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**Importance of Asphaltene Content in Petroleum – Revision of Some Persistent
Stereotypes**

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

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Abstract: A “common knowledge” in petroleum science and technology is that the bulk properties of a crude oil are monotonic functions of its asphaltene content. However unbiased analysis of world’s crude oil databases reveals common peaking of oil density as well of a frequency of oil appearance at specific asphaltene contents, close to structural phase boundaries observed in asphaltene and oil solutions. Another result of database analysis is a new analytical expression for the general trend of density-asphaltene relationship in world’s recovered (dead) crude oils.

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

1. INTRODUCTION

The important characteristic of contemporary production oilfields is large variation in properties of recovered raw petroleum, such as crude oil density, viscosity etc. Petroleum exploration, production and pricing strategies rely significantly on proper assessments of correlations between oil properties and its composition. The development of analytical methods and theoretical and practical methodologies for the determination and interpretation of fluid compositional variations in petroleum reservoirs has been one of foundation stones of reservoir geochemistry and new developments continue to appear (Cubitt et al., 2004). However, surprisingly, in planning of industrial strategies for most reservoirs, property-composition correlations are often ignored (Larter et al., 2008) or interpreted in line with outdated oversimplified stereotypes.

One of these persistent stereotypes is that the density (API gravity) of a crude oil is a uniquely defined monotonic increasing (decreasing) function of oil's asphaltene content (Speight, 1999; Buckley et al., 2002; Yang et al., 2002; Alboudwarej et al., 2006). Accordingly, producers of some °API measuring devices insist that an obtained value of API gravity may be directly converted to an amount of asphaltenes in a crude oil (API Gravity Transmitter, 2005). The apparent principal origin of the discussed stereotype is in an implicit assumption that asphaltenes constitute an inert (dead) colloidal fraction of a crude oil, analogous to suspended fine solids. Another origin may be in consideration of limited oil databases for a single oil family or a number of oil families from one region.

In our earlier publication (Evdokimov, 2005) we have attempted to improve density-asphaltene correlations by collecting a database of several hundreds world's crude oils from a diversity of geographical/geological locations. These preliminary results were evaluated with respect to models of biodegradation and other post-generative alteration effects.

Considerable progress in revealing new information became possible after realization that colloidal asphaltenes are not inert, but belong to a class of so-called association species (Myers, 1999). 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 (Evdokimov et al., 2006; Evdokimov, 2007, 2008). Detailed discussion of this diagram is outside the scope of the present paper. Our current information on the positions and on the probable nature of concentration-defined phase boundaries (numbered as in original publications) may be summarized as follows. Boundary **1** (~5-7 mg/L asphaltene content) apparently corresponds to transition from a solution of monomers to a solution of various oligomers. Boundary **2** (~120-150 mg/L) is due to emergence of nanocolloids 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 complex colloidal clusters 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) and **6** (140-160 g/L).

It should be emphasized that construction of asphaltene phase diagram was largely facilitated by a seemingly trivial, but a crucially important improvement in data analysis. Namely, non-conventional details of analyzed correlations become perceptually well separated only at data plots with log scales for asphaltene concentrations, but not at linear scale plots usually employed in petroleum studies. Note that log concentration scales are recommended in colloid science for presentation and analysis of molecular/colloidal association phenomena (Somasundaran, 2006).

