Visualization Test for Neutralization of Acids by Marine Cylinder Lubricants

Rong Chang Wu and Kyriakos D. Papadopoulos
Dept. of Chemical Engineering, Tulane University, New Orleans, LA 70118

Curt B. Campbell
Chevron Chemical Company, Oronite Global Technology, Richmond, CA 94802

The combustion of high-level-sulfur (2−5%) fuels generates large amounts of sulfuric acid in slow-speed crosshead marine diesel engines. In this study, a video-microscope imaging technique is used to develop an experimental protocol for ranking the ability of marine cylinder lubricants to neutralize sulfuric acid within microcapillaries. The technique was applied to several oils with known rates of acid-neutralization ability to predict these rates. The optical observations allow one to propose a plausible mechanism by which the overbased detergent additive system performs the task of acid neutralization. According to this mechanism, the overbased sulfonate reverse micelles are the site for the neutralization reaction, which occurs at the oil-acid interface. The results confirm that the detergent surfactants are chemically bound to the micellar core. In the case of overbased calcium-carbonate detergents reacting with sulfuric acid, the formation of solid crystals was observed which may form a protective antiwear film on engine metal surfaces.

Introduction

Marine crosshead diesel engines used for ship propulsion operate at slow speeds with engine speeds ranging from about 74 to 200 revolutions per minute (rpm) (Lilly, 1984). The cylinders in these engines are lubricated by injection of a marine cylinder lubricant (MCL) upon each stroke of the piston (Wilbur and Wight, 1984) and the function of such marine cylinder lubricants (MCLs) is to provide lubrication for the moving metal engine parts so as to minimize friction and protect against wear. However, the fuel oil used in these marine engines contains very high levels of sulfur (2−5%), which results in the formation of highly corrosive acids, mainly sulfuric. These acids encroach into the lubrication film and lead directly to the corrosive wear of the cylinder liners and/or piston rings. Acids in the lubricant also lead to the degradation of the oil itself by producing insoluble products that are precursors of carbonaceous piston deposits (Marsh, 1987). Therefore, the ability of MCLs to effectively and efficiently neutralize encroaching acids in the lubrication layer is a "measuring stick" of their quality (Marsh, 1987; Porter, 1990; Benfaremo and Liu, 1996). The major components or additives present in current MCL formulations are overbased detergents, which act as a form of oil-soluble base. These are normally Group-II metal (usually calcium or magnesium) containing organo-metallic complexes, most notably sulfonates, phenates, and salicylates. When these complexes contain a large excess of base, they are commonly referred to as overbased detergents.

Several studies have characterized oil-soluble basic detergents dispersed in lubrication oil, through such experimental techniques as small-angle X-ray/neutron scattering (SAXS/SANS), quasi elastic light scattering (QELS), transmission electron microscopy (TEM), intrinsic fluorescence microscopy (IFM), and extended X-ray absorption fine structure spectroscopy (EXAFS) (Markovic et al., 1984; Markovic and Ottewill, 1986a,b; Jao and Kreuz, 1988; Papke, 1988; O'Sullivan et al., 1991; Roman et al., 1991; Mansot et al., 1993a,b; Griffiths, 1995). It is now generally accepted that the structure of overbased calcium sulfonates and phenates are in the form of reverse micelles with a mixed calcium hy-

---

Correspondence concerning this article should be addressed to K. D. Papadopoulos.

droxide/carbonate core stabilized by an outer alkyl-aryl shell which makes the detergent oil soluble. Markovic et al. (1984) and Markovic and Ottewill (1986a,b) examined two series of colloidal dispersions of calcium carbonate particles, one stabilized by an alkylsulphonic acid and the other by a mixture of an alkylsulphonic acid and nonylphenol. They proposed a core/shell model for the systems studied with core diameters of 2.2 and 6.7 nm for the two series, respectively, and a shell thickness of 1.9 nm in both series. Mansot et al. (1993a,b) further pointed out that the reverse micelles core is made of amorphous calcium carbonate in which the calcium atoms are surrounded by about six oxygen neighbors at a distance of 0.24 nm. Unlike commonly reported reverse micelles, which are dynamic structures and have very short relaxation times (Eicke and Zinsli, 1978), the surrounding alkylaryl sulfonyl groups of the lubrication-oil reverse micelles are chemically bonded to the mineral core, which causes the micelles to remain stable even outside their original medium (Mansot et al., 1993a,b). Molecular dynamics simulations of an overbased calcium carbonate/calcium sulfonate system by Tobias and Klein (1996) showed that in solution the typical micelle is roughly spherical with an average core diameter of 2.3 nm and surfactant layer thickness of 0.9 nm, contributing to a total diameter of approximately 4.1 nm. In addition to the sulfonate systems, Langmuir-trough particle-sizing studies of overbased phenates confirmed the microcolloidal state of the particles (Griffiths et al., 1995). Furthermore, as the total base number (TBN) increased from 150 to 300, the particle size increased from 2.5 to 3.2 nm. TBN is defined as the milligrams of KOH equivalent to the moles of base present in one gram of the sample (Papke, 1988). Another structure aspect of the overbased sulfonate detergents is the apparent presence of free surfactant molecules (that is, the alkylbenzene sulfonic acids or salts) in the compositions (Lewis, 1991).

