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Apparent Disaggregation of Colloids in a Magnetically Treated Crude Oil

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Abstract.

"The new physical mechanism" of viscosity reduction of petroleum fluids was suggested in a series of recent publications. The key idea is that magnetic field treatment aggregates colloidal particles inside a crude oil into larger ones, thus decreasing viscosity. On the basis of new experimental data and of the analysis of well-proven theoretical models, we conclude that this "physical mechanism" in magnetically treated oils appears to be non-existent. In particular, as revealed by our optical measurements, magnetic treatment results in disaggregation of colloidal particles in a crude oil.

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Introduction

Over the past years it has been repeatedly claimed that magnetic/electric field treatment may have beneficial effects on the properties of crude oils. The most frequently reported were cases of significant viscosity improvement. Recently, “the new physical mechanism” of viscosity reduction was suggested in a series of papers in Energy & Fuels and in other publications.[1-7] The key idea is that magnetic (or electric) field treatment aggregates asphaltene (or paraffin) particles inside crude oil into larger ones. In turn, particle aggregation is the cause of the observed viscosity decrease. The authors claim that this basic mechanism of viscosity is universal and powerful for all liquid suspensions with broad applications, present ones and future ones. They also claim that laboratory tests confirm their theory.

It appears, however, that some of the above statements and conclusions are not justified and are at odds with established knowledge. The discussed publications give the impression that the authors may not be familiar with well-known data on asphaltene aggregation effects on petroleum rheology. In fact, there is multiple and conclusive evidence that aggregation of asphaltenes (at constant concentration) *increases* the viscosity of petroleum. E. g., it is well-proven, that when asphaltene particles in the stored (degrading) oil become prone to aggregation, the viscosity of oil increases.[8] Back in 1932, Mack[9] measured viscosity of Mexican asphalts and suggested that the significant viscosity increase is due to strong aggregation of asphaltene particles. In a number of publications it has been concluded that association of asphaltene particles in crude oil and in vacuum residue can be distinguished by a corresponding increase of viscosity.[10-13] Storm and Sheu[14] applied four viscosity models for a colloidal dispersion to experimental data on viscosity of a vacuum residue and concluded that high viscosity was due to increase of volume of asphaltene particles. Fenistein et al.[15] have shown that viscosity variations paralleled those of the volume of asphaltene aggregates as determined from the neutron scattering data. More recent experimental results of Luo and Gu[16] again demonstrated that if the dispersed asphaltene particles aggregate and become large enough, the heavy oil viscosity increases significantly. Finally, Johansson et al.[17] reported experimental decrease of viscosity in asphaltene solutions and attributed it to disintegration of oligomeric aggregates into monomers. They also noted that enhanced asphaltene association increased the viscosity of the solution.

It is true, however, that there are insufficient experimental data on long-term changes in the state of aggregation after magnetic treatment of crude oils, though viscosity reduction has been observed by many authors.[18-27] Some indirect evidence of post-treatment disaggregation was obtained by microscopy of deposits[19-21] and by measuring the number of inhibition (paramagnetic, etc.) centres.[25,27] The direct detailed experiments have demonstrated only temporary orientation of some petroleum constituents under the action of an applied magnetic field.[28-30] In the present paper we describe experimental studies of a magnetically treated crude oil by optical methods which have been shown to be sensitive to the state of asphaltene aggregation.[31-33]

Experimental Section

Crude Oil. The studied virgin crude oil was collected directly from an oil-producing well at Aznakayevsky reservoir in Tatarstan, Russia. After water separation, this oil had a specific gravity (SG) of 0.8756, contained 3.6 wt. % asphaltenes, 1.8 wt. % sulfur, ~6 wt. % paraffins/waxes. Previously, it has been repeatedly demonstrated that crude oils from this origin decrease their viscosity after treatment of flowing oils by constant magnetic fields.[34, 35]

Magnetic Treatment. The experimental set-up was based on a permanent C-shaped magnet with a high-homogeneity field in the 12 mm gap between parallel circular poles. The magnetic field strength was 0.12 T as measured by proton resonance meter. In each of eleven experiments, we employed four 2 ml oil samples in sealed glass tubes inclined by ca. 20^o to the horizontal plane. After filling the tubes, the samples were allowed to equilibrate for 30 minutes. One pair of samples was placed into the pole gap of the magnet; another pair remained outside magnetic field. In each pair, one sample remained stationary; the other was rotated with a frequency of 55-60 revolutions per minute (cf. the scheme of experimental setup in Figure 1). This oil treatment procedure continued for 1 hour at 20-23 ^oC; afterwards optical properties of all samples were measured within 2-3 minutes.