2. NEW DATA ON IMPORTANCE OF ASPHALTENE CONTENT IN PETROLEUM

2.1. Frequency distribution of world's recovered crudes peaks at asphaltene phase boundaries

The importance of asphaltene phase boundaries in native petroleum becomes immediately obvious when the frequency of occurrence of recovered crude oils is analyzed with respect to asphaltene content (in g/L) on a log scale. As an illustration, Figure 1A shows a frequency-asphaltene plot on a conventional linear content scale (oil database from Evdokimov, 2005). The preference of some particular asphaltene contents is poorly revealed and may be interpreted as the result of poor statistics. For comparison, Figure 1B presents a frequency distribution of oils from the same database vs. log of asphaltene concentration. Clearly seen is an anomalous preference of oils with asphaltene contents close to all of the above discussed phase boundaries, as indicated by vertical lines. Appearance of two new boundaries (at ~ 0.4 and ~ 0.8 g/L) may be ascribed to geological time-scales available for equilibration of asphaltene phases in native petroleum, while boundaries 1-6 reflect phase transformations observed at much shorter time scales, characteristic for laboratory experiments (Evdokimov et al., 2006; Evdokimov, 2007, 2008).

2.2. Density (specific gravity) of world's recovered crudes attains maximum values at asphaltene phase boundaries

Figure 2 shows an un-processed (scatter) plot of specific gravity (SG) – asphaltene content (C) relationship for the same crude oil database as in Figure 1. Dashed lines are limits of the conventionally assumed monotonic relationship from Figure 3-25 in Speight, 1999. It is clearly seen that: 1) the conventional monotonic function provides a satisfactory approximation of the general data trend only at high asphaltene contents (>20 - 30 g/L); 2)

minimum values of SG are randomly distributed along some smooth curve; 3) distribution of maximum SG values is not random, these tend to concentrate near several specific values of asphaltene content.

To highlight the last two points, in Figure 3 we show maximum and minimum values of SG from Figure 2, evaluated in consecutive equal intervals of $\Delta\text{Log}(C)=0.05$. The data set for minimal SG was smoothed by a sliding 3-point data window and may be approximated by a simple analytical expression (cf. Section 2.4). Figure 3 clearly demonstrates that anomalous increase of specific gravity is observed in crude oils with asphaltene contents close to the above discussed phase boundaries. Boundary 1 is not reproduced due to poor statistics at low asphaltene concentrations – in most available data sources all values below 0.01 wt. % (~ 0.08 g/L) are classified as zero asphaltene content.

2.3. Importance of asphaltene phase boundaries is supported by any oil database, even by a limited one

To our knowledge, the existence of the above multi-peak correlations has not been reported by any other authors and hence may be regarded as unexpected and dubious. However, log-scale analysis of other published crude oil databases almost invariably reveals anomalous extrema of oil properties at asphaltene phase boundaries. As an example, Figure 4 shows dependencies on asphaltene content of frequency of occurrence and of maximum and minimum specific gravity for a database from Katz and Robison, 2006. The authors did not present a table of oil properties, hence 170 data points analyzed in Figure 4 have been copied from the original graph at which symbols for low asphaltene contents overlap and are indistinguishable. In spite of the loss of low-content data (in the range of phase boundaries 1 and 2), the importance of all other asphaltene phase boundaries is clearly seen.

In fact, “asphaltene phase” effects are so persistent, that once one starts looking for them, they emerge even in very limited data collections. E.g., Mansoori, 2006 describes a collection of just 21 oils with non-zero asphaltene content (from Canada, Venezuela, Mexico, USA, Russia, Brazil, Iraq, France, Algeria). Characteristically, in a recent review of oil properties (Alboudwarej et al., 2006) the linear-scale plot of this data collection (Figure 5A.) is employed to support a stereotype of an “expected” monotonous decrease of API gravity with increasing asphaltene content. However, log-scale presentation of this data set in Figure 5B again reveals peaks of specific gravity at several asphaltene phase boundaries (boundary 3b is not reproduced due to the lack of data points in the respective concentration range).

