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**Importance of Asphaltene Content in Petroleum III – New Criteria for Prediction of
Incompatibility in Crude Oil Blends**

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

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Abstract: Our previous results have shown that macroscopic properties of petroleum media may undergo abrupt changes caused by currently under-investigated microscopic phase transitions in asphaltene nanocolloids. In particular, native crudes of diverse origin exhibit sharp viscosity and density peaking at phase boundaries, defined by specific asphaltene contents. We suggest that when these asphaltene contents are approached in blends of several crude oils, severe incompatibility may be observed, e.g. massive appearance of solid sediments. New criteria for most incompatible and for most compatible blends are formulated in terms of g/L asphaltene concentrations.

Keywords: Crude oils, oil blends, incompatibility, criteria, asphaltene content

1. INTRODUCTION

Multiple studies have shown that blending of different crude oils may lead to precipitation of asphaltenes (Wiehe and Kennedy, 2000a, 2000b; van den Berg et al., 2003; Schermer et al., 2004). This phenomenon, known as crude oil incompatibility, causes more and more problems in transportation and refining especially as economic pressures are forcing many refiners to look at blends of low price crudes to improve margins (van den Berg et al., 2003). In spite of multiple studies performed over the past decades significant gaps remained in the knowledge of the chemistry and physics of incompatibility (Wallace, 1964; Mushrush and Speight, 1995). Recognition of the problem has not yet led to a standard method for the determination and quantification of crude oil incompatibility. Various criteria describing asphaltene stability and allowing prediction of compatibility have been described in the literature.

For example, Asomaning and Watkinson, 2000 introduced a simple colloidal instability index, CII, based on SARA compositional analysis of crude oil blends:

$$CII = \frac{(\text{Saturates} + \text{Asphaltenes})}{(\text{Aromatics} + \text{Resins})} \quad (1)$$

They concluded that blends with $CII > 1$ tend to be incompatible and precipitate asphaltenes.

Another compatibility criterion of Wiehe (Wiehe and Kennedy, 2000a) requires titration of the individual oils with a model solvent, such as toluene, and a model nonsolvent, such as *n*-heptane. This enables measuring the solubility parameter of the mixture at which asphaltenes precipitate. This solubility parameter on a reduced *n*-heptane-toluene scale is called the insolubility number, I_N . In addition, the tests measure the solubility parameter of the oil that on a reduced *n*-heptane-toluene scale is called the solubility blending number, S_{BN} . The criterion for compatibility of any blend is that the volume average solubility blending number is greater than the maximum insolubility number of any component in the blend.

$$(S_{BN})_{\text{blend}} > (I_N)_{\text{max}} \quad (2)$$

Apart from a complexity of required analyses, the common drawback of all existing criteria is their threshold character. Namely, they predict only a single onset of incompatibility in blends with increasing amount of one of crude oils. All mixtures with larger contents of this component are regarded as incompatible. However, as discussed below, close inspection of available experimental data clearly reveals several peaks of incompatibility in oil blends with varying compositions. The suggested new criteria relate incompatibility peaking to a common phase diagram of asphaltenes in petroleum media (Evdokimov 2008b).

2. BACKGROUND OF SUGGESTED INCOMPATIBILITY CRITERIA

Traditionally, thermodynamical descriptions of petroleum phase transformations have been limited to simplest two-phase gas/vapor - liquid models. There has been a considerable progress in modeling liquid-solid phase boundaries for hydrates and waxes, but phase behavior of asphaltenes is still poorly understood. For example, thermodynamic theories presume that asphaltenes dissolve in solution and solid asphaltene precipitation is reversible; colloidal theories hold that asphaltenes disperse in solution and predict irreversible precipitation. All theories explicitly or implicitly imply two-phase behavior of asphaltenes with a single phase boundary.

However, our comparative analysis of available experimental data has shown that formation and evolution of asphaltenes in solutions, as well as in native petroleum proceeds via multiple structurally distinct phases, apparently common for asphaltenes of any origin (Evdokimov et al., 2006; Evdokimov 2007, 2008a, 2009a, 2009b). These phases are delimited by well-defined boundaries on the temperature- composition (T-C) phase diagram of asphaltenes at ambient pressure, illustrated in Figure 1.

