the engine component [1–3]. As a remedy, it is has long been the practice of incorporating basic nanoparticles (additives) in the formulation of oil for the express purpose of giving it the ability to neutralize combustion-generated acids [1,4]. These nanoparticles (additives), commonly referred to as "overbased detergents" (OVB), carry in the oily solution a high amount of inorganic base that is utilized to neutralize the acids when they are dispersed in the lubricant [4,5].

Specifically, overbased sulfonates (OBS) in the form of nanoparticles, are composed of an alkaline earth metal carbonate or hydroxide core, i.e., $CaCO_3/Ca(OH)_2$, surrounded by a shell of organic sulfonate surfactants of varying nature, responsible for the stability of the dispersion of the colloid in the oil [5–7]. These nanoparticles consist of a basic inorganic core stabilized by surfactants in the oil phase in the same mode as reverse micelles solubilize an aqueous phase in oil. This approach successfully enables the oil to store a large basic reserve, and is widely utilized in almost all lubricant oils and adopted on all sorts of engines [4].

The basicity of an additive is the main parameter that characterizes OVBs and it is graded in terms of the total base number (TBN), which is commonly defined as the equivalent amount of potassium hydroxide per gram of detergent (mg KOH/g). Depending on the nature of the oil to which the acid-neutralizing effect is addressed, and on the required performances, oils have been formulated with very different TBN up to 500 [4].

The TBN value of OVBs alone is not sufficient to fully predict its performances and much effort has been devoted to the understanding of their action mechanism especially when they are formulated in complex additives mixtures as can be found in fully formulated oils (FFO) [1,4,8–12]. One key approach to the study of a new lubricant OBS detergent can be related to the determination of the neutralization reaction mechanism occurring on a molecular scale level as proposed in the literature [6,7,13–15]. The neutralization reaction occurs both by transport of the acid onto the surface of the micelles for reaction or by diffusion of the base towards the acid droplets. However, all the neutralization experiments reported were focused on sulfuric acid. Nowadays, the addition of ethanol into gasoline is accepted worldwide, and gasoline/ethanol blends are commonly used [16,17]. Gasoline containing up to volume 10% ethanol are adopted in over 20 countries, and in the USA 90% of the gasoline market has been taken by E10 (gasoline with 10% ethanol) [18].

The introduction of ethanol as a fuel component leads to further problems as far as the engine wear is concerned, since the biofuel introduced constitutes a source of acetic acid that is generated during the combustion [19–22]. The neutralization mechanism of the acids reported in the literature has been up to now focused on the action of the OBS on sulfuric acid and scarcely anything is known on the corrosive action of acetic acid. Recently,

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Nomenclature

[HAc]	concentration of HAc
[Base]	concentration of Base
$V_{reacted\ acid}$	volume of neutralized acid, μm^3
$V_{water\ produced}$	volume of produced water in reaction, μm^3
R	radius of droplet, μm
R_0	initial radius of HAc droplet, μm
R_1	final radius of the remaining droplet, μm
t	time of reaction, s

r_n	neutralization reaction rate, $\mu m/s$
k	neutralization reaction rate constant, $\mu m^4/s\ mol$
k_1	neutralization reaction rate constant
R_{ig}	ideal gas constant, 8.314 J/ mol K
T	temperature, K
E_a	activation energy, kJ/mol
C_A	molar concentration of HAc in droplet, $mol/\mu m^3$
C_{A0}	initial molar concentration of HAc in droplet, $mol/\mu m^3$
C_{HAc}	molar concentration of glacial HAc, $mol/\mu m^3$

Volkswagen set up a new corrosion test, namely PV 1492 [23,24], in which the response to wear of some metallic engine parts (crankshaft) to their exposure to fully formulated lube oils is assessed [24,25]. Using this test, the resistance to wear of some metallic tests is evaluated in well-defined conditions in the presence of acetic acid. Another test on intermediate-level, ethanol-blends engine durability reported acetic acid formation during combustion, and the extra contribution to metal wear of the partial combustion products of ethanol such as acetic acid [25].