Summarizing, the results of previous sections clearly demonstrate a striking coincidence of sharp anomalies of crude oil properties with concentration-defined phase boundaries of petroleum asphaltenes. We may conclude that even subtle changes in asphaltene content of a native crude oil may trigger some processes that have the potential to be detrimental to the oil bulk performance. The exact nature of these processes is not clear yet, one possible mechanism may be deasphalting via a natural geochromatography of oils in course of migration, resulting in a selective removal of asphaltenes with low solubility (Evdokimov, 2005). Even without a precise knowledge of underlying physico-chemical mechanisms, the discussed non-monotonic correlations may be of immediate importance to both upstream and downstream petroleum industry operations. It has been suggested recently, that with the information on common and well documented fine variations of oil properties, oil recovery may be geotailored to target reservoirs in order to improve the economic and environmental performance of the production process (Huang et al., 2008).

While some applications require detailed oil property correlations, others, such as evaluation/prediction of crude oil quality and crude oil pricing, employ analytical

approximations of general property-composition trends in crude oil reserves (de Audemard et al., 1987; Katz and Robison, 2006).

2.4. New analytical criteria for general density-asphaltene trends in recovered crude oils

Figure 1 shows that apart from neglecting the effects of asphaltene phase boundaries, the existing specific gravity – asphaltene approximations do not reproduce the general trends present in crude oil collections. For evaluation of these trends, we have combined all data bases discussed in this paper and in our previous publications (a total of 544 crude oils). To include all samples into evaluation procedure, those with reported absence of asphaltenes have been assigned a ultra-low asphaltene content of 0.0015 g/L. Fitting of various analytical functions to a plot of specific gravity (SG) - asphaltene content (C) correlation has shown that the baseline BL for minimum values of specific gravity may be approximated by a simple power law:

$$BL \equiv SG_{min} = 0.78 + 0.0054 \cdot C^{0.61},$$

where C is in units of g/L.

As illustrated in Figure 6a, maximum values of SG do not exceed the limit of $1.17BL$. For evaluation of the average trend and a standard deviation, the SG data of Figure 6A were re-scaled via dividing by BL approximation (Figure 6B), which resulted in an estimate:

$$SG(C) = (1.064 \pm 0.036)BL$$

The latter limits are indicated by solid lines in Figure 6B, while the dashed lines are the above estimates for minimum and maximum values of SG. These analytical approximations are indicated also in Figure 7, on more familiar to petroleum practitioners plots of wt% asphaltenes versus specific gravity and versus API gravity.

3. CONCLUSIONS

It is usually assumed that the bulk properties of a crude oil are monotonic functions of its asphaltene content. However detailed analysis of world's crude oil databases reveals common extrema of oil properties at contents, close to structural phase boundaries earlier observed in asphaltene and oil solutions. Peaks at asphaltene phase boundaries are revealed even when the frequency of occurrence of recovered crude oils is analyzed with respect to asphaltene content. Moreover, the density (specific gravity) of world's recovered crudes attains maximum values at the same phase boundaries. These maxima are observed not only in large databases, but also in limited collections of no more than 10-20 oil samples. 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. For those practical applications that require knowledge of only general property-composition trends in crude oil reserves we suggest a new analytical expression for the general trend of density-asphaltene relationship.

REFERENCES

Alboudwarej, H., Felix, J., Taylor, S., Badry, R., Bremner, C., Brough, B., Skeates, C., Baker, A., Palmer, D., Pattison, K., Beshry, M., Krawchuk, P., Brown, G., Calvo, R., Triana, J. A. C., Hathcock, R., Koerner, K., Hughes, T., Kundu, D., de Cardenas, J. L., and West, C. (2006). Highlighting Heavy Oil. *Oilfield Rev.* 18(2):34-53.

API Gravity Transmitter (2005). Cd. Madero, México: Sistemas de Medición Especial (SIMES).

Buckley, J. S., Morrow, N. R., Fan, T., Wang, J., Yang, L., and Bays, S. (2002). *Wettability and imbibition: microscopic distribution of wetting and its consequences at the*

core and field scales. *Semiannual Report (DE-AC26-99BC15204)*. New Mexico: PRRC, Institute of Mining and Technology.

