

Bifurcated correlations of the properties of crude oils with their asphaltene content

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Abstract

Asphaltene-based correlations of crude oil properties were analysed for more than 390 recovered (dead) crudes from a new database of the oils of the former USSR, as well as from databases by other authors. For densities, viscosities and pour points the analysis revealed a definite absence of frequently quoted strong linear correlations with asphaltene content and a persistent occurrence of non-linear anomalies for oils with <2.5–3 wt.% asphaltenes. As shown by selective filtering of databases, these anomalies most probably are due to the existence of two distinct types of world's crude oils, as classified with respect to their asphaltene-based correlations. Two separate branches also are observed in most correlations for SARA components, for contents of N, S, O, V and Ni. The analysed correlations show definite imprints of biodegradation and of source types. However, a review of various oil alteration processes shows that an apparent subdivision of crudes into two types is most probably due to deasphalting via a natural geochromatography of oils in course of migration, resulting in a selective removal of a well-defined polar asphaltene fraction, distinguished by its low solubility.

Keywords: Crude oils; Bulk properties; Correlations; Asphaltenes; Deasphalting

1. Introduction

A better understanding of the recovery processes requires a detailed knowledge of the factors that affect composition and physicochemical structure of crude oils [1]. There are considerable difficulties in analysing the original (live) oils in reservoirs, but some valuable information may be obtained by analysing the recovered material (dead/stabilised crude oils). Due to the complexity of oils, hydrocarbon group type analysis is commonly employed [2]. The crude oil components are grouped into four chemical classes based on differences in solubility and polarity (saturates, aromatics, resins and asphaltenes). Knowledge of correlations of crude oil's properties with these major chemical groups is integral to both upstream and downstream operations. Examples are studies related to reservoir evaluation, migration and maturity, degradation processes, processing, and environmental effects [3]. A widely spread problem that decreases the revenue of the petroleum industry is solid deposition [4,5]. When dealing with solubility aspects for crude oils, most of the attention is focused on asphaltenes as prevention of deposition may be based on the phase behaviour forecasting by means of continuous monitoring of correlations between crude oil properties and their asphaltene content [4].

Many other implications in recovering crudes are also invoked by the presence of asphaltenes [1,6]. Revealing of asphaltene-based correlations may especially be useful in interpreting the thermal and alteration histories of oils, in estimating of the oil resources and the risks associated with exploration. The published analyses of oil databases show that the amount of asphaltenes is one of the most significant variables in all cases. E. g. Buckley et al. [7] report a linear correlation between API gravity of oils and asphaltene solvency. Werner et al. [8,9] found that the relationship between the viscosity of crudes and their asphaltene concentration was represented by a single curve. Yang et al. [10] reported correlations between the amount of asphaltenes and RI, API gravity, acid and base numbers of 25 crude oils. In a database of 192 oils, Buckley et al. [11] observed correlations between the amount of asphaltenes and API gravity, average MW, density, amounts of saturates, resins, Ni and V.

Crude oils vary widely in many relevant properties. Thus, a characterisation of an oil family or even of a number of oil families from one region [10,11] may not be relevant to oils in a different part of the world. We have attempted to extend an analysis of correlations to oils from other geographical locations in order to develop a framework for understanding crude oil properties in a generic fashion. A new database of over 220 crude oils from various geographical/geological regions of the former USSR has been analysed for correlation of the oil properties with their asphaltene contents. The results are evaluated with respect to models of biodegradation and other post-generative alteration effects.

2. Database description

For a construction of our database we have used a 4-volume reference book on crude oils from all over the vast territory of the former USSR [12]. The reference book contains information on the geographical location, geological structure, depth, pressure, temperature, gas factor of oil reservoirs, as well as information on the physico-chemical properties of recovered crudes, on their elemental and molecular compositions. All data have been obtained with a unified set of analytical techniques, defined by the USSR State Standards (GOST's). In particular, resins have been analysed by two analytical techniques; in our database we included resin contents determined by adsorption chromatography at silica gels.

In spite of a large number of crude oils, described in Ref. [12], just 191 crudes were included into the database, namely those with complete sets of reservoir and oil properties (24 data positions). The data for additional 33 oils were obtained from Ref. [13], hence the total number of crudes in our database amounted to 224.

3. Correlations of the bulk properties of recovered crudes

3.1. Anomalous occurrence of crude oils with respect to their asphaltene content

An easily observed feature of our database is that crude oils with an asphaltene content somewhat below 3–4 wt.% are singled out by a higher occurrence. This observation was confirmed by an analysis of databases of other authors. Fig. 1 shows a cumulative frequency distribution for 392 crude oils from all databases discussed in this paper. An anomalous preference of oils with 2.5–3 wt.% asphaltenes is clearly seen. As described in the following sections, this anomaly is further reflected in a number of correlations between various properties of crude oils and their asphaltene content. The data of Fig. 1 also show that apparently 99% of world's recovered oils have an asphaltene content below 11.5 wt%; just 4 crudes out of 392 had asphaltene concentrations ranging from 14 to 18 wt.%.

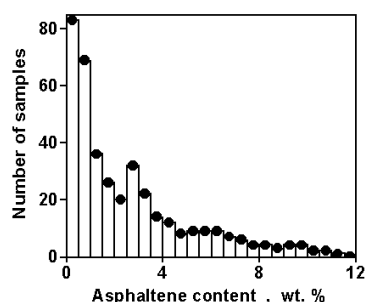


Fig. 1. A frequency distribution for 392 world's recovered crudes with respect to their asphaltene content.

3.2. Correlations of non-filtered data (our database)

Fig. 2 illustrates the methods employed for the analysis of databases. The investigated correlation is between the density of crude oils and their asphaltene content. A linear regression applied to the original scatter plot (straight line in Fig. 2A) reveals a weak correlation with a coefficient of determination $R^2=0.40$. A closer inspection of the plot shows, however, that the small value of R^2 is a consequence not only of a random scatter of data points, but mainly of a systematic occurrence of high densities in oils with asphaltene concentrations below ≈ 3 wt.%, i.e. of a some complex non-linear correlation. To reveal the general trends, a smoothing procedure was applied to the original data. As an example, Fig. 2B shows the scatter plot of Fig. 2A smoothed by a

sliding data window (21 points), the smoothed plots in all other figures have been obtained by the same procedure. The smoothed data of Fig. 2B clearly show the absence of an expected linear correlation [10,11] between density and asphaltene content and reveal an anomalous average increase of densities in oils with 2–2.5 wt.% asphaltenes.

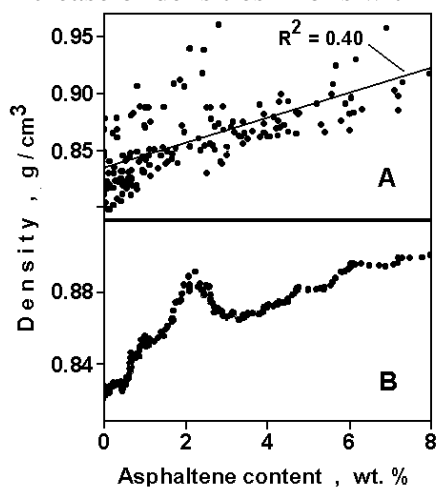


Fig. 2. Density—asphaltene correlations for 224 crude oils from the former USSR. The original scatter plot (A) and the results of its smoothing (B).

Further analysis of the database revealed anomalous correlation between an asphaltene content and a number of other properties of crude oils. In particular, the smoothed scatter plots in Fig. 3 show a sharp increase of kinematic viscosity (50 8C) as well as a deep depression of pour point at the same specific asphaltene content of 2–2.5 wt.%.

To our knowledge, the existence of the above anomalous complex correlations has not been reported previously and hence may be regarded as unexpected and dubious. However, an inspection of publications by other authors proves that anomalous correlations with asphaltene content evidently are universal, world-wide properties of crude oils, not restricted to the territory of the former USSR. Moreover, the discussed anomalies are observed not only in large databases, but also in collections of no more than 7–10 oil samples.