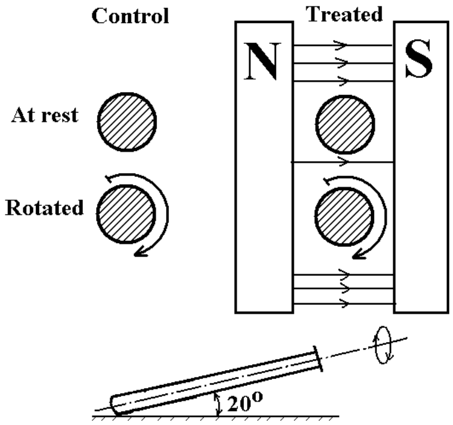

Figure 1. Experimental setup for magnetic treatment of the crude oil (for details – cf. text).

Measurements of Optical Properties. The refractive index (RI) measurements were performed in an Abbe-type refractometer IRF-454-B2M (KOMZ, Kazan, Russia).[33] For toluene at 20 ^oC the measured RI was 1.4967, close to the value of 1.4969 quoted by the producer. The UV-visible extinction (UVVE) spectra in the 205-535 nm range have been measured with a Shimadzu UV-2201 UV/VIS double-beam recording spectrophotometer.[32] The UVVE data were collected with 1 nm wavelength increment and automatically stored. The obtained data sets were computer-processed according to the below described procedures. Extension of UVVE measurements to larger wavelengths (310-750 nm range) was obtained by studying toluene solutions of oils in a spectrometer, equipped with a set of narrow-band light filters (KFK-2 Photocolorimeter).[31] All optical measurements were performed at 20 ^{o}C and at ambient pressure.

Results and Discussion

Experimental evidence of disaggregation in magnetically treated oil. Table 1 shows mean values and standard deviations for RI in four types of oil samples employed in our experiments. In agreement with previously reported studies,[18-27] a statistically significant effect was achieved only in case of magnetic treatment of a flowing (agitated) crude oil. Namely, a decrease of RI by ca. 0.2% was registered in samples rotated in a magnetic field.

Table 1. Results of refractive index measurements in magnetically treated and control samples of a crude oil. Values of specific gravity and of molecular weight are estimated by empirical correlations from Refs.37,38.

Oil samples	In magnetic field		Without magnetic field	
	Rotated	Stationary	Rotated	Stationary
Experimental refractive index	1.5380±0.0006	1.5405±0.0007	1.5404±0.0004	1.5403±0.0007
Estimated specific gravity	0.8706±0.0012	0.8759±0.0014	0.8756±0.0008	0.8755±0.0014
Estimated molecular weight	294±1	297±1	297±0.5	297±1

Multiple experimental studies have proved a strong correlation of RI with a specific gravity (density, API gravity) and an average molecular weight (AMW) of native crude oils,[36-39] which, in turn, are correlated with oil viscosities.[40] Accordingly, two bottom lines of Table 1 show the respective values of specific gravity and AMW estimated from experimental RI data by using empirical correlations from Refs. 37,38. There is an apparent decrease of both SG and AMW by ~0.6% and ~1% by in samples rotated in a magnetic field.