Cubitt, J. M., England, W. A., and Larter, S. R. (eds) (2004). *Understanding Petroleum Reservoirs: Towards an Integrated Reservoir Engineering and Geochemical Approach*. London: Geological Society.

de Audemard, N., Chirinos, M. L., and Layrisse, I. (1987). Physical and Chemical Characterization of Heavy Crude Oil in the Orinoco Oil Belt. In: *Exploration for Heavy Crude Oil and Natural Bitumen*, Meyer, R. F., ed., Tulsa, OK: AAPG. p. 183-191

Evdokimov, I. N. (2005). Bifurcated correlations of the properties of crude oils with their asphaltene content. *Fuel* 84:13-28.

Evdokimov, I. N. (2007). T-C Phase Diagram of Asphaltenes in Solutions. *Pet. Sci. Technol.* 25:5-17.

Evdokimov, I. N. (2008). "Fine Phase Transformations" In Petroleum - The Basis for Emerging Nanotechnologies. In: *Petroleum Science Research Progress*. New York: Nova Science Publishers. pp.235-260.

Evdokimov, I. N., Eliseev, N. Yu., Losev, A. P., and Novikov, M. A. (2006). Emerging Petroleum-Oriented Nanotechnologies for Reservoir Engineering. SPE Paper #102060, *SPE Russian Oil and Gas Technical Conference and Exhibition "Technology for world class resources"*, Crocus Expo, Moscow, Russia.

Huang, H., Bennett, B., Oldenburg, T., Adams, J., and Larter, S. R. (2008). Geological Controls on the Origin of Heavy Oil and Oil Sands and Their Impacts on In Situ Recovery. *J. Can. Petrol. Technol.* 47(4):1-9.

Katz, B. J., and Robison, V. D. (2006). Oil quality in deep-water settings: Concerns, perceptions, observations, and reality. *AAPG Bulletin* 90(6):909-920.

Larter, S. R, Adams, J., Gates, I. D., Bennet, B., and Huang, H. (2008). The Origin, Prediction and Impact of Oil Viscosity Heterogeneity on the Production Characteristics of Tar Sand and Heavy Oil Reservoirs. *Journal of Canadian Petroleum Technology*, 47:52-61.

Somasundaran, P. (2006). *Encyclopedia of Surface and Colloid Science*. New York: CRC Press.

Mansoori, G. A. (2006). *Asphaltene Deposition and its Control*. Internet publication, http://www.uic.edu/~mansoori/Asphaltene.Deposition.and.Its.Control_html (accessed June 26, 2006).

Myers, D. (1999) *Surfaces, Interfaces and Colloids - Principles and Applications*, 2d ed. New York: Wiley-VCH.

Speight, J. G. (1999). *The Chemistry and Technology of Petroleum*. 3rd ed. New York: Marcel Decker Inc.

Yang, S. Y., Hirasaki, G. J., Basu, S., and Vaidya, R. N. (2002). Statistical analysis on parameters that affect wetting for the crude oil/brine/mica system. *J. Petrol. Sci. Eng.* 33:203–215.

FIGURES

Figure 1. Frequency distributions of world's recovered (dead) crude oils with respect to their asphaltene content. Equal histogram intervals on: A – linear g/L scale; B - logarithmic g/L scale. Vertical lines 1-6 denote asphaltene phase boundaries revealed by laboratory experiments with solution of crude oils and of solid asphaltenes. The apparent presence of two new boundaries in may be ascribed to geological time-scales available for equilibration of asphaltene phases in native petroleum.