It should be emphasized that no theoretical models were involved in construction of this diagram. All boundaries are drawn through sets of specific points (inflections, peaks, dips, steps) at directly measured concentration and temperature dependencies of various asphaltene properties. Lists of analyzed original publications may be found in Evdokimov et al., 2006; Evdokimov 2007, 2008a. Note that the still limited amount of data does not allow precise evaluation of phase boundary positions; hence below discussed numerical values of corresponding asphaltene contents should be regarded as approximate. In brief, interpretations of particular boundaries by various authors may be summarized as follows. Concentration-defined boundary *I*, at asphaltene contents of ~5-7 mg/L, corresponds to transition from a solution of monomers (M) to a solution of oligomers (O). Boundary 2, at ~100-150 mg/L, corresponds to emergence of nanocolloids (NC) with basic asphaltene particles 2-4 nm in diameter. Groups of close boundaries *3a* (1.7+3.1 g/L) and *3b* (6+8 g/L) reflect appearance of colloidal clusters (CC) of basic nanoparticles. At higher asphaltene concentrations, these clusters undergo a series of structural transformations (e.g. form fractal flocs $\geq 0.1 \mu\text{m}$ in size) at boundaries 4 (~28 g/L), 5 (55-65 g/L). Boundaries *New* (0.4+0.8 g/L) and 6 (140-160 g/L) were revealed not in laboratory experiments but by later statistical analysis of crude oil databases (cf. below). Temperature-defined phase boundaries *I*, at ~25-35 °C, *II*, at ca. 100 °C, and *III*, at ca. 180 °C, apparently arise from competitive contributions of various types of intermolecular interactions.

The principal, though trivial, reason why such phase diagram has not been revealed earlier is that individual phase boundaries become perceptually well separated only at log scale plots, like that in Figure 1, but not at linear scale plots usually employed in petroleum studies.

Our discussions with petroleum industry practitioners have shown that mere laboratory studies of asphaltene phase behavior in simple solutions may not be persuasive. These specialists

often doubt that delicate processes at molecular nanoscale could be of any significance to bulk properties of native raw petroleum. Hence, to support the data of Figure 1, we analyzed extensive databases (>400 entries) of world's dead crude oils by plotting oil properties as functions of asphaltene contents C in g/L. This analysis has demonstrated that crude oils with asphaltene contents close to phase boundaries 1-6 in Figure 1 are distinguished by: 1) increased frequency of appearance (Evdokimov, 2008a, 2009a); 2) anomalous peaking of viscosity up to two orders of magnitude (Evdokimov et al., 2006, Evdokimov 2007; Evdokimov, 2008a, 2009b); 3) anomalous peaking of specific gravity (Evdokimov et al., 2006; Evdokimov, 2008a, 2009a). To highlight these peaks, we evaluated maximum values of specific gravity in consecutive equal intervals of $\Delta\text{Log}(C)=0.05$ and connected them with straight lines (Evdokimov, 2009a). The obtained multi-peak plot, indicating the apparent importance of asphaltene phase boundaries in native petroleum, is employed for comparison with below discussed incompatibility data in Figures 3-5.

3. CASE DISCUSSIONS

One of the most documented cases (Wiehe and Kennedy, 2000a, 2000b; Mason and Lin, 2003a, 2003b, 2006; Mason et al., 2005; Wiehe and Kennedy, 1999a, 1999b) is incompatibility in blends of a light Forties crude (North Sea, specific gravity – 0.813, asphaltenes – 0.16 %) with a heavy Souedie crude (Syria, specific gravity – 0.910, asphaltenes – 11.8 %). As an example, Figure 2 shows the effect of Souedie content in blends on the volume of asphaltene aggregates (Mason and Lin, 2003a, 2006).

The Wiehe's compatibility criterion (2) predicts that *all* blends with less than 31% Souedie (the hatched range in Figure 2) should be incompatible and precipitate aggregated asphaltenes (Wiehe and Kennedy, 2000a, 1999a, 1999b). However, the presented experimental

data clearly show that noticeable incompatibility is observed only in the narrow range of blend compositions and decreases at smaller Souedie contents. We suggest that this apparent controversy may be explained by the above discussed phase transformations in asphaltenes if incompatibility results are re-scaled as a function of g/L asphaltene concentration in crude oil blends. In Figure 3 re-scaled non-zero data from Figure 2 (filled points, thick line) are superimposed on the multi-peak plot of phase transition effects on specific gravity in dead crude oils from Evdokimov, 2009a (thin line). Figure 3 clearly shows that unexpected incompatibility peaking in blends with ca. 30 % of Souedie most probably is due to asphaltene content approaching and crossing phase boundary 4.

Another reported case (Schermer et al., 2004) is incompatibility in blends of relatively immature marine Arab Medium crude (Saudi Arabia, density - 0.878 kg/L, asphaltenes – 3.25 %) with a mature paraffinic Gippsland crude oil (Australia, density - 0.796 kg/L, asphaltenes ≤ 0.05 %). Blends of these two crudes have shown complex multi-peaked behavior of the mass of sediments, not accounted for by conventional criteria of compatibility. However, re-scaling these data as a function of g/L asphaltene content in blends (Figure 4), again demonstrates that peaks of incompatibility coincide with asphaltene phase boundaries 3a, 3b and 4.