The theoretical expression of RI-density relationship showing closest agreement with experiment is the formula of Lorentz and Lorenz:[41]

$$K_L = \frac{n^2 - 1}{n^2 + 2}\frac{1}{\rho}$$

where K_L is the specific refractivity in terms of the refractive index, n and the density ρ. The specific refractivity has been shown to be substantially independent of the state of aggregation and relatively invariant to change in temperature**.**[36,41,42] Hence, at a constant temperature, the observed lower RI values in magnetically treated samples may be reliably attributed to well-known density (specific gravity) decrease in fluids via bond break-up and deaggregation,[43,44] Computer simulations have shown that these processes should be accompanied by a decrease of fluid's viscosity.[44] An exception is a case where colloidal particles are stabilised by strongly absorbed solvent molecules. In such system structure-breaking in colloidal aggregates is counteracted by structure-building at the increased interface area; hence the net effect is an increase of bulk density.[45-47] The data of Table 1 suggest that such stabilization/absorption effects are negligible in a colloidal system of the studied crude oil.

Additional proof of disaggregation in magnetically treated oil was provided by measurements of optical extinction. Figure 2 shows Shimadzu UV-2201 extinction spectra of non-treated oil (1) and of a crude oil sample rotated in a magnetic field (2); note a log scale for extinction. Clearly seen is a decrease of extinction after magnetic treatment at all wavelengths. The details of this effect were emphasized by computing the ratio of extinction in a treated sample to extinction in the original crude oil, as illustrated in Figure 3. Solid line – the data from Figure 2; open circles connected by dashed line – the data from KFK-2 Photocolorimeter.

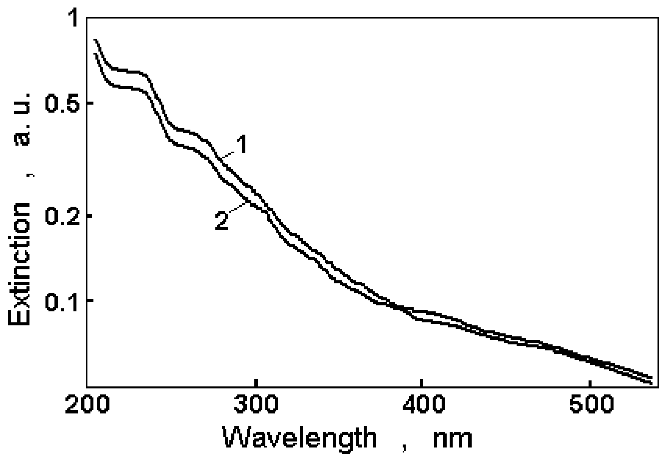

Figure 2. Optical extinction spectra of the original (1) and of magnetically treated (2) crude oil.

Optical extinction of crude oils is conventionally discussed[48,49] within the Rayleigh limit when extinction cross-section is considered to be a sum of the absorbance and scattering contribution, $\sigma_{ext} = \sigma_{abs} + \sigma_{scatt}$. Aggregation effects on absorbance were shown to be negligible at asphaltene concentrations characteristic to non-diluted crude oils,[31,32] while the Rayleigh scattering cross-section is extremely sensitive to any changes in the radii *r* of colloidal particles/aggregates:

$$\boldsymbol{\sigma}_{scatt} = \frac{2^7 \boldsymbol{\pi}^5}{3} \left(\frac{\boldsymbol{n}^2 - 1}{\boldsymbol{n}^2 + 2} \right)^2 \frac{\boldsymbol{r}^6}{\boldsymbol{\lambda}^4}$$

where λ is the wavelength of the incident light and *n* is the ratio of the particle RI to the RI of continuous phase.[49] Accordingly, the overall decrease of extinction may be regarded as a qualitative proof of magnetic field - induced decrease of the size of suspended colloidal particles.

It should be noted, however, that the relative decrease of Rayleigh scattering is expected to be independent on the incident wavelength, while Figure 3 shows a step-like change from a value of ~0.875 below 300 nm, to another fairly constant level of ~0.95-0.96 above ca. 370 nm.

