ARTICLE IN PRESS

Egyptian Journal of Petroleum (2016) xxx, xxx–xxx

HOSTED BY

ELSEVIER

Egyptian Petroleum Research Institute

Egyptian Journal of Petroleum

www.elsevier.com/locate/egyjp
www.sciencedirect.com

REVIEW

Formulation of best-fit hydrophile/lipophile balance-dielectric permittivity demulsifiers for treatment of crude oil emulsions

C.M. Ojinnaka [a], J.A. Ajienka [b], O.J. Abayeh [a], L.C. Osuji [a], R.U. Duru [c,*]

[a] *Pure & Industrial Chemistry Department, University of Port Harcourt, Nigeria*
[b] *Petroleum & Gas Engineering Department, University of Port Harcourt, Nigeria*
[c] *World Bank Africa Centre for Excellence, University of Port Harcourt, Nigeria*

Received 17 September 2015; revised 27 November 2015; accepted 8 December 2015

KEYWORDS

Crude oil;
Emulsion;
Demulsifiers;
Plant extracts;
Screening

Abstract The commerce of crude oil depends heavily on its water and salt contents usually referred to as Basic Sediments and Water (BS&W), which is co-produced with the crude oil in the form of emulsion. The lower the BS&W, the higher the market value of the crude. The presence of water in crude oil causes corrosion, lowers capacity utilization of production and processing plant parts and pipelines, reduces oil recovery and increases the oil content of the effluent water. The stabilizing factors of crude oil emulsions vary from one oil field to the other and with time in the same well as co-produced water increases, or after a well treatment and Enhanced Oil Recovery Operations (EOR). Periodical assessment and possible change of demulsifiers employed is therefore necessary at certain stages of crude oil productions, but this is not encouraged due to lack of general formulation procedures and the rigorous nature of bottle test method that is currently being used for assessment and selection. In this paper, the factors that affect the stability of crude oil emulsions are presented. Efforts of researchers in formulating demulsifiers based on these factors and their screening methods were reviewed. The context sets the stage for further exploration of possible relationship(s) between the physical parameters of the crude oil and the demulsifiers, and exploiting same in the formulation of new demulsifiers capable of resolving crude oil emulsions using chemicals with improved surface activity and crude extracts of indigenous plants.

* Corresponding author.

Peer review under responsibility of Egyptian Petroleum Research Institute.

http://dx.doi.org/10.1016/j.ejpe.2015.12.005
1110-0621

Contents

1. Introduction

In pharmaceutical and cosmetic industries, emulsions are desired for formulation stability. In the petroleum industry, emulsion is undesirable, so chemists and engineers seek means of breaking or destabilizing emulsions formed in the process of producing crude oil from the reservoir.

An emulsion is a type of colloidal dispersion consisting of two incompletely miscible liquids, one (the dispersed or internal phase) being distributed in finite globules in the other [the continuous or external phase (1)]. There are two basic types of emulsion; Oil-in-Water (O/W) and Water-in-Oil (W/O) emulsions. W/O emulsion is formed when water is the dispersed phase and oil is the continuous phase. Conversely, if oil is the dispersed phase and water is the continuous phase, it is termed Oil-in-Water emulsion. Water-in-Oil emulsion is the type that is usually encountered in crude oil production.

The presence of water in crude oil presents a number of problems to its production, transportation and processing leading to increased down-time in the petroleum industries. These problems include [2–6]:

(i) Limitation of space in the processing and transporting vessels leading to reduced net efficiency of the vessels.
(ii) Corrosion of production plant parts and pipelines, an effect which is further enhanced by the presence of dissolved salts in the water phase.
(iii) Emulsion formation may also lead to reduced oil recovery and consequently, environmental concerns due to appreciable oil content of the effluent water.
(iv) Lowering of API gravity.

2. Composition of crude oil

Crude oil contains numerous compounds whose constituent elements are more of carbon and hydrogen in varying proportions. For convenience, the compounds have been grouped into four broad classes – saturates, aromatics, resins and asphaltenes (SARA), using their solubility and polarity parameters. The separation scheme (Fig. 1) into these classes is called SARA analysis [7].

The saturate is the fraction that consists of saturated non polar compounds that are composed of hydrogen and carbon only. Also known as the paraffins, they may be straight-chain, branched or cyclic alkanes. The cycloalkanes may have side chains and multiple rings but the distinguishing characteristic of the saturates is the absence of multiple bonds. Wax (straight chain alkanes with C_{20}–C_{30} carbon range), one of the components that contribute to crude oil emulsion stability belongs to this saturate fraction [7,8].

Aromatics are the fraction that contains cyclic compounds whit benzene ring structure. The rings may be one or more (fused) with or without side aliphatic substituents.

The resin fraction is somewhat similar to the aromatic but differs with the possession of higher molar mass and contains at least one heteroatom in their ring structure making them to be more polar. Operationally, resins can be defined as the fraction that is soluble in light alkanes such as n-pentane and n-heptane but insoluble in propane [7,9,10].

In the SARA analysis procedure, the asphaltene fraction is usually the first to be precipitated out of the crude oil bulk using n-pentane or n-hexane. The structure of asphaltene structure (Fig. 2a) is yet to be well defined but it is generally believed to consist of polycyclic aromatic clusters with estimated molecular weight of 500–2000 g/mol [7]. They are the heaviest and most polar fraction of the crude oil with fused aromatic rings (more than in resins), aliphatic side chains and one or more hetero atoms. As a result, they play the major role of stabilizing water in oil emulsion [7,10,11].

The knowledge about the chemical composition of crude oils, gained from, for instance a SARA-analysis, cannot fully explain the crude oil behavior with regard to emulsion stability, asphaltene deposition etc. but it is valuable in other fields in the petroleum industry such as reservoir evaluation, migration and maturity, degradation processes, processing, and

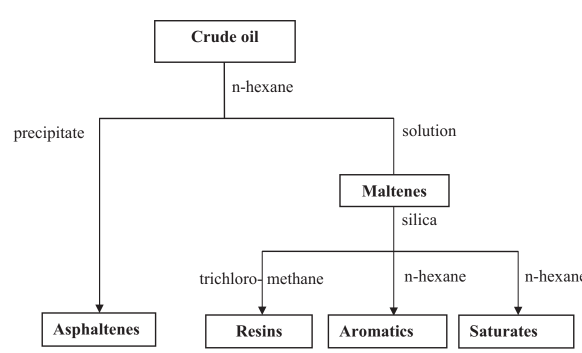

Figure 1 SARA – separation scheme (Aske, 2002) [7].