From the above discussion, it follows that testing the neutralization ability of an MCL has great importance in the design of overbased detergents/detergent systems and formulations. For this reason, several neutralization rate tests have already been developed by previous workers. One technique (Inouye and Mitou, 1988; Lowe, 1974) measures the pH change of a continuously stirred heterogeneous mixture of aqueous acid, lubricating oil, and, optionally, a cosolvent as a function of time. However, it is not clear what is measured through such a test, since in the acid-in-oil emulsion, the measured pH is not necessarily the pH of the suspended sulfuric acid droplets. In another test for detergents containing carbonates, the quantification of carbon dioxide by microelectronic sensors (Wohltjen et al., 1994) is possible. A deficiency of both these tests lies in the fact that they do not provide any information concerning the mass transfer between the two phases, which is necessary for acid neutralization to take place and may be the rate-limiting step in the neutralization reaction. The objective of our study was to use our capillary-microscopy technique (Deshiikan and Papadopoulos, 1995; Hou and Papadopoulos, 1996, 1997) to develop a new experimental protocol for testing the ability of MCLs containing different detergent additives and/or detergent additive systems to neutralize aqueous acids. The technique allows the direct observation of an acid droplet from the instant of its formation inside an oil-filled capillary. To test the neutralization ability of different MCLs, sulfuric acid and nitric acid were used at ambient temperature and pressure.

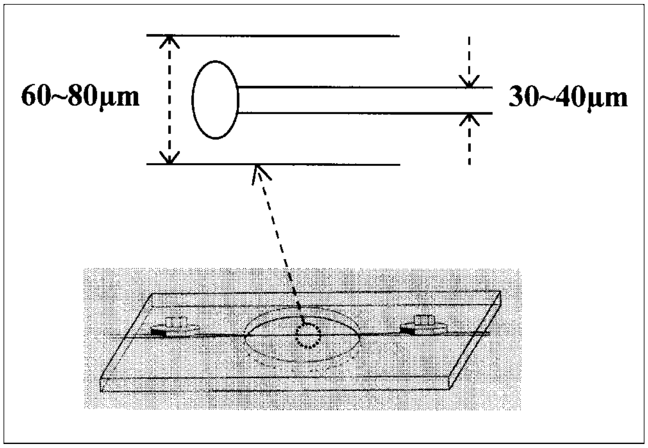


Figure 1. Experimental setup: microcapillary and micropipette.

Materials and Methods

Materials

All lubricating oils tested were provided by Chevron Chemical Company, Oronite Additives Division. The overbased detergent systems used in the oils were overbased calcium carbonate alkyl aromatic sulfonate(s) and, optionally, a supplemental additive dissolved in the Exxon 100N oil, a paraffinic base oil composed of principally alkanes and isoalkanes. Most oils tested had a TBN equal to 70. Both sulfuric and nitric acids were used as received from Aldrich, Inc. The water was deionized and ultrafiltered by a Barnstead E-pure system. Microcapillaries and micropipettes were made from Microcaps (Drummond Scientific).

Methods

Our video-microscope imaging system is described in detail elsewhere (for example, Hou and Papadopoulos, 1997), and the microcapillary setup is shown in Figure 1. The microcapillaries and micropipettes in this work were made by centrally pulling a 30μl micropipette with a 0.275 mm inside diameter and a length of 78 mm using a pipette puller (Narishige, Japan). By controlling the pulling weight, length, and speed, capillaries and micropipettes with different inside diameter could be made. The microcapillary was placed on the microscope (Olympus IMT-2, Japan), and the image was captured by a high-performance camera (Javelin, Japan) and sent to the monitor, VCR, and computer. Recorded and saved images were subsequently analyzed with the availabile software (OPTIMAS 6.1). To successfully produce an acid droplet which does not wet and spread on the wall of an oil-filled capillary, both the inner wall of microcapillary and the outer surface of the injection micropipette had to be hydrophobically treated (Hou and Papadopoulos, 1997). The hydrophobicity of the microcapillary was achieved by immersing it in a 10% octadecyltrichlorosilane (OTS) Iso-par G solution for 2 min, after which it was washed three times with Iso-par G, methanol, and pure water in this order. The micropipette was also immersed in OTS solution for 20 min with nitrogen gas flowing through it during the process.