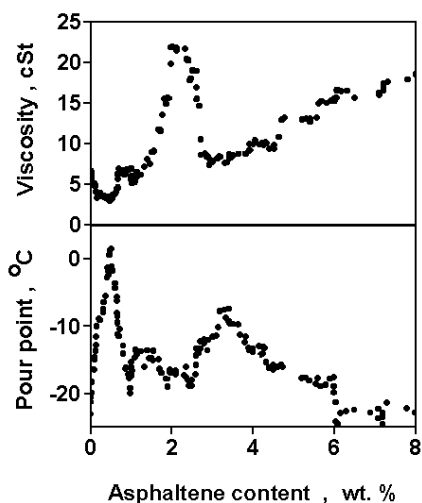


Fig. 3. Viscosity—asphaltene and pour point—asphaltene correlations. The smoothed scatter plots for 224 crude oils from the former USSR.

3.3. Correlations of non-filtered data (databases of other authors)

Fig. 4A shows unprocessed data from a collection of 25 crude oils, described by Yang et al. [10]. The authors claimed an overall linear correlation between API gravity of oils and asphaltene concentration (dashed line in Fig. 4A) with a very small coefficient of determination $R^2=0.13$: It is clearly seen that a linear regression provides much better results when applied separately to oils with asphaltene concentrations below and above 3 wt.% (solid lines in Fig. 4A). This procedure increases the coefficients of determination to 0.41 and 0.24, respectively. Literature analysis has shown that anomalous correlations with asphaltene content may be observed even in more limited data sets. In particular, extrema of density and viscosity at ≈ 3 wt.% asphaltenes may be clearly detected in collections of no more than 15 crudes [14,15]. The scatter plot of a more extended

database of Buckley et al. [11] is shown in Fig. 4B. As in case of our database, a systematic occurrence of high densities in oils with asphaltene content below ≈ 3 wt.% is observed. A thick line shows the smoothed data with a well-defined maximum of density at ≈ 2.7 wt.% asphaltenes, in a good coincidence with the smoothed results of Fig. 2B.

Finally, Fig. 4C presents a smoothed scatter plot obtained by combining all the above databases (a total of 392 crude oils). A presence of an extremum at asphaltene concentrations close to 2.5 wt.% is clearly seen, indicating that the above discussed peculiarities of correlations with asphaltene content may be general characteristics of world's recovered crudes.

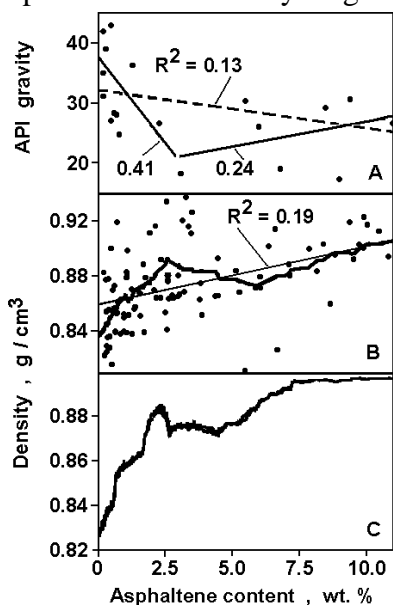


Fig. 4. Density (API gravity)—asphaltene correlations. The unprocessed scatter plots are from the databases of Ref. [10] (A) and of Ref. [11] (B). Straight lines are linear correlations. The smoothed scatter plot (C) is for 392 crude oils from all analysed databases.

3.4. Filtered data

It is well known that an analysis of a database may provide more information in case the data are filtered with respect to some groups, selected according to certain basic assumption. Selective filtering of the above databases was performed in the assumption that any correlations between the properties of a single type of natural objects (e.g. natural crudes) should be described by smooth functions, lacking any sharp inflections or extrema. Hence, the peculiarities observed in Figs. 2–4 were regarded as ‘artefacts’ due to existence of more than one type of oils, as classified with respect to their asphaltene content.

Fig. 5 illustrates the criteria used for filtering of oil databases; the smoothed data are those from Fig. 2B (note a log scale). The solid line is a polynomial (2nd order) approximation of an evidently prevailing smooth relationship between densities and asphaltene contents. This prevailing relationship was further regarded as representative of the more abundant type of crude oils ($\approx 82\%$ of entries in our database), in the following denoted as type ‘B’. All data entries with asphaltene content below 5 wt.% and with densities, exceeding the polynomial approximation by more than 3%, were regarded as representative of the other type of crudes, in the following denoted as type ‘A’.

The scatter plot of the filtered USSR database is shown in Fig. 6A. Filled circles and open triangles denote the data for crude oils ‘A’ and ‘B’, respectively. Straight lines are the respective linear correlations with $R_A^2=0.83$ and $R_B^2=0.79$, much higher than $R^2=0.40$ for the non-filtered scatter plot in Fig. 2A. The difference of density-asphaltene correlations for two types of crudes, as well as a non-linear manner of correlations, is emphasised by smoothing the original scatter plots, as illustrated in Fig. 6B. The same selective filtering was applied to the database of Buckley et al. [11] (cf. Fig. 4B). The filtered data for oil types ‘A’ and ‘B’ (≈ 36 and 64% of data entries) are denoted in Fig. 7A by filled circles and by open triangles, respectively. Linear correlations in the filtered data sets with $R_A^2=0.45$ and $R_B^2=0.74$, are both notably stronger than the one with $R^2=0.19$ for non-filtered data in Fig. 4B. The smoothed tendencies in Fig. 7B are close to those for our database (cf. Fig. 6B).

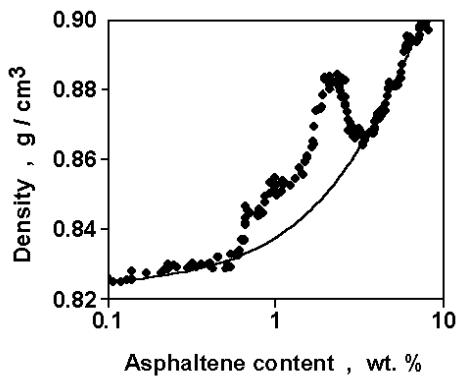


Fig. 5. The criteria used for selective filtering of oil databases.

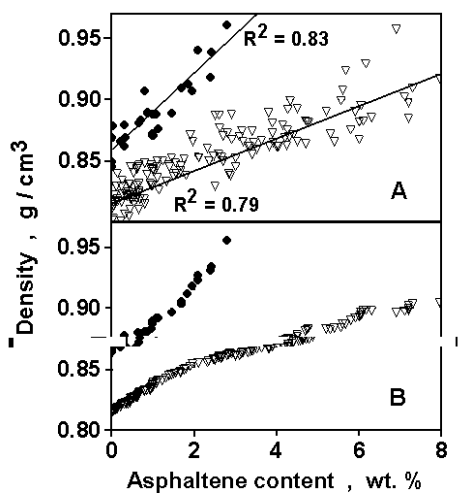


Fig. 6. Filtered density—asphaltene correlations for 224 crude oils from the former USSR. The filtered scatter plots (A) exhibit improved linear correlations with respect to non-filtered data of Fig. 2. The existence of two types of oils is further emphasized by smoothening of the filtered scatter plots (B).

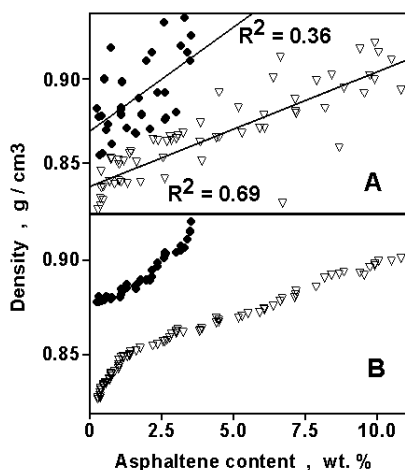


Fig. 7. The same as in Fig. 6 for the database of Ref. [11] (cf. Fig. 4B).