The purpose of the current research is to study the behavior of some OBS when introduced in a FFO for passenger cars and to determine their neutralization efficiency when exposed to acetic acid in conditions similar to those normally encountered in the WV PV 1492 test. Using capillary video-microscopic technique as described in the previous work and applied to the study of the neutralization of sulfuric acid in oily media, [6,7,26,27] the novelty of the current study lies in its focus on the determination of reaction kinetics of the acetic acid droplets in overbased lubricant oil.

By monitoring the shrinking radius and ultimate fate of acid droplets that are being neutralized as a function of time, it was possible to determine the kinetics governing such reactions. The equations describing unsteady-state systems were numerically solved to model the processes.

2. Theoretical

The reaction process is observed as the shrinkage of an acetic acid droplet, and interface-reaction-controlled reaction kinetics is considered and described in detail.

Assuming diffusion-control, our calculations based on solving Fick's 2nd-Law equation along the lines of previous studies [28,29], could not fit the experimental data in Fig. 3; as seen in Fig. 3, the interface-controlled assumption fits these data very well.

This type of reaction occurs when the bulk phase contains overdosed amount of base and the diffusion of base towards the reaction interface is fast enough so that the overall reaction rate is only dependent on the rate of reaction on the interface in contact. In this case, the following assumptions are made to set up a model to depict the fate of a droplet when the reaction is only limited by the interface reaction rate:

– The base in the oil is ample in the bulk phase, and diffuses fast enough to the interface to keep neutralizing the acetic acid droplet and does not change in interface concentration.
– The droplet at the end contains only water, which is the product of neutralization reaction.
– If the initial acid droplet's radius is R_0 and final radius of the remaining water droplet is R_1, total volume of $4/3\pi R_1^3$ water is

the product from reaction of acid droplet with the volume of $4/3\pi R_0^3$.
– The volume fraction of water and acetic acid are cumulative in the droplet.

For the simplest scenario, the neutralization of glacial acetic acid droplet, the derivations of the equations for reaction process are described as follows:

At any given time when the droplet radius is $R(t)$, the volume of water produced from neutralization, $V_{water\ produced}$, is proportional to the reacted volume of acid, $V_{acid\ reacted}$.

$$V_{water\ produced} = \frac{\frac{4}{3}\pi R_1^3}{\frac{4}{3}\pi R_0^3} V_{acid\ reacted} \tag{1}$$

The volume of reacted acid when the droplet radius is $R = R(t)$ can be calculated via

$$\frac{4}{3}\pi R_0^3 - \frac{4}{3}\pi R^3 = V_{acid\ reacted} - V_{water\ produced} \tag{2}$$

because the change in droplet volume is the result of both acid consumption and water accumulation.

Therefore, we obtain:

$$V_{water\ produced} = \frac{\frac{4}{3}\pi R_1^3}{\frac{4}{3}\pi R_0^3}\left(\frac{4}{3}\pi R_0^3 - \frac{4}{3}\pi R^3 + V_{water\ produced}\right) \tag{3}$$

or

$$V_{water\ produced} = \frac{4}{3}\pi R_1^3 \frac{R_0^3 - R^3}{R_0^3 - R_1^3} \tag{4}$$

It is assumed that the total water volume (product of neutralization) in the droplet when the radius is $R = R(t)$ (at time t), is described by Eq. (4).

– Neutralization is assumed to be first-order interfacial reaction:

$$r_n = k_1[HAc][Base] = k[HAc] \tag{5}$$

where r_n is the overall reaction rate, defined as the volume of acid neutralized per second per unit surface contacting area. k, and k_1 are the reaction rate constants. In this paper, r_n has the unit of $\mu m/s$ and molar concentration is used for acetic acid droplet. In Eq. (5), the concentration of base is considered constant as per the ample-base assumption.

A lumped-parameter model is also assumed for the acid-concentration distribution in the droplet, so that it is considered uniform throughout. The injected acetic acid droplet is in liquid state and has a large diffusion coefficient of $1.24 \times 10^{-9}\ m^2/s$ in water phase [30]. For the diffusion of molecules in the droplet, Einstein's Relation, $(\Delta x)^2 = 2Dt$ [31,32], can be used to calculate the time for a molecule to diffuse a certain distance. Δx is the mean displacement of the molecule, D is the diffusion coefficient and t is the duration of diffusion. If a droplet has the radius of 50 μm, the