The rate of acid neutralization for the test oils was also measured according to a modified procedure previously described (Lowe, 1974) using a Mettler model DL21 automatic titrator programmed to record pH-vs.-time profiles. A Mettler Toledo DG 115-SC glass electrode was equilibrated for 5 min by soaking in 50 mL of 0.002 N H_2SO_4 contained in a plastic titration cup for the Mettler titrator at room temperature with stirring (magnetic stir bar at stirrer setting 4). To this stirring solution was quickly (1–2 s) added 10 mL of the test oil by syringe and the time required for the electrode to register pH = 9.0 was recorded. At the end of the neutralization rate experiment, the electrode was cleaned by rinsing with hexane followed by acetone and then water.

Results and Discussion

Neutralization rate tests

Six lubricants were tested for their neutralization ability based on the observed visual behavior of an acid (H_2SO_4 and HNO_3) droplet in the oil and compared to their rate of neutralization ability determined by a pH measurement test (Lowe, 1974). The six lubricant oils tested are numbered A-1 to A-6. Oil A-1 has the fastest neutralization ability according to a pH-measurement test and the oils' rate of neutralization ability decreases in the order A-1 to A-6 (Campbell, 1998). Figure 2 shows the behavior of a sulfuric acid droplet (4.7 mol/L) in the six oils 2 min after injection. At the time of injection and before the neutralization reaction has progressed ($t = 0$), the appearance of the acid droplet bears no signs of alteration due to chemical reaction. However, by 2 min after injection, the acid droplet in lubricating oil A-1 is seen to be completely destroyed with the reaction products being amorphous debris. For the same time interval, the visual destruction of the acid droplets becomes progressively smaller as we move towards the oils with slower rates of acid neutralization ability by the pH measurement technique. For the worst oil (A-6), the droplet has almost the same appearance as when it was freshly injected, the difference being two crystals formed on its surface. Based on these images, and similar ones after 5 min from injection (not shown here), a comparison of the different oils' rate of acid neutralization ability determined by the pH technique with their visual neutralization ability is shown in Table 1. While the agreement between the microcapillary technique and the pH method is acceptable, it is noteworthy that, whenever there are differences, the predictions of the microcapillary technique are inherently more reliable, because the pH of a water-in-oil emulsion is by its nature ambiguous.

The shrinking of acid droplets with time is not measurable in most experiments due to crystal formation (see ''formation of crystals'' section) and droplet breaking. For two of the oils (A-3 and A-6), and for some experiments the acid-droplet shrinking with time was clear enough to be measured, thus