The process of filtering improves correlations with asphaltene content not only for the density, but also for other properties of crude oils. As an example Fig. 8 shows smoothened data sets from our database for a kinematic viscosity (50 °C) and for a pour point. As above, filled circles and open triangles correspond to crude oils of the types ‘A’ and ‘B’, respectively. In contrast to non-filtered data (Fig. 3), the expected ‘natural’ smooth tendencies are revealed in Fig. 8 for both types of oils.

Summarising, strong correlations, revealed by the filtering procedure, indicate that the existence of two types of crudes, as classified with respect to their asphaltene content, may in fact be a generic characteristic of the world’s petroleum resources.

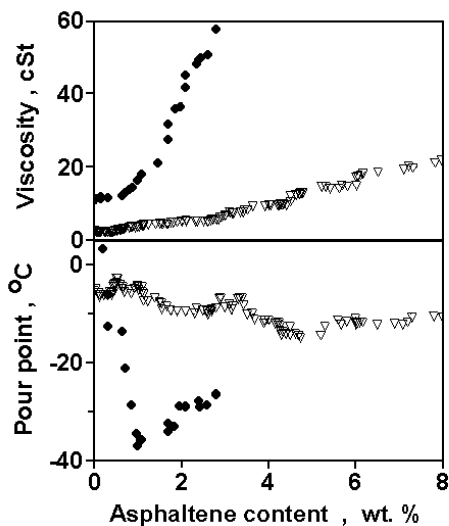


Fig. 8. Filtered data reveal notably different viscosity—*asphaltene* and *pour point*—*asphaltene* correlations for crude oils of types ‘A’ (filled circles) and ‘B’ (open triangles) (compare with non-filtered results in Fig. 3).

3.5. *Non-asphaltene correlations of filtered data*

For the above defined two types of crudes, we have tested correlations between several properties, other than the asphaltene content. Surprisingly, with respect to most of these correlations, these types of crude oils appeared to be virtually indistinguishable, as shown in Fig. 9.

Filled circles and solid lines denote the smoothed scatter plots for crudes ‘A’ and ‘B’, respectively. It is clear that both types of oils exhibit the same correlations between viscosity and density as well as between pour point and wax content, in sharp contrast with asphaltene-based correlations of Fig. 8. A comparison of Figs. 8 and 9 allows to suggest that: (1) for such crude oil properties as density, viscosity and pour point, asphaltene content is not a determining factor; (2) oil types ‘A’ and ‘B’ are distinguished only by their asphaltene concentrations, while the relationships between most other properties are identical; (3) more abundant ‘B’ oils represent ‘normal’ crudes, while ‘A’ crudes (18–36% of entries in different databases) are the same oils subjected to fractional deasphalting, which did not notably affect such properties as density, viscosity, etc. As shown above, with respect to the asphaltene content there appears to be a sharp distinction between crude oils of the types ‘A’ and ‘B’, implying that the suggested deasphalting is not a gradual process, but a selective loss of a well-defined fraction of asphaltenes, common for all ‘natural’ crudes.

The existence of two major fractions of asphaltenes has been indeed demonstrated experimentally over the past years [16–19]. The difference between fractions A1 and A2 [17] is manifested by their strikingly different solubilities.

The fraction A1 is almost insoluble, in toluene at RT its solubility does not exceed 93–100 mg/l [17,20–22] and formation of molecular aggregates commences at concentrations not higher than 6 mg/l [23], apparently even at 1–2 mg/l [20–22]. The solubility of the fraction A2 is 59 g/l in toluene [17], higher by almost three orders of magnitude than that for of A1 asphaltenes. The relative amounts of A1 and A2 in C5I and C7I asphaltenes may depend on the type of the parent crude. Strausz et al. [19] observed that $\approx 20\%$ of precipitated asphaltenes (apparently A1 ones) did not dissociate to monomeric state in CH_2Cl_2 . Gutierrez et al. [17] reported that the relative amount of A1 asphaltenes in samples of various origin was between 48 and 70%.

Asphaltenes with low solubility (A1) are apparently more polar and hydrogen bonding; this fraction has a lower H/C ratio (0.90) and higher N, V, Ni, and Fe contents than the more soluble fraction A2 [16,18].

We suggest that these polar and poorly soluble A1 asphaltenes are the ones that are shed by the crudes in course of the assumed selective deasphalting. In Section 5 we present more arguments in favour of this suggestion, based on the analysis of correlations between molecular and elemental compositions in crude oils.

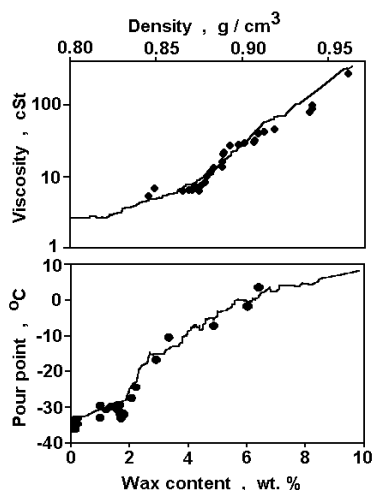


Fig. 9. Non-asphaltene correlations of viscosity and pour point for the same database as in Figs. 3 and 8. The smoothed trends for ‘A’ oils (filled circles) and for ‘B’ oils (solid line) are virtually undistinguishable.

3.6. Correlations of filtered data with reservoir properties

In search of particular mechanisms of the suggested deasphalting, for crude oils ‘A’ and ‘B’ from our database we have tested pair cross-correlations between all available reservoir properties (perforation depth, pressure, gas factor, temperature, geographical location, collector’s type). It appeared that with respect to most of these correlations both types of oils are indistinguishable. Notably, both data sets are characterised by virtually similar pressure-depth and temperature-depth scatter plots.

We have found only two apparent differences between two types of crudes with respect to reservoir properties. The first is in their frequency distributions vs temperatures of reservoirs. Namely, the more abundant ‘B’ crudes are encountered in the entire range of temperatures, with a moderate frequency peaking below 40 °C. In contrast, type ‘A’ oils are recovered only from reservoirs with temperatures in the narrow range from ≈ 22 to 78 °C, with $\approx 90\%$ of oils found at temperatures ≤ 67 °C. It is generally accepted that oils in reservoirs with temperatures below 75–80 °C may change their composition via biodegradation, while the oil-degrading bacteria have an optimum growth temperature of only 60 °C [24–26].

The other difference is that ‘A’ oils almost exclusively originated from the southern regions of the former USSR, namely from the provinces close to the Caspian Sea (Azerbaijan, Kazakhstan, Astrakhan, Volgograd, Krasnodar) and from the Sakhalin Island. All these areas are characterised by the presence of deep faults and by fracturing of reservoir structures [27], implying a significant role of migration. Petroleum has long been known to undergo fractionation during migration [28]. Some of the processes that may affect the contents of oil compounds during migration are adsorption on mineral surfaces [29] and ‘geochromatographic’ size exclusion [30]. Interaction between crude oil and reservoir rocks also may be responsible for compositional modification of crude oils in course of recovery [31]. Moreover, oil-producing areas of Azerbaijan and of Sakhalin Island are accompanied by mud volcanic manifestation [27]. Faults and fractures serve as conduits for flow of hot water and hydrocarbon gases from great depth. Hence the oils may have been subjected to significant water washing [32–34] and gas deasphalting [35,36].

The above observations should not be interpreted as indications that crude oils ‘A’ and ‘B’ are inherent to different locations, well separated geographically. Some of the databases [14,15] (cf. Section 3.3) show that both types of oils may be encountered in the same fairly small geographical region, namely in the North Sea. Apparently, spatial co-existence of ‘A’ and ‘B’ crudes also follows from databases of Refs. [10,11]. The authors do not specify the exact locations of oil wells, but presumably the majority of oil samples described in both publications originated from New Mexico and Texas, USA.

