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Importance of Asphaltene Content in Petroleum II – Multi-Peak Viscosity Correlations

[*a shortened version of the title*: Importance of Asphaltene Content in Petroleum II]

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Abstract: A "common knowledge" in petroleum science and technology is that viscosities of dead crude oil are monotonic functions of oil's asphaltene content. However analysis of crude oil databases reveals multiple peaking of oil viscosity (up to two orders of magnitude) at specific asphaltene contents, close to structural phase boundaries observed in asphaltene and oil solutions. Due to strong viscosity –density correlation maxima of viscosity practically coincide with earlier reported maxima of specific gravity in dead crude oils.

Keywords: Asphaltenes, crude oils, phase boundaries, viscosity-asphaltene, viscosity-density, correlations

1. INTRODUCTION

Petroleum exploration and production strategies rely significantly on proper assessments of correlations between oil properties and its composition. Regretfully, property-composition correlations are often interpreted in line with outdated oversimplified stereotypes. One of these persistent stereotypes is that the viscosity of a crude oil is a monotonic increasing function of oil's asphaltene content (Al-Mamaari et al., 2006; Argillier et al., 2001; Henuat et al., 2001). Monotonous viscosity-asphaltene relationships are implied even by the authors who acknowledge the importance of the structural state in asphaltene nanocolloids (Chandra et al., 1998; Mason and Lin, 2003; Luo and Gu, 2007). The apparent principal origin of the discussed stereotype is in an implicit assumption that asphaltenes constitute an inert colloidal fraction of a crude oil, analogous to suspended fine solids. However, in our previous publications (Evdokimov et al., 2006; Evdokimov, 2007, 2008; Evdokimov, 2009) we have argued that colloidal asphaltenes are not inert, but belong to a class of so-called association species. Consequently, association asphaltene colloids are subjected to consecutive structural transformations characterized by a well-defined phase diagram apparently common to asphaltenes of any geographical/geological origin. Concentration-defined phase boundaries at this diagram delimit, consecutively, solution of asphaltene monomers, solution of oligomers, suspension of nanocolloids with basic asphaltene particles 2-4 nm in diameter, suspensions of various colloidal clusters of basic nanoparticles, suspensions of micrometer-sized fractal flocs.

It should be emphasized that the existence of the discussed phase boundaries become immediately evident only at data plots with log scales for asphaltene concentrations, but not at linear scale plots usually employed in petroleum studies. In particular, in the preceding paper (Evdokimov, 2009) it was demonstrated that the frequency distribution of world's recovered crudes peaks at asphaltene phase boundaries and that the specific gravity of dead crude oils crudes attains maximum values at these phase boundaries.

2. MULTI-PEAK VISCOSITY-ASPHALTENE CORRELATIONS IN DEAD CRUDE OILS

2.1. Correlations of viscosity with specific gravity in the analyzed crude oil database

On the basis of the above information, peaking of viscosity at asphaltene phase boundaries may have been expected in view of the frequently quoted strong viscosity – density (API gravity) correlations in dead crude oils (Khan et al., 1987; Sattarin et al., 2007; and references therein). Figure 1 shows a fairly low scatter of data points in the relationship between kinematic viscosity at 20 ^{o}C with specific gravity for the analyzed database of more than 200 dead crude oils from a variety of geographical/geological locations in the former USSR (Evdokimov, 2005). Solid line is a recent analytical correlation for dead crude oils at fixed temperature (Sattarin et al., 2007, equation 6).

2.2. Viscosity of world's recovered crudes exhibits orders of magnitude increase at asphaltene phase boundaries

Figure 2A shows an un-processed (scatter) plot of the relationship between viscosity at 20 oC and asphaltene content C for the same crude oil database as in Figure 1. This plot demonstrates that minimum values of viscosity are randomly distributed along some smooth curve, while distribution of maximum viscosity values is not random, these tend to concentrate near several specific values of asphaltene content. To highlight these observations, in Figure 2B we show maximum and minimum values of viscosity from Figure 2A, evaluated in consecutive intervals of ΔLog(C). The respective data points sets are connected by solid lines.

Figure 2A clearly demonstrates anomalous peaking of viscosity (up to two orders of magnitude) in crude oils with some specific asphaltene contents.