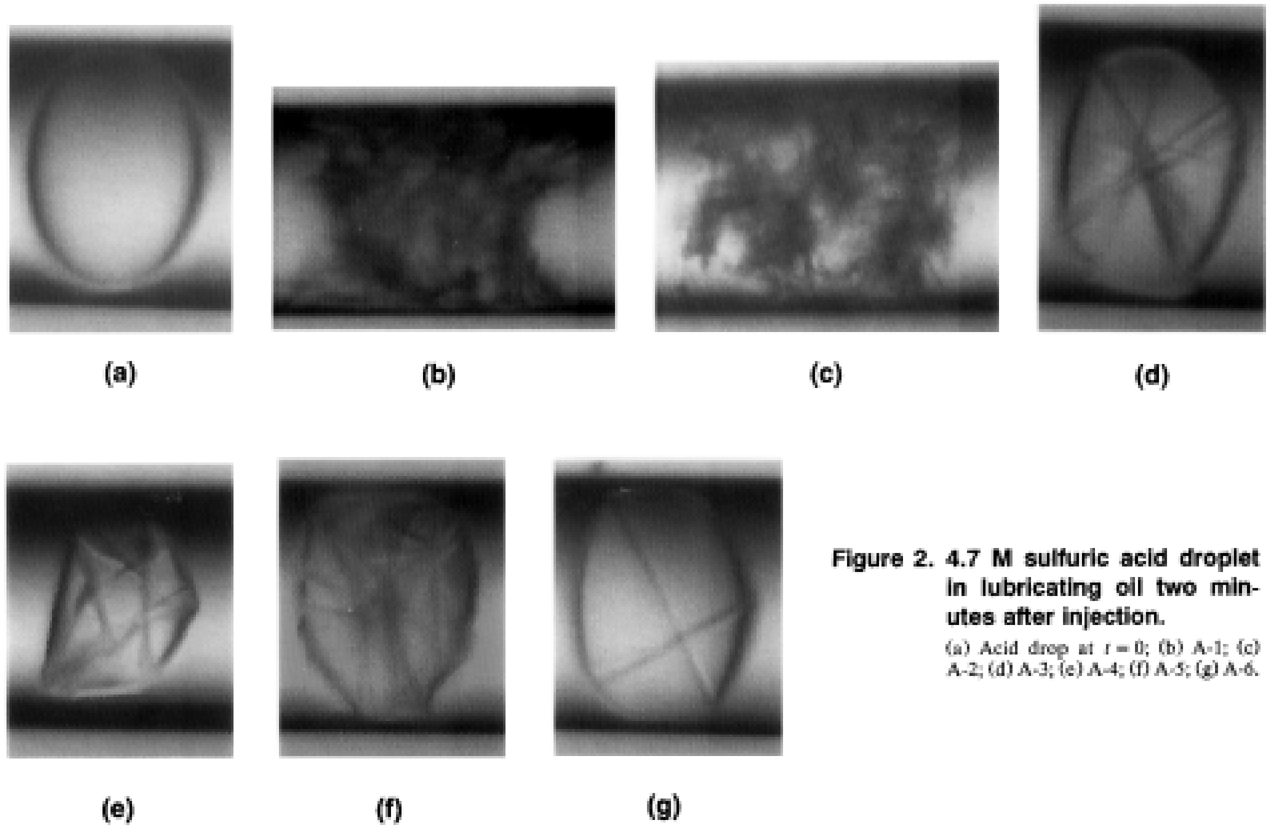

(a) (b) (c) (d) (e) (f) (g)

Figure 2. 4.7 M sulfuric acid droplet in lubricating oil two minutes after injection.

(a) Acid drop at $t = 0$; (b) A-1; (c) A-2; (d) A-3; (e) A-4; (f) A-5; (g) A-6.

Table 1. Comparison of Different Oils on the Rate of Sulfuric Acid (4.7 M) Neutralization

Oil Sample	pH Meas. Technique	Microscope Technique	
		2-min Image	5-min Image
A-1	26	* * *	* *
A-2	58	* * *	* *
A-3	67	* *	* *
A-4	115	* *	*
A-5	344	* *	*
A-6	708	*	*

*Slowest neutralization ability.
***Fastest neutralization ability.

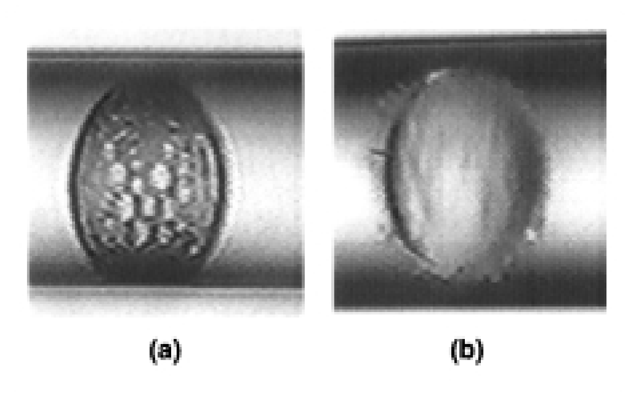


Figure 4. Visualized acid neutralization reaction in a microcapillary.

(a) Oil droplet in nitric acid phase; (b) nitric acid droplet in oil phase.

providing quantitative information on the neutralization reaction (Figure 3). The injected acid droplets never had a perfect spherical shape, probably due to the high viscosity of the oil sample and also the immediate, though not visually seen, formation of solid reaction products on the oil-acid interface. Droplet shrinkage was measured as the longest axial dimension L, with L_0 being the same length at the beginning of the experiment. Figures 3a, 3b, and 3c show the ratio L/L_0 as a function of time from the injection of the acid-droplet into the lubricating oil. In oil A-3, a nitric-acid droplet shrinks more than a sulfuric acid droplet (Figure 3a), even though the normality of the H_2SO_4 droplet (18.8 N) is about twice that of HNO_3 (11.1 N). This difference is discussed in the following section in terms of the deposition of solids in the sulfuric acid case. It is not surprising that the higher concentrated nitric-acid droplet shrank much more than the lower concentrated acid one in the same oil (Figure 3b). Figure 3c compares the shrinking rate of an acid droplet in oils A-3 and A-6, verifying the better rate of neutralization of the former.

Mechanism of neutralization reaction

Nitric acid was used to study the reaction mechanism by observing the fate not only of an acid droplet in oil, but also of an oil droplet in acid. Typical images of the oil-in-acid and the acid-in-oil experiments are shown in Figure 4. In both cases, there was visible production of small bubbles of CO_2, always appearing first at the oil-side of the oil-acid interface. These bubbles then migrated into the bulk oil phase as is apparent in the images in Figure 4. These observations suggest that the neutralization reaction takes place in the oil-side of the oil-acid interface, and that the overbased sulfonate reverse micelles are the sites of the neutralization reaction.