Summarising, the analysis of reservoir properties suggests that the systematic difference in composition may indeed be the result of some specific alteration processes. Most of these processes are distinguishable from each other by comparing the changes of oil constituents other than asphaltenes (e.g. saturates, aromatics, resins, N, O, S, V and Ni). The results of such comparative evaluation are described below.

4. Unified re-scaled correlations for two types of crudes

The proposed concept of fractional deasphalting implies that a well-defined percentage of the initial asphaltenes is shed by an oil in a single specific process, the contents of other constituents (as well as the oil's density) being virtually unaltered. In such a case, asphaltene-based correlations for deasphalted 'A' oils may be re-scaled to correlations for the initial ('B') crudes via dividing asphaltene contents by the (constant) relative amount of the remaining asphaltenes. In the upper part of Fig. 10 we present the results of such re-scaling for density-asphaltene correlations from Fig. 6A for our USSR database. The data for oils 'A' and 'B' are denoted by filled circles and by open triangles, respectively. The scatter plot for 'A' oils is rescaled in the assumption that 30% of the initial asphaltenes remained in the crudes after a supposed fractional deasphalting. It is clearly seen that after re-scaling both scatter plots intermix and may be described by a single density-asphaltene correlation (solid line) with $R^2=0.78$ remaining as high as in case of non-scaled correlations in Fig. 6A. The universal correlation for the re-scaled data is in a good agreement with a general biodegradation path of oils (dashed line), as specified by Miiller et al. [37].

The data for the USSR database in Fig. 10 support the hypothesis of deasphalting via shedding a specific fraction of asphaltenes, obviously common for all crude oils, and indicate that such deasphalting and oil alteration via biodegradation may be independent (and even unrelated) processes. In such a case, selective deasphalting may occur in oils at any stage of biodegradation or, in other words, a continuous process of bio-alteration is not interrupted or notably altered by the supposed deasphalting.

These conclusions are further supported by an analogous re-scaling of the scatter plots from Fig. 7A for the database of Ref. [11], as shown in the lower part of Fig. 10. The scatter in the re-scaled plot is larger than in our data, but $R^2=0.63$ still is indicative of a sufficiently strong correlation. The agreement with a biodegradation path [37] (dashed line), also is not as good as in the upper part of Fig. 10, but the general trend is reproduced.

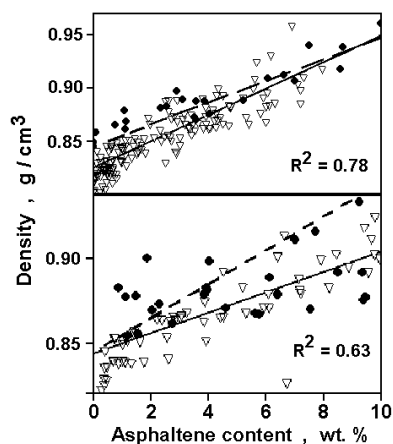


Fig. 10. Density—asphaltene scatter plots from the USSR database (above) and from the database of Ref [11] (below). The data for 'A' oils are rescaled to account for deasphalting. Solid lines—linear correlations. Dashed lines—a typical biodegradation path [37].

5. Correlations of the molecular and elemental contents of recovered crudes

5.1. SARA correlations

The complete sets of SARA contents for 101 out of 192 crudes are provided in the database of Buckley et al. [11]. Fig. 11 illustrates respective correlations between contents of saturates, aromatics, resins and the content of asphaltenes (note a log scale). To emphasise the trends, scatter plots for 'A' and 'B' oils were smoothed (cf. Section 3.2), as shown by filled circles and by a solid line, respectively. Open triangles denote the data for 'A' oils re-scaled in the same assumptions as in Fig. 10.

As expected, in both types of oils with increasing asphaltene content the content of saturates decreases, the content of resins increases, while there is only a marginal decrease in the content of aromatics [6,37,38]. The data of Fig. 11 show that crude oils 'A' and 'B' may be easily differentiated by the markedly different rates of their saturates-asphaltenes and resins-asphaltenes correlations. These again may be re-scaled to universal bio-degradation tendencies [37] in the assumption of 30% asphaltenes retained after a supposed deasphalting. After re-scaling, the

smoothened data for 'A' oils (open triangles in Fig. 11) practically coincide with those for 'B' crudes. The coincidence for saturates (the upper part of Fig. 11) is somewhat worse, indicating that 'A' oils may be slightly more paraffinic than the 'B' ones. Practically similar non-scaled and re-scaled correlations between silicagel resins and asphaltenes were obtained for 27 'A' oils and 149 'B' crudes from our USSR database.

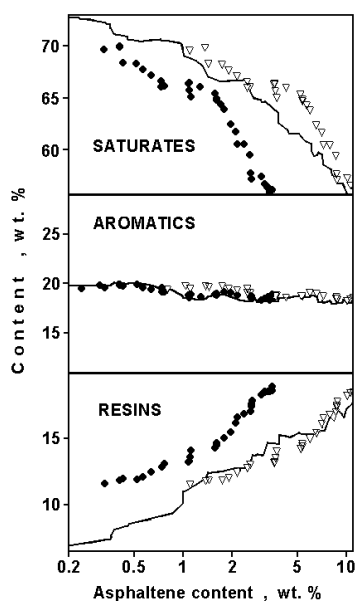


Fig. 11. SAR–asphaltene correlations for the database of Ref. [11]. Solid lines—smoothened original scatter plots for 'B' oils. Filled circles—smoothened data for 'A' oils. Open triangles—smoothened data for 'A' oils re-scaled as in Fig. 10.

The SARA contents are commonly regarded as the major variables in revealing the compositional changes during crude oil alteration. To illustrate this point, Tissot and Welte [38] plotted a triangular (saturates; aromatics; resins+asphaltenes) composition diagram for 636 world's crude oils and showed that all compositions fell into a comparatively narrow band extending from thermally mature crude oils, enriched in aliphatic hydrocarbons, to biodegraded crude oils, with low amounts of aliphatic hydrocarbons. This is illustrated in Fig. 12, where solid lines show the 'global' contour plot from Tissot and Welte [38]. Filled circles and open triangles, respectively, are the data for 'A' and 'B' oils, analysed in Fig. 11. It is clear that the two types of oils are indistinguishable with respect to their SARA biodegradation trends. Both data sets fall onto a sharp slope near the maximum of Tissot and Welte's distribution, hence both 'A' and 'B' oils apparently are in the states from a low to a moderate level of biodegradation.

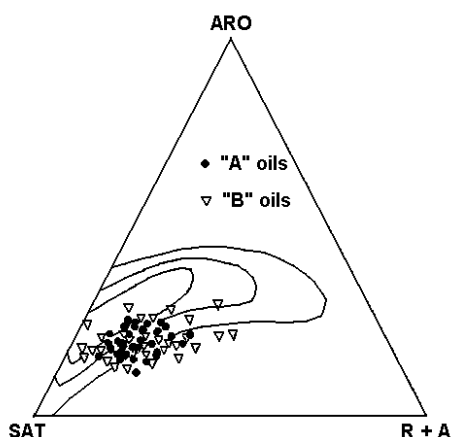


Fig. 12. Composition diagram for 'A' and 'B' oils (filled and open symbols, respectively) from the database of Ref. [11]. Solid lines show the contour plot for a global distribution of crude oils from Tissot and Welte [38].

A useful indicator of oil alteration is a ratio of the cumulative content of saturates and aromatics to the cumulative content of resins and asphaltenes [39]. In Fig. 13 the ratios $(SAT+ARO)/(R+A)$ are plotted for the same data sets as in Figs. 11 and 12. In the upper part of the figure, the non-scaled data for oils 'A' (filled circles) and 'B' (open triangles) exhibit markedly different strong ($R^2 > 0.7$) correlations with asphaltene content. In the lower part of Fig. 13, the

above described re-scaling of the data for ‘A’ oils reduces the scatter and results in a single strong correlation ($R^2=0.72$), indicative of a common biodegradation trend.