The third well-documented case (Saleh et al., 2005) is incompatibility in blends of four crude oils used in Australia - Bach Ho (density - 0.82 kg/L, asphaltenes – 1.48 %), Gippsland (density - 0.79 kg/L, asphaltenes – 0.35 %), Cossack (density - 0.79 kg/L, asphaltenes – 0.08 %), and Kutubu (density - 0.80 kg/L, asphaltenes – 0.11 %). According to CII criterion (1), all blends should have been incompatible, while Wiehe's criterion (2) predicted incompatibility only in one blend of 75% Bach Ho with 25 % Gippsland. However, experimental results revealed complex behavior of various incompatibility parameters. Again, re-scaling these results as functions of g/L

asphaltene content in blends reveals that most obvious peaks of incompatibility coincide with asphaltene phase boundaries. As an example, filled points connected with a thick line Figure 5 show the mass of final filterable insolubles in the studied blends with a prominent peak at phase boundary *3b* and an obvious increase towards phase boundary *New*.

4. SUGGESTED CRITERIA

Summarizing, consideration of several documented studies of crude oil blends apparently reveals common conditions of incompatibility. In particular, maximum amounts of aggregated asphaltenes, solid sediments, filterable insolubles obviously are observed in blends with asphaltene contents close to the newly revealed phase boundaries of asphaltene nanocolloids. In turn, fairly compatible blends appear to possess asphaltene contents far from phase boundaries. On the basis of the above discussion, in Table 1 we suggest new criteria of incompatibility according to final contents of asphaltenes in blends of several dead oils.

It should be specially noted that the above criteria imply that the blends are homogeneous and equilibrated fluids. These requirements are fulfilled only in cases of correct blending order (Wiehe and Kennedy, 1999a, 1999b; Buckley et al., 2006). E.g., blending of small amounts of a heavy asphaltic crude oil with a large volume of a light paraffinic one can create heterogeneous mixing zones where asphaltenes precipitate rapidly (Buckley et al., 2006), as their local concentrations are close to the above discussed phase boundaries. Instantaneous compatibility of blends mixed under these conditions may deviate from predictions of Table 1, while reaching an equilibrium homogeneous state may require days or even months. With respect to immediate practical applications, it should be also reminded that Figure 1 and Table 1 describe

only “the most obvious” nanophase boundaries, reflect our current knowledge of structural transformations in petroleum and should be subjected to further investigation.

4. CONCLUSIONS

In conclusion, this paper describes research aimed at modification of traditional incompatibility criteria by accounting for molecular processes in nanocolloids of native petroleum fluids. Such modification now becomes possible on the basis of the newly assembled temperature-composition phase diagram of asphaltenes in solutions, as well as in native dead crudes. In particular, this diagram reveals some critical asphaltene contents, highly unfavorable for industrial processing of petroleum. Namely, industrially important macroscopic properties of recovered (dead) crude oils (density, viscosity, etc.) may undergo undesirable abrupt changes caused by currently under-investigated microscopic phase transitions in asphaltene nanocolloids. Blends of several dead crude oil with final asphaltene contents near phase boundaries may exhibit severe incompatibility.

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Table 1. The criteria for incompatibility based on final asphaltene concentrations in blends of several crude oils.

Asphaltene phase boundaries	6		5		4		3b		3a		3a		2
	Asphaltene content , g/L												
Most incompatible blends	150		70		27		7.5		2.7		1.8		0.12
Most compatible blends		80		45		11		4.5		2.3		0.65	

FIGURES

Figure 1. Multiple structural phases of asphaltenes in petroleum (at ambient pressure), revealed by analysis of experimental data. 1-6 – concentration-defined phase boundaries. I-III - temperature-defined phase boundaries. Types of asphaltene species: M – monomers; O – oligomers; NC – nanocolloids; CC – colloidal clusters.