A greater understanding of the neutralization reaction will lead to the development of better additive systems for the neutralization of acids in lubricating oils. Based on a rotating diffusion cell (RDC) technique, Lewis (1991) proposed a "droplet formation and transfer mechanism" for the neutralization reaction between surfactant-dispersed colloidal metal carbonate particles in oil and aqueous acid (Figure 5a). According to this mechanism, there are some "excess" (free) surfactant molecules in the oil phase, which will form a surfactant layer at the oil-acid interface when the acid phase is introduced. This surfactant layer reduces the interfacial ten-

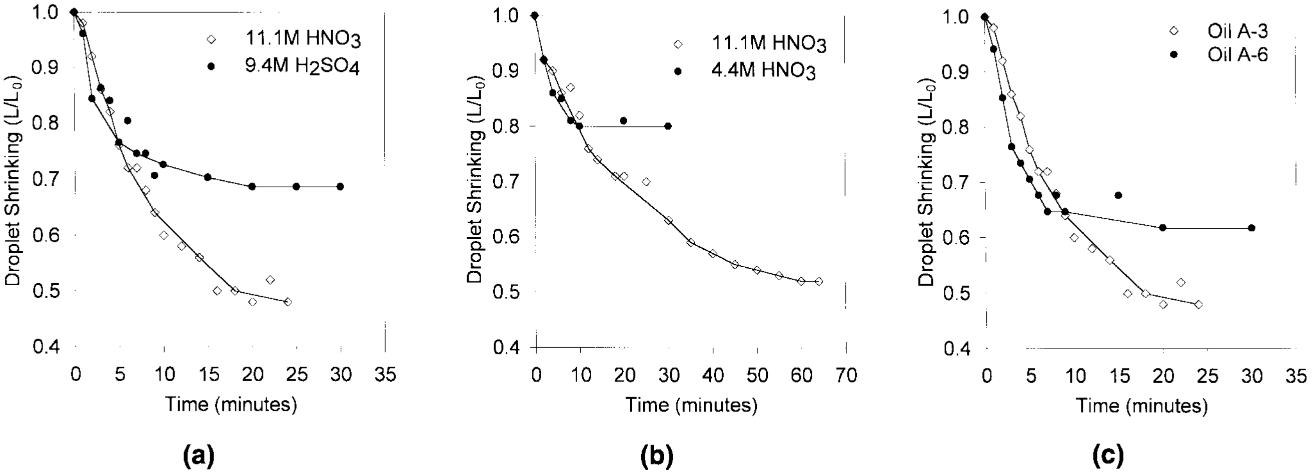


Figure 3. Shrinking of acid droplet in lubricating oil.

(a) Effects of acid; (b) effects of acid concentration; (c) effects of oil formulation.

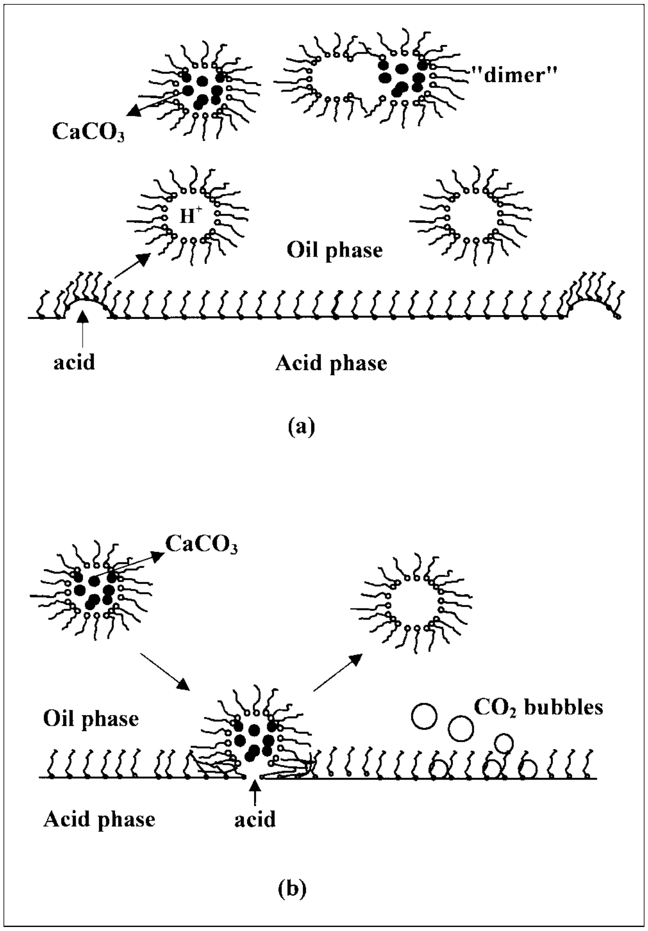


Figure 5. Mechanism of neutralization reaction in lubricating oil.

(a) Proposed by Lewis (1991); (b) proposed for systems studied in this article.

