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RESEARCH

# Studies of Water-in-Oil Emulsions: Stability Studies

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**Rheological studies were conducted on the water-in-oil emulsions of three crude oils: Arabian Light; Green Canyon; and Sockeye. The emulsions were found to fall into three categories on the basis of both rheological properties and visual appearance: stable; mesostable; and unstable. Stable emulsions are characterized by high viscosities and elasticities and are indefinitely stable. In this study stable emulsions showed true viscosities (viscosity with elasticity separated) approximately 700 times that of the starting oil and mesostable emulsions approximately 50 times that of the starting oil. Mesostable emulsions break into water, oil and sometimes emulsion within about 3 d. © 1997 Elsevier Science Ltd**

*Keywords:* **Water-in-oil emulsion, emulsification, mousse, weathering.**

## Introduction

Previous work by the authors showed that water-in-oil emulsions might be characterized into three categories (stable, mesostable and unstable) (Fingas *et al.*, 1995). These categories were established by visual appearance, elasticity and viscosity differences. It was also shown that water content was not an important factor. Literature reviews show that these emulsion phenomena were noted, but not classified in the same manner (Fingas *et al.*, 1995). A consensus of the literature is that:

- Stable and less-stable emulsions exist.
- Emulsion stability derives from the viscoelastic films at the oil–water interface of asphaltenes, which behave as amphiphiles.
- Asphaltenes produce more rigid films than do resins.
- Stable emulsions show differing viscoelastic and dielectric properties from less stable or unstable emulsions.
- Water content does not appear to relate to stability, however, very low or very high water contents will not yield stable emulsions (<30% or >90%).
- Most researchers use visible phase separation to classify emulsions as stable or not, but state that this is not an optimal technique.

The purpose of this study was to further both the study of emulsion stability and the development of tools to probe stability.

## Methodology and Results

Emulsions were formed in a rotary agitator (Associated Design) and the rheology measured over time. The properties of the three crude oils used did not vary significantly, other than that Green Canyon was more dense and viscous and Sockeye had almost twice the asphaltene content of the other two oils. Viscosities were characterized by a Haake RS100 rheometer under a variety of tests that included controlled stress and forced oscillation. For comparison purposes, a Haake RV20 and a Brookfield viscometer were used. The latter was not capable of shear rate control. The rheometer provided data capable of distinguishing elasticity and viscosity components. The combination of the viscosity and elasticity is not distinguished by most viscometers. Readings from these types of

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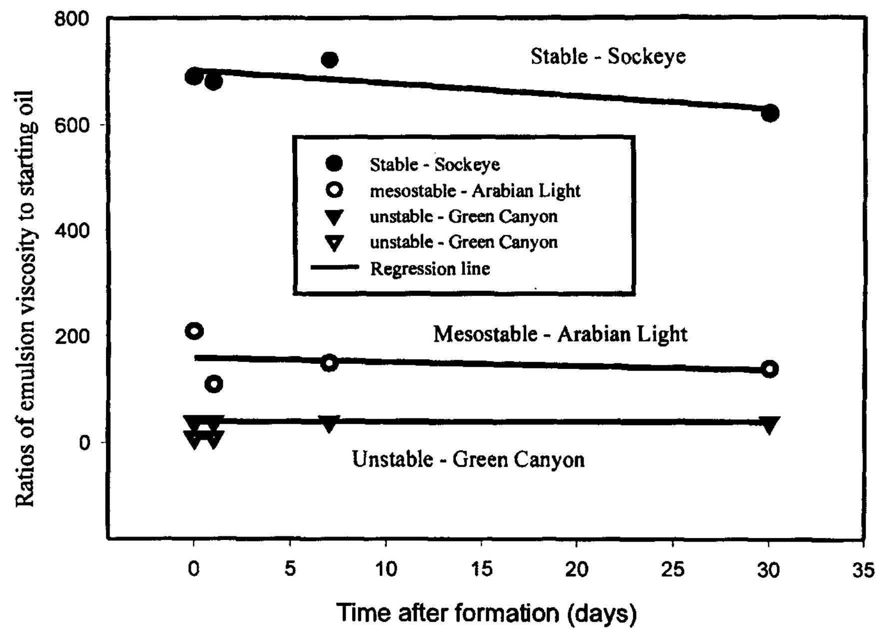


**Fig. 1** Ratios of viscosities of emulsion to starting oil.

**Table 1** Summary of emulsion characteristics

| Parameter | Mesostable emulsion | Stable emulsion |
|---|---|---|
| True viscosity difference from starting oil | 20-200 | 700 |
| Apparent viscosity difference from starting oil | 80-600 | 3000 |
| Lifetime | <3 d | Indefinite |
| Appearance before breaking | Viscous brown mass | Solid-like brown mass |
| Appearance after breaking | 3 layers | Does not break |
| Main stabilizing force | Viscoelasticity | Asphaltene film |
| Secondary stabilizing force | Asphaltene film | Viscoelasticity |

viscometers are known as 'apparent' viscosity as opposed to 'true' viscosity, when only the viscosity component is measured.

The true viscosity of the emulsions compared with that of the starting oil was found to vary significantly, as shown in Fig. 1. This figure also shows that there is a large gap between the viscosities of stable and unstable emulsions. There are no significant changes in the viscosity of all three types of emulsions over time.

The rheometer studies show that large differences exist in the properties of the stable, mesostable and unstable emulsions. The record of the visual appearances of the emulsions over the period of time corresponds to the rheological properties.

The comparison of measurement techniques shows that viscometers that do not apply controlled stress are not accurate for characterizing unknown emulsions. This results from the fact that elasticity and viscosity are measured together. Stable emulsions have large elasticities. Furthermore, viscometers that do not have controlled shear rates show variances in readings, because the high shear rates break the emulsions over time.

## Conclusions

Water-in-oil emulsions made from crude oils have different classes of stabilities as a result of the asphaltene contents. The differences in the emulsions are summarized in Table 1.

### *References*

Fingas, M. F., Fieldhouse, B., Gamble, L. and Mullin, J. V. (1995) Studies of water-in-oil emulsions: stability classes and measurement. In *Proceedings of the Seventeenth Arctic and Marine Oil Spill Program Technical Seminar*, pp. 21–42. Environment Canada, Ottawa, Ontario.