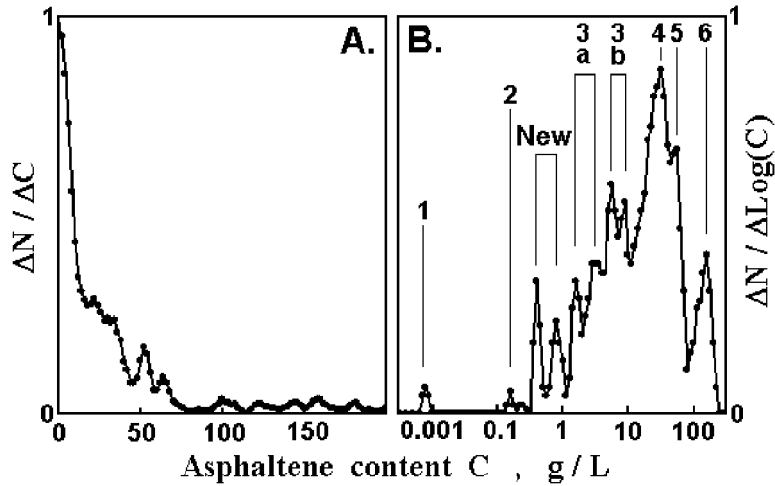


Figure 2. Specific gravity – asphaltene correlation for crude oil database from Evdokimov, 2005 (filled symbols). Dashed lines delimit the monotonic relationship assumed in Speight, 1999.

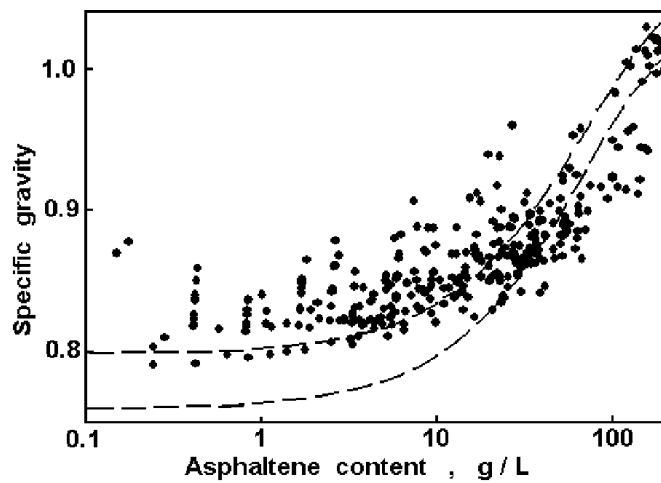


Figure 3. Maximum and minimum values of specific gravity from Figure 2. Note specific gravity peaking at asphaltene phase boundaries denoted as in Figure 1.

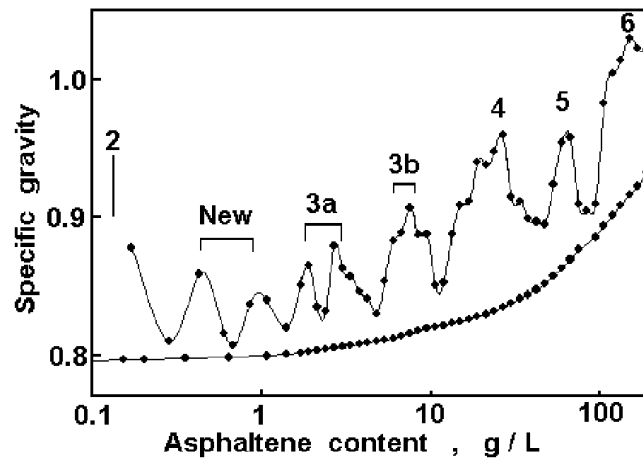


Figure 4. The importance of asphaltene phase boundaries in the oil database of Katz and Robison, 2006. A - Frequency distribution of crude oils; B - Maximum and minimum values of specific gravity.