sion to the extent that spontaneous curvature of the interface can occur and the formation of acid-containing reverse micelles occurs. These reverse micelles, containing aqueous acid, can then move into the oil phase and may collide with the dispersed calcium carbonate particles leading to the formation of a transient "dimer," where the neutralization reaction can take place. Following neutralization, surfactant molecules depleted of acid are released and can return to the interface. This mechanism shows the neutralization reaction occurring in the core of reverse micelles in the oil phase and not at the interface. However, in all our observations of acid droplets in the oils tested, we have never observed the products of the neutralization reaction appearing first in the bulk oil phase. Hence, any mechanism for the neutralization reaction between the overbased detergent $CaCO_3$-containing reverse micelles studied in the current work and aqueous acid must account for this observation. Such a mechanism is shown in Figure 5b, which is consistent with the reports that overbased-detergent reverse micelles are not dynamic structures (Mansot et al., 1993a, b) and is supported by our visualization experiments. Considering that the dimensions of the acid droplets in our microcapillary experiments (usually in the range of 60–80 μm) are much greater than those of reverse micelles (in the range of several nanometers), we are illustrating the interface as a plane (Figure 5). The mechanism envisions that the detergent $CaCO_3$-containing reverse micelles in the bulk oil approach collides with the oil-acid interface by Brownian motion. A successful (sticky) collision results in the "adsorption" of the reverse micelles on the interface followed by the formation of channels between the reverse micelles and the bulk aqueous phase, through which mass transfer can occur. The acid is then transferred into the core of the reverse micelles, and reacts with the calcium carbonate. This type of mechanism has been proposed for mass transfer between the aqueous phase and water-in-oil microemulsion by Plucinski and Nitsch (1994), and it is used to study the solubilization of triolein into nonionic surfactant solutions by Chen et al. (1997). Additionally, molecular dynamics simulations have shown exchange of oil molecules between a large oil droplet and micelles during collisions (Karaborni et al., 1994). Therefore, we believe that the interfacial collision and the adsorption of overbased reverse micelles onto the acid droplet play an important role in the neutralization, and may be the rate-controlling step.

Formation of crystals

When sulfuric acid is used instead of nitric acid, the formation of needle-like crystals is observed. These crystals are believed to consist of hydrated calcium sulfate and their formation can be easily understood assuming the neutralization-reaction mechanism proposed in the previous section. Figure 6 shows the appearance of solid crystals in the case of a 4.7 mol/L and a 9.4 mol/L sulfuric-acid droplet in oil A-4, and in Figure 7 we illustrate the origination of the crystals via a proposed mechanism. Several effects, such as the concentration of sulfuric acid and the basicity of the oil (TBN), determine the shape of particular crystals. In the case of low sulfuric acid concentration and low TBN oil, the solids are in the shape of long, needle-like crystals, while in the case of high acid concentration and high TBN oil, the solids become amorphous. In the former case, the neutralization reaction is slower allowing the crystal nucleus to grow. In the high-acid-concentration high-TBN case, the amorphous solids may deposit on the sulfuric acid droplet thus inhibiting further

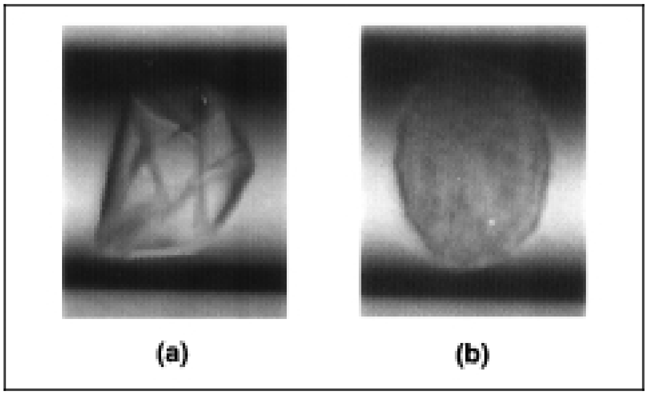


Figure 6. Visualized crystals in the neutralization reaction.

(a) 4.7 M sulfuric acid droplet in oil A-4; (b) 9.4 M sulfuric acid droplet in oil A-4.

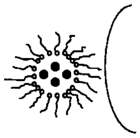
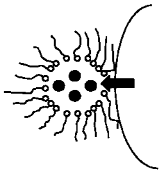
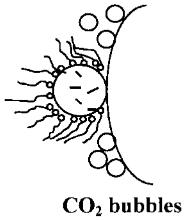
Stage	Phenomena
1. Reverse micelle moves close to the interface of acid droplet	
2. Aqueous acid transports into the core and contacts the $CaCO_3$ particles	
3. $CaCO_3$ reacts with acid, and nucleus of hydrated calcium sulfate is formed, together with CO_2	
4. Once the nucleus is formed, the crystal grows	

Figure 7. Mechanism of crystal formation.

reaction. This may explain why in Figure 3a the nitric-acid droplet shrinks more than the sulfuric-acid droplet. It is also the reason why measurements of droplet shrinkage were unreliable, or even impossible, for most experiments involving sulfuric acid.