A plausible interpretation may be a different degree of magnetic action on smaller and larger crude oil molecules. The most effective absorbers below 300 nm are known to be low molecular weight species with 1-2 ring aromatic chromophores, while absorbance in the visible and in the near-IR ranges is due to the presence of heavier asphaltene molecules with multiple-ring aromatic systems.[50]

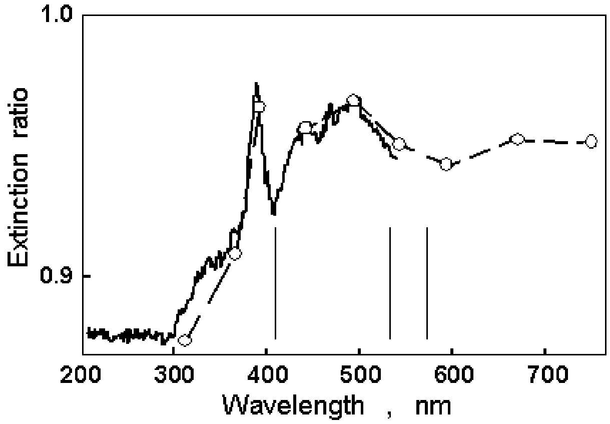

Figure 3. Relative decrease of crude oil's optical extinction after magnetic treatment.

The appearance of two local minima in the longer-wavelengths part of Figure 3 may be regarded as an additional support of the above interpretation as these are indicative of relatively stronger magnetic field effects on the specific molecular species. In particular, the position of these minima coincide with positions of the strong Soret and the weaker Q_α and Q_β absorption bands in vanadyl porphyrins[51] (at 410, 553 and 573 nm as indicated by vertical lines in Figure 3). Furthermore, it has been experimentally demonstrated that vanadyl porphyrins are accumulated only in asphaltene sub-fractions with the lowest molecular weights.[52,53]

Theoretical models do not support "the new physical mechanism" of viscosity reduction via particle aggregation. As discussed in Introduction, the authors of Refs.1-7 claim that this "basic mechanism of viscosity" is universal and powerful for all liquid suspensions. However, their theory of this mechanism obviously is the result of false assumptions and serious misinterpretations. In particular, consider the following statement from Ref. 2 on relation of viscosity η to the particle size at constant volume fraction ϕ:

"*While a profound theory for this size effect is still lacking, the following qualitative explanation helps our understanding. Generally, the effective viscosity depends on how much freedom the suspended particles have in the suspension. The less freedom for the particles, the faster the energy dissipates and the higher the effective viscosity. The mean free path of the spheres inside the suspension is given by* $l \approx a/(3\phi)$*, where a is the particle radius. As a gets bigger, l becomes longer, indicating that the suspended particles have more freedom to move in the suspension. Thus,* η *goes down*."

This qualitative conclusion of increasing l with increasing a may have followed only from an over-simplified elementary kinetic theory of ideal gases[54] with an additional restricting assumption that primary suspended particles do not flocculate (retaining their identities) into irregular-shaped aggregates but coalesce into new spherical species. Under these assumptions, $l \sim 1/na^2$ where n is the number density of particles. At constant ϕ, $n \sim 1/a^3$; hence it may be concluded that $l \sim a$.

In fact, realistic theories of disordered media, free from simplifying assumptions, show that the larger are the diffusing particles, the smaller is the mean free path at constant volume fraction.[55,56]

Another argument for the new "basic mechanism of viscosity" concerns the behaviour of a maximum volume fraction, ϕ_m, an important "crowding" parameter in a number of models, e.g. in the Krieger-Dougherty's formula for effective viscosity of a liquid suspension:[57]

$$\eta=\eta_0(1 - \phi/\phi_m)^{-[\eta]\phi m},$$

where η_0 is the viscosity of a base liquid and $[\eta]$ is a so-called intrinsic viscosity (equal to 2.5 for hard spheres).

In Ref.1 the authors of "the new mechanism of viscosity" insist that magnetic field "*aggregates the small particles into large ones. ... While this change in rheology does not alter* ϕ*, it makes* ϕ_m *increased as a result of the increase of ... average particle size. Hence, the effective viscosity* η *is reduced*."