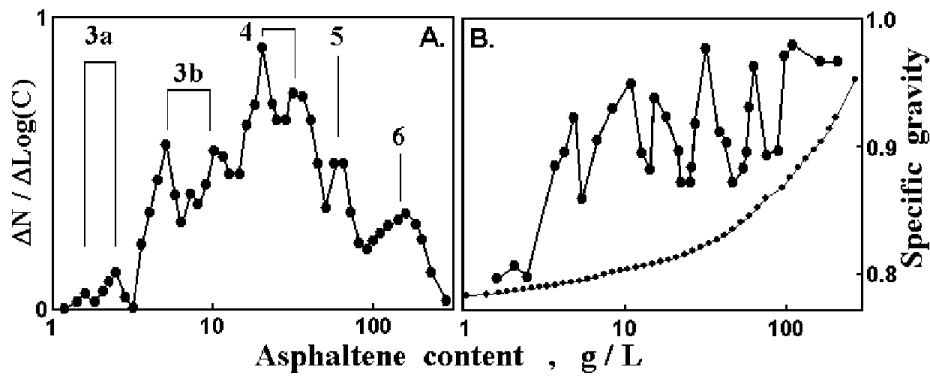


Figure 5. Analysis of a limited database of 21 crude oils with non-zero asphaltene content from Mansoori, 2006. A. – Linear-scale plot presumably confirming the stereotype of a monotonic API-asphaltene relationship (after Alboudwarej et al., 2006); B – log-scale presentation revealing specific gravity peaking at asphaltene phase boundaries.

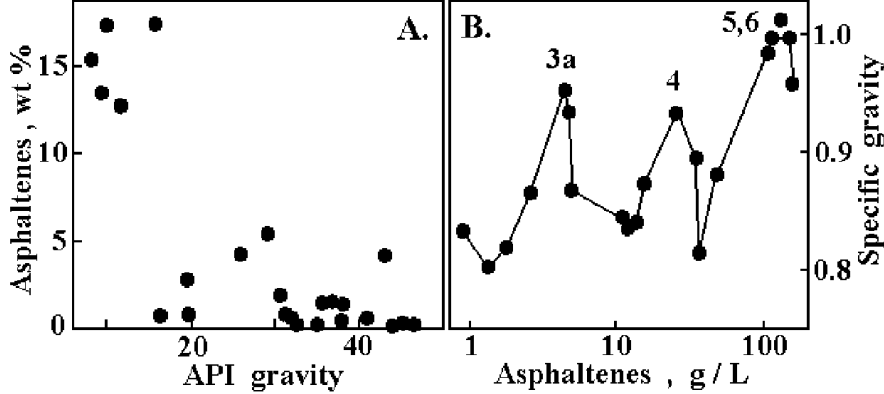


Figure 6. Evaluation of analytical approximations for general specific gravity – asphaltene content trends in a combined database of 544 crude oils.

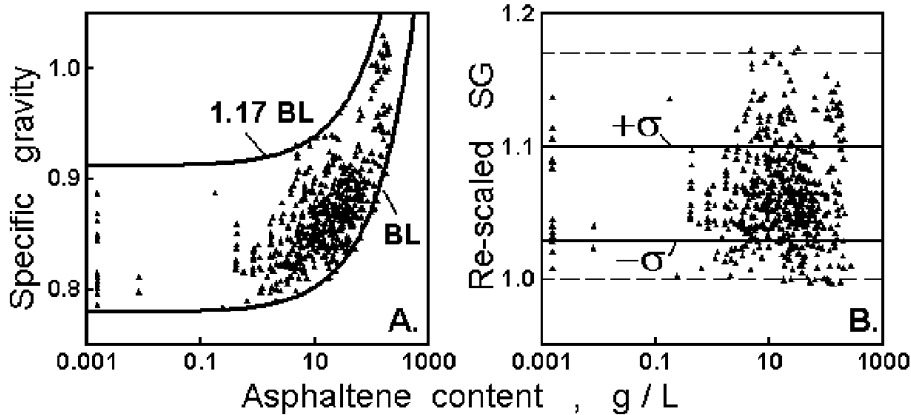


Figure 7. Standard deviations from the mean tend (solid lines) and approximations of maximum and minimum limits (dashed lines) on conventional plots of wt% asphaltenes as functions of crude oil specific and API gravities.