Tribological studies on the behavior of colloidal additives indicate that $CaCO_3$ overbased detergent micelles can provide good antiwear properties (Mansot et al., 1993b). Accordingly, overbased micelles first adsorb onto the metal friction surfaces and then, as the movement of the surfaces shears them, the micelles lose their surfactant shell and their cores crystallize and/or aggregate on the metallic surfaces. The resulting polycrystalline film provides wear protection. Here, it should be pointed that Mansot et al.'s (1993b) experiments were carried out in friction tests, without the presence of sulfuric acid. It has been indicated, however, that the dew point for sulfuric acid is around 170°C in crosshead engines and that, at temperatures as much as 30°C below the dew point, there is considerable formation of aqueous sulfuric acid (Shott and MacDonald, 1988). Therefore, in marine crosshead diesel engines, considerable amounts of aqueous sulfuric acid in dilute concentration are believed to be present following the combustion of high-sulfur containing fuel. Based on our observation of the formation of solid crystals of hydrated calcium sulfate as a result of the neutralization of sulfuric acid by $CaCO_3$ overbased detergents, hydrated calcium sulfate crystals may also play a role in the formation of antiwear films.

Other systems of interest

In this study we have shown that, using our capillary video-microscopy technique, it is possible to study the interfacial reaction between a droplet and its suspending medium in a biphasic system. Besides the MCL acid-neutralization reaction, there are several other biphasic systems involving interfacial reaction and/or mass transfer, which can be studied visually using our technique. As one example, we may refer to the hydrolysis of water-insoluble fatty acid anhydride oil drop in water, which leads to the formation of self-reproducing fatty acid giant vesicles with diameters up to a few micrometers (Walde et al., 1994; Wick et al., 1995). With our technique, both the oil drop and the self-reproduced giant vesicles could be monitored from the very beginning, and this would provide additional insight in the hydrolysis process. Other systems that can be studied via our technique are those involving enzymatic lipolytic reactions, where water-soluble lipolytic enzymes act mainly at the water/lipid interface and the catalytic reactions are coupled with various interfacial transport and adsorption phenomena (Panaiotov et al., 1997). Quantitative measurements on oil droplet size would provide kinetic data and may also help to investigate the mechanism of the lipolysis process. Our technique may also be useful in ''inverse phase-transfer catalysis'' (IPTC) (Mathias and Vaidya, 1986) studies, which involve transport of an organic-soluble reactant into an aqueous phase followed by reaction with a hydrophilic species.

Conclusion

In this study a novel experimental protocol has been developed for testing the neutralization ability of MCLs, based on a video-microscopic technique, which allows observation of the destruction of acid by MCLs inside a microcapillary. Our observations have also led us to propose a mechanism for the neutralization reaction in MCLs focusing on the bending of the detergents' tails. Solid crystals, believed to be hydrated calcium sulfate, were observed in our experiments, and this implies that, in marine diesel engines where large amounts of aqueous sulfuric acid are generated by combustion of high-sulfur-containing fuel, there may also be a considerable presence of solid crystals. These crystals may contribute to the antiwear properties of detergent additives in the real-engine situations. Other biphasic systems, where interface reaction and/or mass transfer take place, may also be studied using our technique.

Acknowledgments

We would like to thank M. Singh for carrying out acid neutralization rate tests and Chevron Chemical Company, Oronite Division, for supporting this work. Financial support was also provided by the Louisiana Board of Regents under grant LEQSF-RD-B-14.

Literature Cited

Benfaremo, N., and C. S. Liu, ''Crankcase Engine Oil Additives,'' *Lubrication*, **76**, 1 (1996).

Campbell, C. B., private communication (1998).

Chen, B. H., C. A. Miller, and P. R. Garrett, "Rates of Solubilization of Triolein into Nonionic Surfactant Solutions," *Colloids Surf.*, **128**, 129 (1997).

Deshiikan, S. R., and K. D. Papadopoulos, "London-vdW and EDL Effects in the Coalescence of Oil Drops," *J. Colloid Interface Sci.*, **174**, 302 (1995).

Eicke, H. F., and P. E. Zinsli, "Nanosecond Spectroscopic Investigations of Molecular Processes in W/O Microemulsions," *J. Colloid Interface Sci.*, **65**, 131 (1978).

Griffiths, J. A., R. Bolton, D. M. Heyes, J. H. Clint, and S. E. Taylor, "Physico-Chemical Characterisation of Oil-soluble Overbased Phenate Detergents," *J. Chem. Soc. Faraday Trans.*, **91**, 687 (1995).

Hou, W., and K. D. Papadopoulos, "Stability of Water-in-Oil-in-Water Type Globules," *Chem. Eng. Sci.*, **51**, 5043 (1996).

Hou, W., and K. D. Papadopoulos, "W1/O/W2 and O1/W/O2 Globules Stabilized with Span 80 and Tween 80," *Colloids Surf.*, **125**, 181 (1997).

Inouye, K., and T. Mitou, "Acid Neutralization Capacity of Overbased Detergents," *Nisseki Review*, **30**, 197 (1988).

Jao, T. C., and K. L. Kreuz, "Rigidity of Alkylaryl Sulfonate Micelles Monitored by Intrinsic Fluorescence Probes," *J. Colloid Interface Sci.*, **126**, 622 (1988).