As above, this conclusion obviously comes from misunderstanding of aggregation phenomena in solid suspensions. An increase of ϕ_m with increasing size is possible only in very rare cases (e.g. in emulsions) where new compact particles (aggregates) are formed by total coalescence of smaller ones.[58,59] In solid suspensions, however, aggregation always proceeds via flocculation of smaller particles into non-compact clusters (open structures containing entrapped liquid).[58-61]

Since Mooney,[60] ϕ_m is interpreted as the volume fraction at which particles (aggregates) fill the available space and the viscosity increases because of mechanical interlocking. For rigid individual spheres, independent of size, the maximum ϕ_m=0.74 is achieved in hexagonal close packed arrays. However in suspensions of flocculated open clusters space-filling commences at much lower concentrations of primary particles, i.e. ϕ_m *decreases* (and effective viscosity increases) with increasing size. The magnitude of these effects depends on the volume fraction of particles inside a cluster, $\phi_{int} \leq 0.74$, as illustrated in Figure 4. Solid curves are theoretical evaluations of relative viscosity $\eta_{rel}=\eta/\eta_0$ which have shown a good agreement with experiment.[61]

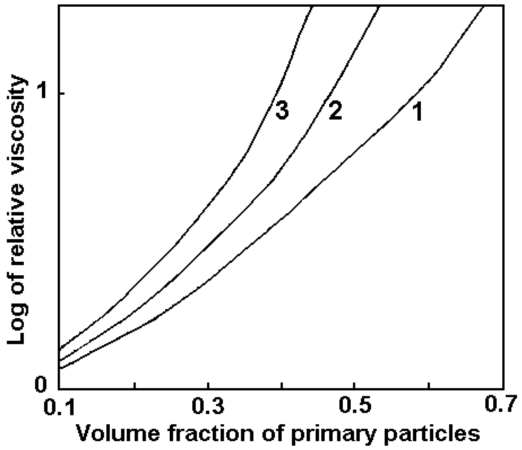

Figure 4. Increase of relative viscosity as a result of particle aggregation in a suspension. Curve 1: primary particles do not form aggregates; curve 2: $\phi_{int}=0.65$ (cubic centered packing of particles inside aggregates); curve 3: $\phi_{int}=0.56$ (simple cubic packing of particles inside aggregates). After Ref. 61.

Summarizing, the crucial theoretical arguments in Refs. 1-7 supporting the ”basic mechanism of viscosity” are not justified and are at odds with well-established knowledge in rheology of aggregating suspensions. Characteristically, some of these publications recently were also criticized for claims and conclusions that violate the first law of thermodynamics.[62]

Possible molecular mechanisms of magnetic treatment. After this paper was submitted for publication, one of the reviewers requested more discussion for particular chemical (molecular) mechanisms of magnetic treatment effects in crude oils. Regretfully, literature analysis shows that at the moment this subject is still under-investigated, hence any suggested model would be merely speculative. Various mechanisms of magnetic action have been proposed, but not proven conclusively. E.g., some groups of scientists ascribe a key role to charged species in petroleum and to arising Lorentz forces which can destroy molecular aggregates.[19] Other authors discuss the magnetic treatment effects in terms of intrinsic magnetic properties of asphaltene colloids.[18,27] Presumably, asphaltene particles may be either ferromagnetic (due to ferrous micro-contaminants),[63] paramagnetic[27,64] or diamagnetic.[65] However, the implicit controversy in models with magnetic asphaltenes is that such particles may be expected not to disaggregate, but to flocculate under the action of a magnetic field.[66] Some other molecular mechanisms are discussed in publications on specially formulated electrorheological and magnetorheological fluids,[67-69] in particular, external field effects on hydrogen bonding.[69] In our previous publication we have discussed the importance of easily disrupted hydrogen bonds in asphaltene aggregates.[70] Hence, a plausible cause of the above discussed disaggregation of petroleum colloids may be a transient break-up of hydrogen bonds between asphaltene molecules.

Conclusions

Recent suggestion of “the new physical mechanism” of viscosity reduction via particle aggregation has added unnecessary confusion to a still controversial topic of magnetic field effects in crude oils. On the basis of the above experimental and theoretical evidence, we may conclude that this “physical mechanism” in magnetically treated oils appears to be non-existent. The widespread circulation of scientifically untenable "explanations" does little to inspire confidence in any beneficial effects of magnetic treatment of petroleum. However, unbiased experiments increasingly report evidence that magnetic treatment may significantly alter the colloidal properties of asphaltenes and paraffins in crude oils. Further research is needed to reveal the true molecular nature of these effects.

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