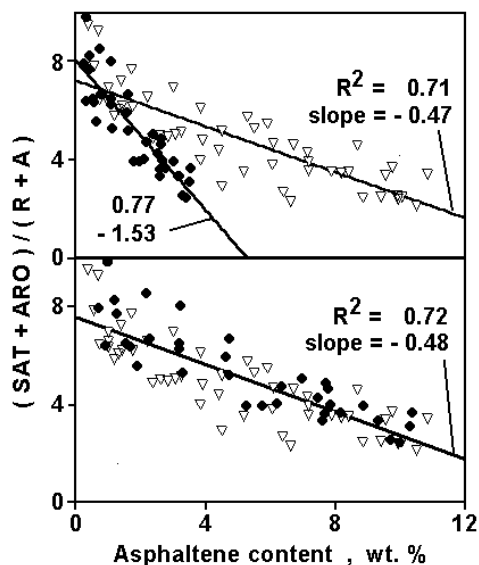


Fig. 13. Correlations with asphaltene content of a SARA—determined indicator of crude oil alteration. The data sets are the same as in Figs. 11 and 12. Above—the original scatter plots for ‘A’ and ‘B’ oils. Below—the scatter plot for ‘A’ oils re-scaled as in Fig. 10. Solid lines—linear correlations.

5.2. N, S, O correlations

Such heteroatoms as nitrogen, sulphur and oxygen are known to concentrate in high-MW oil constituents [6,40, 41]. Accordingly, N,S,O contents may have been expected to exhibit simple correlations with the contents of asphaltenes and with the density (API gravity) of oils. Our analysis of the databases has shown that, at least in the case of sulphur, these correlations are far from being simple.

In the databases [10,11] there is no information on the contents of N, S and O. In our database of the USSR oils N and S contents are listed for the majority of oils, while the oxygen contents—only for about one third of the crudes. This may be one of the reasons why both in ‘A’ and ‘B’ oils oxygen has shown no apparent relationship to the content of asphaltenes. For both types of oils nitrogen contents exhibited a common sufficiently strong ($R^2=0.78$) linear correlation with asphaltenes.

The remarkable difference between ‘A’ and ‘B’ oils is manifested by two branches of their sulphur-asphaltene correlations. Namely, the major trend for ‘B’ oils is a “high-S” branch with an expected continuous increase of sulphur concentration with the increasing content of asphaltenes. On the other hand, all ‘A’ oils belong to a “low-S” branch characterised by a very small sulphur content (the average value 0.32 wt.%), only marginally increasing with the content of asphaltenes. The same property also is inherent to some of the ‘B’ oils, indicating a possibility that not all of ‘A’ oils have been identified by the filtering procedure (Section 3.4). Another possibility is that our ‘A’ and ‘B’ originate from different source types (cf. the data of Ref. [42] in Fig. 15). However, on the basis of below discussed V and Ni correlations, we conclude that the source hypothesis is less likely.

It is frequently assumed that the most sour are heavy oils, i.e. that S concentration exhibits a straightforward correlation with the oil’s density (API gravity) [6,7,10,11,43]. Hence, in the upper part of Fig. 14 the obtained sulphur – asphaltene correlations are re-plotted with respect to the densities of oils (here all data in the ‘low-S’ branch are denoted by filled symbols). Again, the presence of distinctly different branches is clearly seen. The ‘high-S’ oils are characterised by a strong increase of S content with increasing density and a large coefficient of determination ($R^2=0.83$). The linear fit for ‘low-S’ oils has a slope smaller by more than an order of magnitude, indicating a very weak correlation, further emphasised by a very small coefficient of determination ($R^2=0.13$). The lower part of Fig. 14 shows sulphur - density correlations for oils from filtered data sets, reported in Ref [42]. Easily observed are two different types of correlations, both very close to those in the upper part of the figure. It should be noted that in Ref. [42] data filtering was not with

respect to asphaltene-dependent properties (as for our ‘A’ and ‘B’ oils), but with respect to different source types.

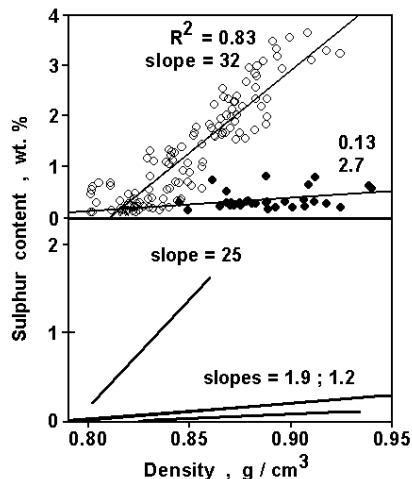


Fig. 14. Low-S and high-S branches of sulphur—density correlations for world’s crude oils. Above—a scatter plot for the USSR database, solid lines are linear correlations. Below—linear correlations, reproduced from Kaufman [42] of the scatter plots (not shown) for oils from various source types.

To conclude this section, we may note that the existence of a double character of S-density correlations may be implicitly reflected in the system of pricing of oils at the world’s markets. These prices are constructed on the basis of five types of oils defined by their S contents and API gravities (densities). One type is an average standard: API=35 (0.850 g/cm³), sulphur - 1.0%. The other two pairs apparently reflect ‘high-S’ and ‘low-S’ branches of Fig. 14, namely: (1) Light Sour (40; 0.825 g/cm³; 2.0%) and Heavy Sour (30; 0.876 g/cm³; 2.0%); (2) Light Sweet (40; 0.825 g/cm³; 0.1%) and Heavy Sweet (30; 0.876 g/cm³; 0.1%).

5.3. H/C correlations, apparent solubility limits

The H/C ratio in a crude provides an inverse measure of the oil’s aromaticity [6], which is affected by oil alteration processes. In particular, as crude oils biodegrade from light to heavy ones, their H/C ratio decreases, while (N+S+O)/C ratio (a measure of polarity) increases [44]. On the other hand, an increase of H/C ratio of an oil decreases solubility of asphaltenes and increases their state of aggregation [45,46]. Solubility parameter mapping shows that aromaticity of the solvent (not polar or hydrogen bonding interactions) may be the major determinant of asphaltene solubility [47]. Hence, we suggested that asphaltene-related properties of crude oils would show some correlation with their H/C ratios. In Fig. 15 this suggestion is verified with respect to asphaltene contents of oils from our database. The data for ‘A’ and ‘B’ oils are denoted by filled and open symbols, respectively. The original (non-scaled) ‘A’ and ‘B’ scatter plots in the upper part of the figure are well separated. However, after rescaling (in the above described assumptions), both data sets completely intermix, as shown in the lower part of the figure. The common scatter plot exhibits a sufficiently strong asphaltene-H/C correlation ($R^2=0.45$) while a general increase of asphaltenes with decreasing H/C ratio is consistent with a biodegradation trend [44].

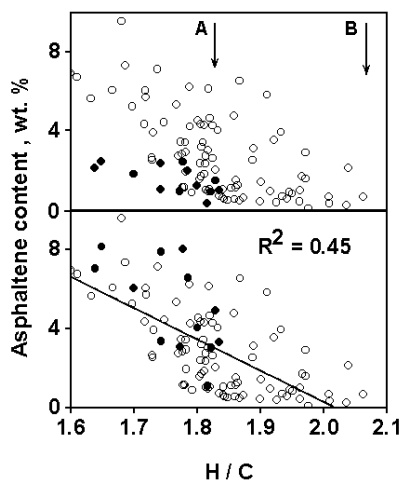


Fig. 15. Correlations of asphaltene content with H/C ratio for ‘A’ oils (filled symbols) and ‘B’ oils (open symbols) from the USSR database. Above—the original scatter plots. Below—the data for ‘A’ oils are re-scaled as in Fig. 10. Solid line—the common linear correlation for re-scaled data. Arrows—apparent solubility limits for asphaltenes in ‘A’ and ‘B’ oils.