Karaborni, S., N. M. van Os, and P. A. J. Hilbers, "Molecular Dynamics Simulations of Oil Solubilization in Surfactant Solutions," *Langmuir*, **9**, 1175 (1994).

Lewis, J., "Mechanism of Action of Overbased Additives in Hydrocarbon Media," PhD Diss., University of East Anglia, U.K. (1991).

Lilly, L. R. C., *Diesel Engine Reference Book*, Chap. 27, Butterworths, London, U.K. (1984).

Lowe, Warren, "Acid Neutralizing Accelerating Compositions," U.S. Patent 3,856,687 (1974).

Mansot, J. L., M. Hallouis, and J. M. Martin, "Colloidal Antiware Additives: 1. Structural Study of Overbased Calcium Alkylbenzene Sulfonate Micelles," *Colloids Surf.*, **71**, 123 (1993a).

Mansot, J. L., M. Hallouis, and J. M. Martin, "Colloidal Antiware Additives: 2. Tribological Behaviour of Colloidal Additives in Mild Wear Regime," *Colloids Surf.*, **75**, 25 (1993b).

Markovic, I., R. H. Ottewill, D. J. Cebula, I. Field, and J. F. Marsh, "Small Angle Neutron Scattering Studies on Non-aqueous Dispersions of Calcium Carbonate: I. The Guinier Approach," *Colloid Poly. Sci.*, **262**, 648 (1984).

Markovic, I., and R. H. Ottewill, "Small Angle Neutron Scattering Studies on Non-aqueous Dispersions of Calcium Carbonate: II. Determination of the Form Factor for Concentric Spheres," *Colloid Poly. Sci.*, **264**, 65 (1986a).

Markovic, I., and R. H. Ottewill, "Small Angle Neutron Scattering Studies on Non-aqueous Dispersions of Calcium Carbonate: III. Concentrated Dispersions," *Colloid Poly. Sci.*, **264**, 454 (1986b).

Marsh, J. F., "Colloidal Lubricant Additives," *Chem. Ind.*, 470 (1987).

Mathias, L. J., and R. A. Vaidya, "Inverse Phase Transfer Catalysis. First Report of a New Class of Interfacial Reactions," *J. Amer. Chem. Soc.*, **108**, 1093 (1986).

O'Sullivan, T. P., M. E. Vickers, and R. K. Heenan, "The Characterization of Oil-Soluble Calcium Carbonate Dispersions Using Small-Angle X-Ray Scattering (SAXS) and Small-Angle Neutron Scattering (SANS)," *J. Appl. Cryst.*, **24**, 732 (1991).

Panaiotov, I., M. Ivanova, and R. Verger, "Interfacial and Temporal Organization of Enzymatic Lipolysis," *Current Opinion in Colloid Surf.*, **2**, 517 (1997).

Papke, B. L., "Neutralization of Basic Oil-Soluble Calcium Sulfonates by Carboxylic Acids," *Tribol. Trans.*, **31**, 420 (1988).

Plucinski, P., and W. Nitsch, "Mechanism of Mass Transfer between Aqueous Phase and Water-in-Oil Microemulsion," *Langmuir*, **10**, 371 (1994).

Porter, M. R., "Corrosion Inhibitor Properties of Surfactant," *Recent Developments in the Technology of Surfactants*, M. R. Porter, ed., Elsevier Science, Essex, U.K., p. 163 (1990).

Roman, J. P., P. Hoornaert, D. Faure, C. Biver, F. Jacquet, and J. M. Martin, "Formation and Structure of Carbonate Particles in Reverse Microemulsions," *J. Colloid Interface Sci.*, **144**, 324 (1991).

Shott, F. H., and A. G. MacDonald, "The Influence of Acid Strength on the Corrosive Wear of Grey Cast Iron in Oil-Surfuric Acid Mixtures," *Wear*, **122**, 343 (1988).

Tobias, D. J., and M. L. Klein, "Molecular Dynamics Simulations of a Calcium Carbonate/Calcium Sulfonate Reverse Micelle," *J. Phys. Chem.*, **100**, 6637 (1996).

Walde, P., R. Wick, M. Fresta, A. Mangone, and P. L. Luisi, "Autopoietic Self-Reproduction of Fatty Acid Vesicles," *J. Amer. Chem. Soc.*, **116**, 11649 (1994).

Wick, R., P. Walde, and P. L. Luisi, "Light Microscopic Investigations of the Autocatalytic Self-Reproduction of Giant Vesicles," *J. Amer. Chem. Soc.*, **117**, 1435 (1995).

Wilbur, C. T., and D. A. Wight, *Pounder's Marine Diesel Engines*, 6th ed., Chap. 6–12, Butterworths, London, U.K. (1984).

Wohltjen, H., N. L. Jarvis, and M. Klusty, "Solid State Microsensors for Lubricant Condition Monitoring: II. Total Base Number," *Lubrication Eng.*, **50**, 861 (1994).

Manuscript received July 14, 1998, and revision received Mar. 25, 1999.