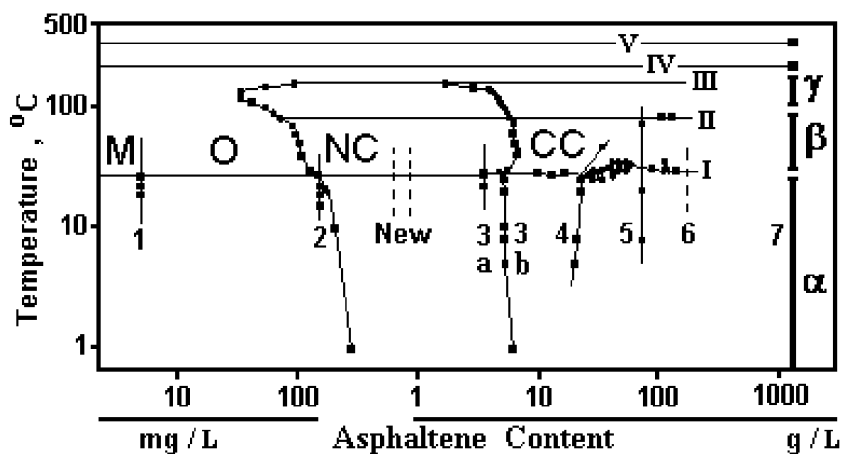


Figure 2. Volume of asphaltene aggregates in blends of a light crude with a heavy one (after Mason and Lin, 2003a, 2006). The existing incompatibility criteria predict massive aggregation in the entire hatched region.

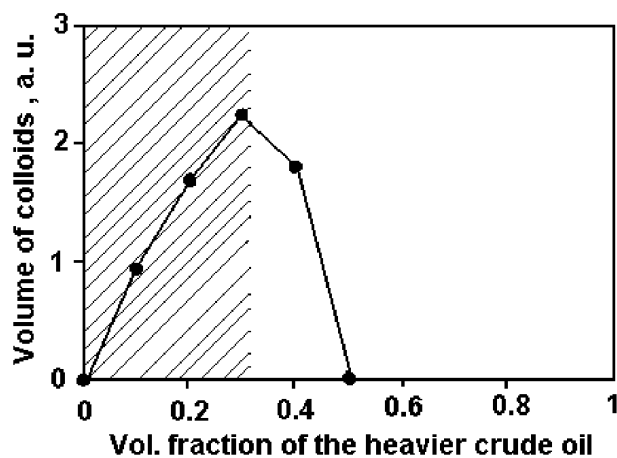


Figure 3. The data of Figure 3 (filled circles), superimposed on a general plot of asphaltene phase transition effects in crude oils (Figure 2).

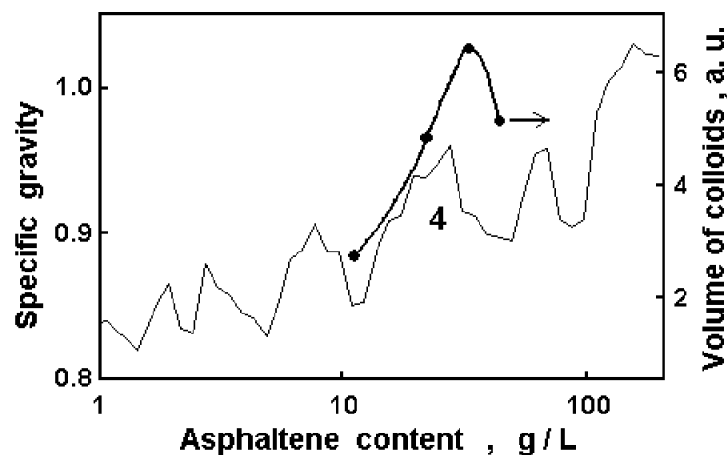


Figure 4. Filled circles – the mass of sediments in blends of two crude oils (data from Schermer et al., 2004, re-scaled to g/L asphaltene contents in blends). Solid lines - a general plot of asphaltene phase transition effects in crude oils from Figure 2.

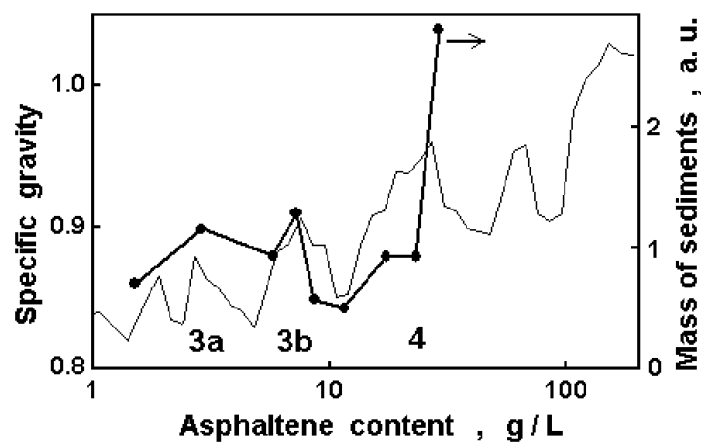


Figure 5. Filled circles – the mass of final filterable insolubles in blends of four Australian crudes (data from Saleh et al., 2005, re-scaled to g/L asphaltene contents in blends). Solid lines - a general plot of asphaltene phase transition effects in crude oils from Figure 2.

