Petroleum Science and Technology

ISSN: 1091-6466 (Print) 1532-2459 (Online) Journal homepage: http://www.tandfonline.com/loi/lpet20

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To cite this article: L. Oyekunle & O. Adeyanju (2011) Thermodynamic Prediction of Paraffin Wax Precipitation in Crude Oil Pipelines, Petroleum Science and Technology, 29:2, 208-217, DOI: 10.1080/10916460903330163

To link to this article: https://doi.org/10.1080/10916460903330163

Published online: 07 Feb 2012.

Petroleum Science and Technology, 29:208–217, 2011

ISSN: 1091-6466 print/1532-2459 online
DOI: 10.1080/10916460903330163

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Thermodynamic Prediction of Paraffin Wax Precipitation in Crude Oil Pipelines

L. OYEKUNLE[1] AND O. ADEYANJU[1]

[1]Department of Chemical Engineering, University of Lagos, Akoka-Yaba, Lagos, Nigeria

Abstract *Crude oils are generally very complex chemical systems consisting predominantly of hundreds to thousands of hydrocarbon compounds from simple low-molecular-weight paraffins to high-molecular-weight waxes. At low temperatures these paraffins precipitate as a wax phase, which may cause the plugging of pipes and many other problems. In this study the cloud point and the amount of the precipitated wax at different temperatures were determined using a modified multi-solid wax model at stock tank conditions and at high pressure for three live crudes and synthetic oil. The model is based on the description of the nonideality of the phases in equilibrium using the Peng-Robinson cubic equation of state for the liquid phase with a modified a-function and the universal quasi chemical (UNIQUAC) equation for the solid phase, which takes into account the effects of temperature, pressure, and composition on the wax precipitation. The model assumes the crystalline nature of wax formed. The experimental data and model predictions reveal that the cloud point decreases with increased pressure and increases when the crude oil is mixed with more light hydrocarbons. The values predicted by the new model show very little deviation from experimental data.*

Keywords crude petroleum, paraffins, thermodynamic modeling, wax deposition

Deposition of crystalline paraffinic waxes is frequently encountered during the production and transportation of crude oil and its products. In the petroleum industry, wax precipitation causes severe operational problems by plugging the valves and the flow lines.

One of the most important measurements that characterize the waxing potential of fluids is the cloud point. This is the temperature at which "cloudiness" of a relatively transparent petroleum fluid is observed upon cooling. As long as the operating temperature remains above the cloud point, wax precipitation will not occur. Typically, cloud point measurements used in industry are inadequate. The standard ASTM D2500-88 or IP 219/82 cloud point measurement methods are only applicable for clear fluids because they rely on visual observation of the wax crystals. For dark crude oils, cloud points are estimated from viscometry and differential scanning calorimetry (DSC). Oftentimes, the viscosity or DSC data are misinterpreted. A more serious problem with these methods is that sufficient wax must crystallize before the cloud point can be detected.

A number of engineering models have been proposed for calculating oil-wax equilibria (Hansen et al., 1988; Erickson et al., 1993; Prausnitz et al., 1999; Banki and Firooz-

Address correspondence to Layioye Oyekunle, Department of Chemical Engineering, University of Lagos, Akoka-Yaba, Lagos 101017, Nigeria. E-mail: layioyekunle@yahoo.com