120 AR

WATER-IN-OIL EMULSIONS: HOW THEY ARE FORMED AND BROKEN

Merv Fingas and Ben Fieldhouse
Emergencies Science Division
Environment Canada
Environmental Technology Centre
3439 River Road
Ottawa, Ontario K1A 0H3
Canada

Joe Mullin
U.S. Minerals Management Service
381 Elden Street
Herndon, Virginia 22070

ABSTRACT: *Studies on the formation of emulsions were summarized, and analytical methods used to determine the final results of the emulsion breaking process were evaluated. These include visual appearance, viscosity, zero-shear-rate viscosity, elasticity, water content, and conductivity. All but the latter two are useful for determining the stability of an emulsion.*

The development of four new tests was reviewed. These test the effectiveness of emulsion breakers in open and closed systems and emulsion preventers in open and closed systems. Results of testing on commercial products are presented.

The most important factor in emulsion work is the understanding of the physics of emulsification. It was not recognized until recently that the basics of water-in-oil emulsification were understood in the surfactant industry, but not in the oil spill industry. The literature shows that there is now basic understanding of the formation of water-in-oil emulsions.[1] Information on the kinetics of formation at sea is less abundant. Emulsion formation is a result of the behavior of the polar and asphaltene compounds. These similar compounds both behave like surfactants when they are not in solution. When amounts of volatile aromatic components are insufficient to solubilize the asphaltenes and polars, these precipitate and are available to stabilize water droplets in the oil mass. The minimum mass percentage of either asphaltenes or resins required to stabilize an emulsion is about 3 percent. Emulsions begin to form when the chemical conditions mentioned above prevail and sea energy is sufficient. This energy is not measurable with current state-of-the-art techniques. The literature indicates that the relative energy required to form emulsion varies, but is not high. The understanding of emulsion physics is important to the understanding of optimal emulsion-breaking techniques.

Emulsion stability

The most important question related to emulsions analysis is whether or not they are stable. In the strict thermodynamic sense, all emulsions are unstable; however, experimental evidence has shown that some emulsions will persist over a matter of weeks.[2] A commonly accepted definition is that an emulsion is considered stable if it persists at least five days at 15° C. An assessment of a number of tests for stability have been correlated to the basic definition. These tests include: observation of the colour of the emulsion, viscosity, elasticity, 0-shear-rate viscosity, water content, and conductivity. The latter two measures are not, in themselves, reliable indicators of emulsion stability. It has been noted that most, if not all, stable emulsions are reddish in appearance, and those that are not are black. The viscosity of a stable emulsion at a shear rate of one reciprocal second, is at least three orders of magnitude greater than that of the starting oil. An unstable emulsion usually has a viscosity no more than two orders of magnitude greater than that of the starting oil. The 0-shear-rate viscosity is at least six orders of magnitude greater than the starting oil for a stable emulsion. For an unstable emulsion, it is usually less than two or three orders of magnitude greater than the starting oil viscosity. A stable emulsion has a significant elasticity, whereas an unstable emulsion does not. These measures can then be used in the design of any emulsion-breaking test as a quick analytical tool. It should be noted that very few emulsions have questionable stability. The usual situation is that emulsions are obviously either stable or unstable. Analytical techniques are then largely required to test the few questionable emulsions or to confirm the stability of the others rapidly.

Treating agent effectiveness tests

Twelve tests for emulsion breakers have been developed. New tests were developed to solve difficulties or shortcomings in older tests. Recent testing focused on developing four types of agent tests, one series for emulsion breaking and one for inhibition of emulsion formation. Tests for each of these were developed for open and closed systems. This is necessary to test properly agents that have water solubility and those that do not. This also corresponds to use patterns. Open-system tests represent the application of an emulsion breaker or inhibitor at sea. Closed-system tests represent the addition of agent to skimmers and tanks. Table 1 shows the basic parameters of these tests and results of testing with two commercial products, Vytac and Alcopol. Test results are given as minimum effective dose. The tests employ the stability measurement techniques noted above, to characterize remaining emulsion after treatment.