The notable feature of Fig. 15, not affected by the scaling procedure, is the apparent presence of distinctly different asphaltene solubility limits for two types of oils, indicated by arrows in the upper part of the figure. There are clearly no asphaltene-containing 'B' oils with $H/C > 2.06$, while no 'A' oils have the H/C ratio higher than 1.84. The re-scaled data of Fig. 15 should be further corrected to reflect initial H/C ratios in crudes before the supposed deasphalting. Namely, asphaltenes are characterised by H/C ratios, not exceeding 0.9–1.2 [48], so when asphaltenes are removed, the products ('A' oils) should have higher H/C ratio than the original crudes. In the assumption of $H/C=1.0$ for asphaltenes, the corrected solubility limit in original non-deasphalted crudes shifts from $H/C=1.84$ to $H/C=1.77$.

A common density - H/C correlation for two types of crude oils is shown in the upper part of Fig. 16. Both (nonscaled) data sets form one intermixed scatter plot which exhibits a strong linear correlation ($R^2=0.7$). The presence of two apparent solubility limits is clearly seen again. Markedly different H/C correlations for 'A' and 'B' oils were observed for their $(N+S+O)/C$ ratio, a measure of the polarity of oil's constituents [16,18]. The respective scatter plot in the lower part of Fig. 16 consists of two branches—the 'low NSO' and the 'high NSO' ones, as in case of S correlations in Fig. 14. Here also, as in case of sulphur, 'A' oils (filled symbols) are confined to the 'low NSO' branch, while 'B' oils (open symbols) are distributed among both branches. The apparent low polarity of 'A' oils may be regarded as another argument in favour of deasphalting via removal of a polar fraction of the initial asphaltenes. Compared to density- H/C correlation, the 'low NSO' and the 'high NSO' branches are characterised by smaller R^2 values (0.59 and 0.30) which may be due to a smaller number of oils with their oxygen content listed in the database (cf. Section 5.2).

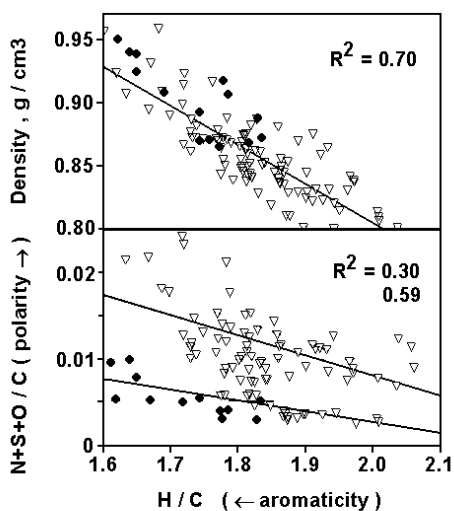


Fig. 16. Above—a single density- H/C correlation for 'A' and 'B' oils from the USSR database (unscaled scatter plots). Below—two branches of polarity-aromaticity correlations for the same data sets.

5.4. Correlations of metal contents

The most important oil foulants, nickel and vanadium, are mainly complexed with nitrogen atoms in asphaltenes and resins [49,50]. Consequently, V and Ni concentrations may be expected to parallel the contents of these heavy MW constituents of crude oils. Accordingly, much of the literature states that there is an inverse relationship of Ni , V content and API gravity [51]. Our database of USSR oils does not contain information on the contents of metals, but these are provided for a number of oils in the database of Ref. [11]. For such oils, Ni and V correlations with asphaltene content are shown in Fig. 17 (note the double-log scale). The data for 'A' and 'B' oils are denoted by filled and open symbols, respectively. Once again, as in S and $(N+S+O)$ correlations, the scatter plots for Ni and V develop two branches, one with an almost constant metal content. This time there is no unique preference of 'A' oils to the 'low content' branch. There is a possibility that the appearance of two branches is due to Ni and V being sourcesensitive elements [50]. In particular, V/Ni ratio would be constant in crudes of the same origin, while absolute metal concentrations may increase with biodegradation [51]. To test the source hypothesis, in Fig. 18 we have plotted correlations of V/Ni ratios with asphaltene content. The plots show two separated 'layers' with low and high V/Ni ratios, indicative of different source rocks. In the upper part of Fig. 18 there are non-scaled data for 'A' and 'B' oils, in the lower part both data sets become intermixed

after the above described re-scaling of the ‘A’ data. Dashed lines indicate the average V/Ni values (0.17 and 2.04) in two ‘layers’. For the ratio $V/(V+Ni)$, another source indicator [38,52], the respective averages are 0.15 and 0.67.

Summarising, the V and Ni data may be regarded as evidence that source rocks do make an imprint on the discussed asphaltene-related correlations (cf. Section 6.1). However, this does not exclude an independent occurrence of a suggested selective deasphalting, as the presumably deasphalted ‘A’ oils are evenly distributed among both ‘layers’ in Fig. 18.

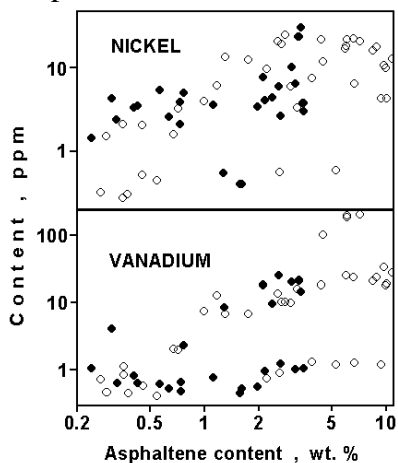


Fig. 17. Two branches of V and Ni correlations with asphaltene content for ‘A’ and ‘B’ oils (filled and open symbols, respectively) from the database of Ref. [11].

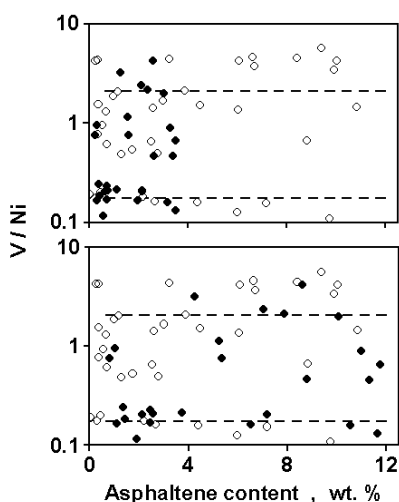


Fig. 18. Correlations with asphaltene content of V/Ni ratio for the same data as in Fig. 17. Dashed lines are averages for ‘high’ and ‘low’ branches, indicative of different source types. Above—unscaled scatter plots; below—the data for ‘A’ oils are re-scaled as in Fig. 10.

6. Discussion. Possible causes of the revealed correlations

In this publication we have presented the asphaltene-related correlations for databases, totalling more than 390 recovered (dead) crudes from a variety of geographical/ geological locations. The data analysis was performed without any modelling assumptions and revealed an apparent bi-modal distribution of the world’s crudes, as classified with respect to their asphaltene-determined properties. Of the two revealed types of oils, the less abundant type (‘A’) may be described as ‘asphaltene-deficient’ as the relevant correlations of oil properties may be re-scaled to respective correlations in the predominant type of oils (‘B’) merely by multiplying the current asphaltene content by an universal constant factor (<3.3).

By itself, this purely statistical evidence may be of importance for reservoir evaluation and management through interpretation of geophysical/geochemical data. However, a better understanding of the recovery processes requires a more detailed knowledge of the factors that determine the bifurcation of analysed correlations. Below we present some preliminary conclusions regarding a possible nature of such factors.

6.1. Source signature

It is well known that in a particular basin several distinct oil families, originated from different source rocks, may be identified by different correlation between oil properties [42,53,54].

