

# Breaking of Water-in-Crude Oil Emulsions. 1. Physicochemical Phenomenology of Demulsifier Action

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Water-in-oil emulsions formed during oil slicks or petroleum production are known to be stabilized by surfactant molecules that naturally occur in the crude oil, e.g., asphaltenes, which are quite lipophilic in nature. Demulsifier substances combine with naturally occurring surfactants to attain a so-called optimum formulation at which the stability of the emulsion is minimum. The attainment of this formulation is related to the hydrophilicity and concentration of the added demulsifier, and a general phenomenology of the demulsification process is outlined.

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## Introduction

Petroleum is most often produced as a water-in-oil emulsion and the water must be removed (down to a level of <1%), in a process that is usually called demulsification or dehydration, which consists of forcing the coalescence of water droplets and producing their separation by settling. After decades of research and encouraging results, the breaking of water-in-petroleum emulsions is not completely understood, particularly as far as the added chemical demulsifier role is concerned, and much research is still required.<sup>1,2</sup>

Physical–chemical conditions, such as formulation (i.e., the nature of the substances, temperature, and composition), are known to be related to the emulsion properties, particularly its stability or persistence. The high stability of water-in-crude emulsion is generally due to the effect of amphiphilic substances present in the petroleum, i.e., asphaltenes and resins compounds, which actuate as lipophilic emulsifiers.

The target of demulsifier action is to offset the stabilization of emulsion both from the thermodynamic and kinetic points of view. Because the stabilization is dependent on the nature and proportion of the different components, particularly the surfactant species, it is intrinsically linked with the physicochemical formulation.

**1. Influence of Formulation on Emulsion Stability.** In the past century, several attempts have been proposed to relate the formulation concept to emulsion stability. The first proposal, the so-called Bancroft's rule,<sup>3</sup> stated in 1913 that the external phase of the emulsion is the one that contains most of the surfactant, i.e., a W/O (or O/W) emulsion results from the use

of a lipophilic (or hydrophilic) surfactant. This was a very qualitative rule, and a numerical description of the effect of the different species involved in the phenomena was desirable. In 1949, the hydrophilic–lipophilic balance (HLB) concept was introduced by Griffin<sup>4</sup> as an empirical scale that was intended to describe the balance in the effects of the hydrophilic and lipophilic groups of a surfactant molecule. The HLB was defined for polyoxyethylated surfactants as 20 times the weight fraction of the polyoxyethylene part.<sup>5</sup> For instance, for a pure nonylphenol with five EO groups, the HLB results to be 10. Because this species has exactly the same weight in the hydrophilic and lipophilic parts, an approximate rule of thumb is that  $HLB < 8$  (or  $HLB > 12$ ) indicates a lipophilic (or hydrophilic) surfactant and, hence, results in a W/O (or O/W) emulsion, according to Bancroft's rule. Original studies on the HLB effect on emulsion properties reported the presence of a stability maximum at some value, the so-called required HLB, which is dependent on the nature of the oil; however, there was no systematic screening until the investigation by Boyd et al.,<sup>6</sup> which indicated that there are two stability maxima (one at  $HLB < 10$  (W/O emulsion) and one above it (O/W)), and, therefore, there is an implicit stability minimum between them, at  $HLB \approx 10$ . The HLB scale was empirical and had several shortcomings, particularly the fact that it was inaccurate when comparing different surfactant families and it did not take into account the effects of temperature, salinity, and the nature of the hydrophilic group. It may be said that the HLB scale, which is still used today, because of its extreme simplicity, is only valid to compare substances in a same family of surfactants.

The enhanced oil recovery research drive in the 1970s allowed researchers to improve upon Winsor's *R*-ratio<sup>7</sup> and Shinoda's phase inversion temperature (PIT) concepts<sup>8</sup> to describe the

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(1) Angle, C. W. *Encyclopedic Handbook of Emulsion Technology*; Sjöblom, J., Ed.; Marcel Dekker: New York, 2001; Chapter 24, pp 541–594.

(2) Kilpatrick, P. K.; Spiecker, P. M. *Encyclopedic Handbook of Emulsion Technology*; Sjöblom, J., Ed.; Marcel Dekker: New York, 2001; Chapter 30, pp 707–730.

(3) Bancroft, W. D. *J. Phys. Chem.* **1913**, *17*, 501–519.

(4) Griffin, W. C. *J. Soc. Cosmet. Chem.* **1949**, *1*, 311–326.

(5) Griffin, W. C. *J. Soc. Cosmet. Chem.* **1954**, *5*, 249–256.

(6) Boyd, J.; Parkinson, C.; Sherman, P. *J. Colloid Interface Sci.* **1972**, *41*, 359–370.

(7) Winsor, P. *Solvent Properties of Amphiphilic Compounds*; Butterworth: London, 1954.

(8) Shinoda, K.; Arai, H. *J. Phys. Chem.* **1964**, *68*, 3485–3490.