2.3. Peaks of viscosity and of specific gravity in dead crude oils are observed at the same of asphaltene phase boundaries

In Figure 3 the behavior of maximum viscosity values is compared to maxima of specific gravity from Evdokimov, 2009. Close coincidence of both data sets allows to attribute the above specific asphaltene contents to phase boundaries of asphaltene nanocolloids, numbered as in previous publications (Evdokimov et al., 2006; Evdokimov, 2007, 2008; Evdokimov, 2009). Note the absence in viscosity data of phase boundary 6 which is an attribute of non-flowing extra heavy crudes and bitumen. The exact mechanisms of simultaneous viscosity and density increase at phase boundaries should be a subject of further investigations. One possibility is a transient disaggregation of spacious asphaltene clusters into compact subunits on a route to a new structural state.

3. CONCLUSIONS

A "common knowledge" is that the bulk properties of a crude oil are monotonic functions of its asphaltene content. However analysis of dead oil databases reveals maxima of oil viscosity and of specific gravity at asphaltene contents, close to structural phase boundaries earlier observed in asphaltene and oil solutions. Even without a precise knowledge of underlying molecular mechanisms, the revealed multi-peak correlations may be of immediate importance to both upstream and downstream petroleum industry operations.

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FIGURES

Figure 1. Data points – correlation of viscosity and specific gravity in the analyzed database of more than 200 dead crude oils. Solid line – analytical correlation from Sattarin et al., 2007.

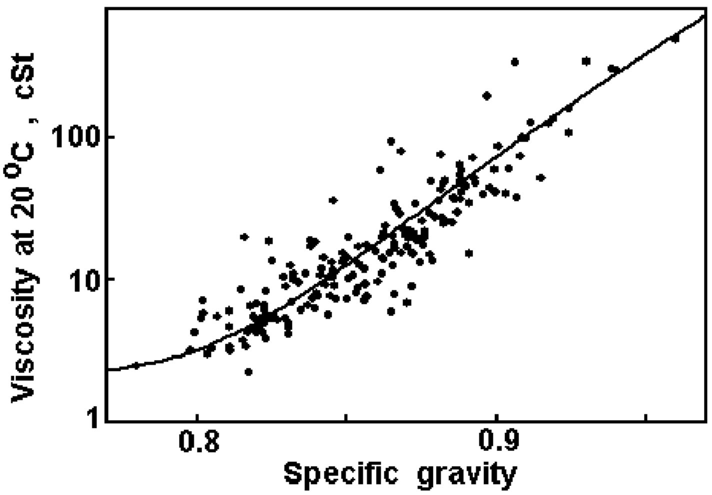

Figure 2. A. - Scatter plot of viscosity – asphaltene correlation for crude oil database from Evdokimov, 2005. B. - Maximum and minimum values of viscosity in the scatter plot. Note viscosity peaking by two orders of magnitude at some specific asphaltene contents.

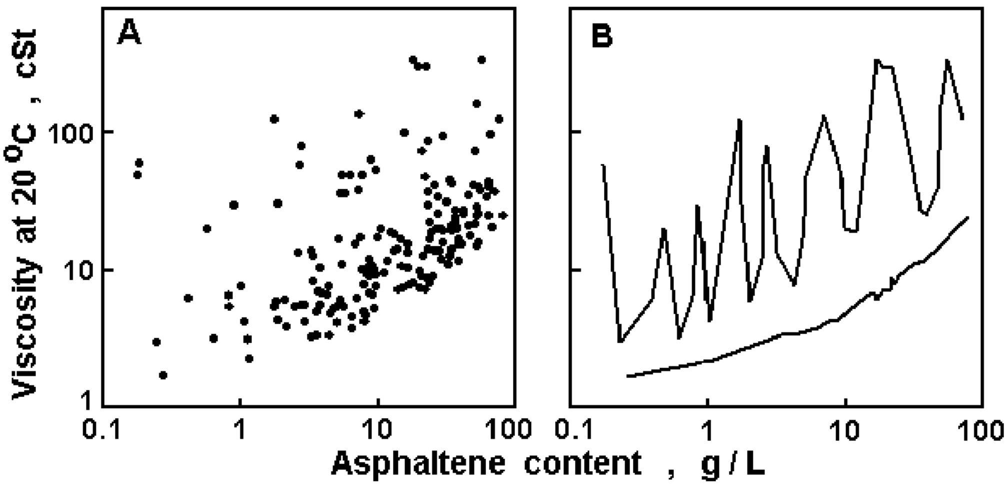

Figure 3. Attribution of viscosity and specific gravity maxima in dead crude oils to particular phase boundaries of asphaltene nanocolloids.