Common source indicators are oil's V/Ni or V/(V+Ni) ratios. In particular, V/Ni<0.1 is associated with alkaline lacustrine environments, V/Ni=0.1–1.0 with acid lacustrine environments and V/Ni>1.0 is typical of marine environments deposited under low-oxygen conditions [52]. V and Ni contents seem to be related to the content of sulphur, as S and metals may be introduced into crudes concomitantly [55]. In higher density, high-S oils, V and Ni concentrations increase with asphaltene content, while in paraffinic low-S crude oils Ni predominates over V and the V/(Ni+V) ratio is typically below 0.5 [38,52]. The V/Ni ratio also may be related to the age of source deposits [51,56] While the average V/Ni ratio and the S content reflect the type of a source rock, variations of V/Ni and S across a reservoir may be related to migration-determined oil alteration [57].

On the basis of this information, we may ascribe the 'high' and the 'low' branches of scatter plots in Figs. 14, 16–18, respectively, to marine and terrestrial source types (or to sources of different age). In this case a confinement of 'A' oils from our USSR database to a single branch (Figs. 14 and 16) may have indicated that the suggested deasphalting is a specific property of oils originated from a particular type of source rocks. However, 'A' oils from the database of Ref.[11] evidently are related to both source types. Moreover, the possibility of a universal re-scaling (cf. Figs. 10, 11, 13, 15, 18) indicates that the average ratio of asphaltene contents in 'A' and 'B' oils from a variety of geographical/geological locations (and from independent databases) apparently is the same (<0.3), which is difficult to account for by source-determined mechanisms. Hence, we may conclude, that selective deasphalting is a post-generative alteration process not directly related to the origin of crudes, though some details of this process may be determined by a type of the oil's source.

6.2. Post-generative alteration

Currently, there still dominates an opinion that post-generative alteration of crudes occurs via a gradual fractionation of components in the sequence: asphaltenes>resins>aromatics>branched alkanes>*n*-alkanes, the latter being preferentially expelled with respect to the former compound [58]. On the other hand, the results of the present study indicate that the main cause of the differences in 'A' and 'B' oils may be a step-wise fractional asphaltene precipitation, dominating over alteration of lighter compounds. Selective asphaltene separation also may result in pronounced differences in correlations of geochemical parameters previously considered to be influenced solely by source or thermal maturity. If biomarker profiles can be altered by asphaltene precipitation, then correlation studies, and assessments of paleodepositional environments, maturity, biodegradation, and other geochemical parameters important to exploration can be compromised [59].

In reservoirs alteration of crude oil is assumed to follow two main tracks: (1) alteration by bacteria and water which decrease oil quality and occurs in shallow, cool reservoirs; (2) alteration by gas and thermal energy which improves oil quality and occurs in deep, hot reservoirs [53,60]. The processes, which may cause massive asphaltene precipitation, have been reviewed by Spieght [1]. He points that asphaltenes form stable suspensions in crude oils provided that there are no disturbances made to the system. The main disturbances leading to deasphalting are: (1) the alteration of natural abundance of oil fractions; (2) the chemical or physical alteration of the constituents during migration and recovery, including changes brought on by temperature and pressure variations; and (3) alteration of the polar group distribution during oxidation by exposure to aerial oxygen or water. The important cause of changes in the abundance of polar species also is selective adsorption at mineral surfaces [29,61,62]. The material that deposits from the crude oil as a separate phase is more aromatic and richer in heteroatom compounds than the original crude or deasphalted oil. The models of precipitation suggest that the loss of asphaltene solubility (deasphalting) can be explained by a change in the molecular equilibria in petroleum through a change in the balance of oil composition [1]. The ratio of polar to non-polar molecules and the ratio of high- to low-MW molecules are factors responsible for solubility of asphaltenes, which varies with the solubility parameter of the surrounding oil medium. The latter may be affected either by dissolution of gas or alkane in the deasphalted oil phase or by changes in temperatures.

6.2.1. Biodegradation

The most widespread alteration process is that of biodegradation. Type 'A' oils are found exclusively in reservoirs with temperatures below ≈ 77 °C (cf. Section 3.6), i.e. in those subjected to effective biodegradation [26].

Biodegradation clearly is one of the major factors, which determine the manner of correlations between most of the properties of 'A' and 'B' oils. Specifically, biodegradation in an oil reservoir is known [24,37] to gradually increase the relative asphaltene content due to a loss of lighter fractions and, concomitantly: (1) to increase oil's density - cf. Fig. 10; (2) to decrease the relative contents of saturates and aromatics and to increase the content of resins - cf. Figs. 11–13; (3) to increase the content of sulphur - cf. both branches of correlations in Fig. 14; (4) to decrease H/C ratio and to increase (N+S+O)/C ratio [44] - cf. Figs. 15 and 16; (5) to increase the absolute concentration of metals, in particular of Ni and V [51] - cf. both branches of correlations in Figs. 17 and 18. However, from a physicochemical point of view, biodegradation of petroleum would be expected to increase (not decrease) asphaltene solubility [35], and hence should not be significant in the suggested processes of selective deasphalting.

6.2.2. Thermally-induced alteration

If reservoir oil is buried deeper after accumulation, it is thermally degraded-cracked into lighter hydrocarbons and gas, especially if the original oil was rich in sulphur compounds [53,60]. Because evolved gas contains more hydrogen than oil, excess carbon is precipitated into pyrobitumen and oil will decrease in density. A particular mechanism of thermal deasphalting may be a non-pyrolitic deposition of asphaltenes due to the heat-induced removal of the solvating layer around polar asphaltene cores [63]. At 100 °C the heat-induced deposition is not significant. It is beginning at 175 °C, and is very evident at 250 °C. Hence, thermal degradation of the oils is evidently ruled out by low temperatures (< 80 °C) in reservoirs from which type 'A' oils are recovered (cf. Section 3.6).

6.2.3. Oil–water interaction

Hydrothermal fault zones, with their high water/rock ratios, may be enriched in heavy end-member water-washed petroleum, as the faults provide a conduit for the invasion of meteoric waters into hydrocarbon accumulations. The process of water washing of crudes selectively removes water-soluble compounds such as aromatics and cycloalkanes [32,33]. Oils may be so altered by water washing that they form semisolid bitumen [34] and tar mats [35]. Hence, water washing can not be regarded as a cause of a selective deasphalting, as this alteration process gradually increases the asphaltene content.

6.2.4. Gas-related alteration

An important process to consider when interpreting geochemical data for altered oils is phase fractionation which may occur when a gas phase evolves and migrates away from a crude oil, leaving a residual oil depleted in light hydrocarbons [64,65]. Experimental simulation indicates that the residual oil is enriched in aromatic and cyclic hydrocarbons [64]. On the other hand, migrating gas from high-pressure zones can enter oil reservoirs where it selectively removes low-carbon number compounds that are most soluble in gas under pressure. This process of gas stripping (gas washing), also called 'evaporative fractionation', is experimentally proven to concentrate naphthenic and aromatic hydrocarbons in the parent oil phase; most efficient gas washing occurs in deeply buried continuous sands, where as much as 91% of the oil's original n-alkanes may be removed [66]. The above gas-related processes increase asphaltene content in altered oil. However, asphaltene precipitation may be caused by an increased gas solution in oil. Such an effect (gas deasphalting) [1,6] may arise from an increase of reservoir pressure and may result in formation of tar mats with high asphaltene content (20–60 vol.%) compared with the altered oil leg (1–5%) [35]. Asphaltene also may precipitate due to pressure depletion [67]. At high pressures in the reservoir, the asphaltene are dissolved in the monophasic crude oil. When the pressure is reduced (e.g. during production) the solubility parameter difference between asphaltene and the crude oil increases towards a maximum at the bubble point of the crude. As a result of the reduced solvating power,

asphaltenes may start to precipitate at some onset pressure above the bubble point. Once gas evolves, the light alkane fraction of the liquid phase is reduced, and thereby the solvating power for asphaltenes increases again. The relative change in asphaltene solubility has been shown to be highest for light crude oils that are undersaturated with gas, and which usually contain only a small amount of asphaltenes, though a high fraction of saturates. Hence light reservoir oils are considered to be more likely to experience asphaltene pressure depletion than heavier, less undersaturated, asphaltenic oils.