Table 1. Summary results of emulsion breaking and inhibiting tests

Action	System	O:W ratio	Shaker/device	Min. operative dose
Breaking	Open	1:5,000	New Brunswick	Vytac 1:300 Alcopol 1:200
	Closed	1:200	Burrell	Vytac 1:250 Alcopol 1:280
Inhibition	Open	1:25	Rotary	Vytac 1:6,000 Alcopol 1:2,000
	Closed	1:4	Blender	Vytac 1:7,000 Alcopol 1:2,500

Conclusions

Emulsion stability measurement is useful for the development of emulsion breakers or inhibitor testing. It is important to test emulsion treating agents separately as breakers or inhibitors, and with varying water ratios. Each of these tests ranks treating agents differently depending on the properties of that agent.

References

1. Fingas, M. F. and B. Fieldhouse, 1994. Studies of water-in-oil emulsions and techniques to measure emulsion treating agents. *Proceedings of the 17th Arctic and Marine Oil Spill Program (AMOP) Technical Seminar*, Environment Canada, Ottawa, Ontario, pp213–244
2. Fingas, M. F., B. Fieldhouse, I. Bier, D. Conrod, and E. Tennyson, 1994. Laboratory effectiveness testing of water-in-oil emulsion breakers. *in* The Use of Chemicals in Oil Spill Response, Peter Lane, ed., ASTM STP 1252. American Society for Testing and Materials, Philadelphia

Author

Merv Fingas in the chief of the Emergencies Science Division of Environment Canada. He has worked on oil spill research over the past 20 years and specializes in spill behavior, dynamics, and analysis. He has bachelor degrees in arts and chemistry and masters degrees in business, mathematics, and chemistry.

EVALUATION OF DISPERSANT TOXICITY USING A STANDARDIZED MODELED-EXPOSURE APPROACH

Lisa Weetman, Ina Lee, Michael Singer, Saji George, Susan Jacobson, Ronald Tjeerdema
Department of Chemistry and Biochemistry
University of California, Santa Cruz
34500 Highway 1, Granite Canyon
Monterey, California 93940

Michael L. Sowby
Office of Oil Spill Prevention and Response
Sacramento, California

ABSTRACT: *A spiked-exposure toxicity test procedure has been developed, in which initial dispersant concentrations are diluted at a standardized rate to provide a simple model of exposure experienced in the field. Traditionally, acute dispersant toxicity has been described using constant-concentration exposures of 24 to 96 hours. Constant concentrations are unrealistic in the field because of the dilution effects of wind and wave conditions required for dispersant application. The spiked-exposure procedure has been adopted in California as a standardized tool for comparing dispersant toxicity. Five dispersants have been tested using four Californian species. Tests using oil and dispersant-oil mixtures are being developed.*

Exposure regime

Traditionally, toxicity evaluation of dispersants has been accomplished mainly with standard, constant-concentration procedures, which are unrealistic and characterized as "worst-case scenarios." These exposures are artificial because of the physical and chemical nature of these agents and the dilution effects experienced under conditions required for dispersant use; sea swell, wind, and wave intensity must be sufficiently high to achieve proper chemical mixing. In sea trials, dispersant concentrations have been measured from <1 to 13 ppm at various depths and times after application. In all cases, concentrations dropped below detectable limits within hours.

Constant-exposure data may not give insight into delayed mortality, or increased or decreased sensitivity under realistic conditions. For example, short-term episodic exposures to pesticides have elicited delayed toxic effects not seen in constant-exposure tests. Short-burst exposures of some toxicants may allow for greater amelioration of toxic effects by detoxification or other "repair" processes.

Spiked-exposure test procedures

To provide a simple model of exposure experienced in the field, a spiked-exposure toxicity test procedure has been developed in which initial dispersant concentrations are diluted at a standardized rate over a 6- to 8-hour period. The state of California has adopted these procedures as a standardized tool for comparing dispersant toxicity. This research program was designed to provide the state with stan-

Proceedings

1995 International Oil Spill Conference

(Achieving and Maintaining Preparedness)

February 27–March 2, 1995
Long Beach, California

USCG API EPA

IMO IPIECA

Sponsored by

U.S. Coast Guard

American Petroleum Institute

U.S. Environmental Protection Agency

International Maritime Organization

International Petroleum Industry Environmental Conservation Association