The discussed bi-modal character of correlations between the properties of crude oils is presumably determined by the presence of two distinctly different fractions in the oil's asphaltenes. One of the main differences between the fractions is their solubility (cf. Section 3.5). Hence, pressure-related changes of solvating powers of crude oils indeed may lead to a step-wise loss of a low-soluble fraction of asphaltenes, resulting in the appearance of type 'A' crude oils. However, we conclude, that gas-determined process apparently is not the main cause of a presumed selective (fractional) deasphalting of 'A' oils. The reason for this conclusion is that in our USSR database 'A' and 'B' oils are indistinguishable with respect to correlations involving either reservoir pressure or gas factor (cf. Section 3.6).

6.2.5. Oil-rock interaction

Petroleum may migrate up to several hundred kilometers from source to reservoir. This flow is affected by a number of properties ultimately controlled by oil-rock interactions. In particular, adsorption on mineral and organic solid surfaces and retention by molecular size exclusion in the mineral pore space are active mechanisms of oil alteration during primary and secondary migration [39, 68]. Crude oils contain surface-active molecules with a strong affinity for solid phases, which are concentrated in the NSO compounds, including asphaltenes. The properties of asphaltene adsorption onto solids are of technological importance due to their effects on permeability within reservoir rocks. This reason alone was enough to justify the large number of studies dealing with asphaltene adsorption onto different materials [69,70]. It has been proven that not only individual asphaltene molecules but also comparatively large asphaltene flocs have a high adsorption affinity to solid surfaces [70,71]. In a review of earlier publications, Anderson [72] presented evidence of a high asphaltene adsorption onto carbonates, exceeding adsorption onto quartz sands at least by a factor of 2.3 (in some experiments-by an order of magnitude). Asphaltenes appear to be strongly adsorbed onto clays due to their high surface area and charge density [62,69,72]. Consequently, the resin and asphaltene components of migrated petroleum may display strong correlations in terms of concentration and composition with clay content of reservoirs [73]. Adsorption onto clays and carbonates may lead to a selective removal of a specific fraction of oil's asphaltenes. Namely (cf. Section 3.5) the low-soluble fraction is also the most polar one, while studies of the degree of adsorption of organic compounds on clays show a strong relationship between the degree of adsorption and polarity. The more polar a compound is the stronger the complex is that is formed with the clay [74].

Collectively, compositional changes brought about by oil/rock partition, were termed 'geochromatography' effects [75], which mainly accompany primary migration as oil leaves the source rock but also occur during secondary migration [76]. E.g. in petroleum systems of the North Sea and of the Western Canada sedimentary basins, migration in clastic carrier beds over distances of more than 100 km resulted in the reduction of absolute concentrations of some oil constituents (benzocarbazoles) by over an order of magnitude [76]. Larter et al. [61] presented a conclusive experimental evidence that geochromatography does occur in course of oil migration through siltstone under realistic subsurface carrier bed or reservoir conditions of temperature and pressure. They observed that hydrocarbon oil fractions showed little fractionation, while the more polar non-hydrocarbon fractions, containing nitrogen and oxygen, showed substantial compositional change. The depletion of polar compounds during the experiment was similar to the compositional changes seen in migrated oil field data [76], proving that such compounds do respond to petroleum migration. In particular, Larter et al. [61] report that the first oil samples produced from the core were a clear orange colour, contrasting with the black colour of the initial oil. The authors do not specify the nature of the polar pigmented species retained in the core, but darkness of heavy oils is

known to be determined by the specific colour of asphaltenes, which is a part of their definition [40,77].

Chromatographic models show that concentrations of oil constituents in a reservoir are not simple functions of the distance migrated but depend critically on sorption properties of the rocks and on the relationship between the volume of carrier rock accessed by the oil and the volume of oil migrated through it to reservoirs [61]. Hence, large fractionations are most likely to be observed in basins with small fields at the end of long migration routes, as in foreland basins [78] or where rocks involve highly sorptive siltstones or mudstones. Thus, large geochromatography effects are seen [61,76] in reservoired petroleum systems in the foreland basin settings of Western Canada and Oman and for vertically migrated oils in the Gulf of Mexico and in the Kekeya Field of the Tarim Basin (Oman) which must have migrated through kilometres of mudstones. In contrast, in prolific basins, large volumes of oil will be charged through the same rock volume, ultimately saturating it with the feed oil, with little geochromatography effects seen in the final reservoired oil. According to Larter et al. [76], an example is the Kimmeridge Clay Formation (source)—Hugin Formation/Paleocene/Eocene sand (carrier/reservoir) petroleum systems of the Tertiary reservoirs in the Viking Graben, North Sea, where many reservoir volumes of oil have been charged through a single pathway.

The above conclusions that geochromatography may be observed only in basins with the small volumes of migrated oil, is based on the assumption that the absorbed quantity of any oil's component can not exceed a certain saturation limit. However, this may not be so in the particular case of fractionation of asphaltenes. Indeed, the results derived from studies at various solid surfaces revealed a multilayer manner of adsorption for asphaltenes [70,79,80]. In some asphaltene/mineral systems multilayer adsorption onto formation rock evidently is a no-saturation process by which the quantity of adsorbed asphaltene increases continuously [81]. Hence, selective (fractional) deasphalting due to geochromatography may be a relatively common phenomenon. Moreover, this phenomenon apparently should not be restricted to oils of some specific compositions, i.e. to specific solubilities of asphaltenes. Wiehe et al. [82] remarked that it is frequently implied that the higher is the solvating power of the oil, the less tendency the asphaltenes will have to adsorb at a surface. In fact, as demonstrated in a number of experiments [79,80,82], strong adsorption is observed well below the solubility limit (or even the CMC) of asphaltenes, which suggests that asphaltene–solid interaction is more important than the effects of asphaltene interaction with other oil constituents and, hence, asphaltene solubility. Solid surfaces may act as nuclei, facilitating asphaltene association as they are concentrated onto the solid. The assumption, that a well-defined fraction of asphaltenes may be removed from oils by selective adsorption at mineral surfaces, is supported by experimental results of Ref. [83]. The authors concluded that with respect to adsorption (deposition), asphaltenes may be regarded as a two-component system.

The 'less soluble asphaltenes' are irreversibly (chemically) adsorbed at mineral surfaces. The 'more soluble asphaltenes' remain in solution, or are only weakly (physically) adsorbed at strongly bound deposits and are easily desorbed again by a moving fluid.

To conclude this section, it should be noted that in some cases fractionation of asphaltenes during secondary migration might be obscured by source facies and maturity effects [76]. While for clastic oil source rocks migration fractionation effectively removes any source related maturity influence on the secondary migrated oil, in the carbonate-sourced petroleum systems maturity effects do sometimes dominate over the effects of geochromatography [76]. However, quite commonly the effects of source maturity and secondary migration fractionation appear to operate in concert, both reducing concentrations of polars in the further migrated and least mature oils [76].

7. Conclusions

Several independent databases of more than 390 crude oils, were analysed with respect to correlations between oil properties and their asphaltene content. For densities, viscosities and pour points the analysis revealed a definite absence of linear correlations with asphaltene concentration, described in some publications. Moreover, we found persistent anomalous deviations of bulk properties in oils with 2–2.5 wt.% asphaltenes. The nature of these deviations was investigated by filtering of the original databases. The results of this procedure suggest the existence of two types of

world's crudes, well distinguished with respect to their asphaltene-based correlations. A possible mechanism of subdivision of crude oils may be a certain widely spread process of a selective (fractional) deasphalting.

Bifurcated correlations with asphaltenes also were observed for saturates, aromatics, resins and for of S, V and Ni. The correlations show definite imprints of biodegradation and of source types. However, a review of various oil alteration processes shows that an apparent subdivision of crudes into two types is most probably due to deasphalting via a natural geochromatography of oils in course of migration, resulting in a selective removal of a well-defined polar asphaltene fraction, distinguished by its low solubility.

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